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## New structural insights into the stability of Au<sub>22</sub>(SR)<sub>16</sub> nanocluster under ring model quidance†

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This study presents thorough structural insights into the stability of crystallized  $Au_{22}(SAdm)_{16}$  (HSAdm = 1-adamantanethiol) nanocluster. With the recently developed Ring Model for describing the interaction between inner gold cores and outer protecting ligands in thiolate-protected gold nanoclusters, the experimental spontaneous transformation from the crystallized Au<sub>22</sub>(SAdm)<sub>16</sub> to Au<sub>21</sub>(SAdm)<sub>15</sub> could be well understood as structurally unfavorable for the current  $Au_{22}(SAdm)_{16}$  and could also be attributed to the weaker aurophilic interaction between the inner Au<sub>4</sub> core and the surrounding rings in Au<sub>22</sub>(SAdm)<sub>16</sub> over that in Au<sub>21</sub>(SAdm)<sub>15</sub>. Furthermore, with the Ring Model and the grand unified model, two new Au<sub>22</sub>(SCH<sub>3</sub>)<sub>16</sub> isomers with evident lower energies, higher HOMO-LUMO gaps as well as distinct optical properties over the available crystallized isomer were obtained. This study deepens the current knowledge on the structure of the Au<sub>22</sub>(SR)<sub>16</sub> cluster from a new structural point of view and also confirms the validity as well as practicability of the Ring Model in understanding and predicting the stable structures of thiolate-protected gold nanoclusters.

#### Introduction

Understanding the structural stability of thiolate-protected gold nanoclusters is still a challenging task. 1-4 Although numerous X-ray crystallography gold nanoclusters show high stability, 5-8 several with low thermostability were also observed. For example, the experimentally crystallized Au<sub>38</sub>(PET)<sub>24</sub> (referred as  $Au_{38T}$ , PET =  $SC_2H_4Ph$ ) nanoclusters can irreversibly transform to their another crystallized isomer Au<sub>38</sub>(PET)<sub>24</sub> (referred as Au<sub>380</sub>) at 50 °C in toluene, indicating the low thermostablity of Au<sub>38T</sub> with respect to Au<sub>38Q</sub>. Besides, in principle, the 18-electron closed-shell  $Au_{44}(2,4-DMBT)_{26}$  (2,4-DMBTH = 2,4dimethylbenzenethiol) is expected to be more stable than 16electron Au<sub>44</sub>(TBBT)<sub>28</sub> (TBBTH = 4-tert-butylbenzenelthiol).<sup>10</sup> Dynamic UV/vis/NIR spectra confirms that Au<sub>44</sub>(2,4-DMBT)<sub>26</sub> can transform to other gold nanoclusters under 80 °C. Under the same conditions, similar transformation was not observed for Au<sub>44</sub>(TBBT)<sub>28</sub>, which indicates that Au<sub>44</sub>(2,4-DMBT)<sub>26</sub> is actually less thermostable than

Over the past decades, this field has seen tremendous progresses. 13-20 Several models including divide and protect concept, <sup>13</sup> superatom complex model, <sup>21</sup> superatom network model, <sup>22</sup> super valence bond model, <sup>23</sup> polyhedra method, <sup>24</sup> inherent structure rule,25 grand unified model (GUM)26 as well as Ring model<sup>27</sup> have been developed to gain a better understanding of the stabilities of thiolate-protected gold nanoclusters. Among them, the Ring model was recently developed to describe the interfacial interaction between the inner gold cores and the outer protecting motifs of thiolate-protected gold nanoclusters. Several thiolate-protected clusters have been predicted via the Ring model, which demonstrates the usefulness in understanding the structural characters of ligand clusters. 28,29 In the Ring model, thiolate-protected gold nanoclusters can be decomposed into several fusing or interlocking  $[Au_a(SR)_p]$   $(q = 4-8, 10, 12, and 0 \le p \le q)$  rings. With the Ring model, this study presents new structural insights into

Au<sub>44</sub>(TBBT)<sub>28</sub> under 80 °C.<sup>10</sup> In addition, Au<sub>22</sub>(SAdm)<sub>16</sub> (SAdm = 1-adamantanethiol) was recently found to be metastable in a solution and can spontaneously transform into Au<sub>21</sub>(SAdm)<sub>15</sub>. <sup>11,12</sup> These structural alternations clearly show that some crystallized thiolate-protected gold nanoclusters with low thermostability do exist. However, the structural insights on the geometrical transformation of these crystallized structures, and if there exists a more stable isomer, are yet to be unravelled.

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the less thermostability of crystallized Au<sub>22</sub>(SAdm)<sub>16</sub> with respect to the Au<sub>21</sub>(SAdm)<sub>15</sub> nanocluster. Furthermore, another two isomeric structures of Au<sub>22</sub>(SR)<sub>16</sub> (R = CH<sub>3</sub>) were obtained, which own lower relative energies and higher HOMO-LUMO gaps over the available crystallized structure.

#### Results and discussion

# Structural understanding of Au<sub>22</sub>(SR)<sub>16</sub> via the Ring model and

We first focused on the structural analysis of crystallized  $Au_{22}(SR)_{16}$  and  $Au_{21}(SR)_{15}$  (R = SAdm) nanoclusters in a straightforward manner following GUM. As shown in Fig. 1, GUM suggests that both clusters own one green-colored Au<sub>4</sub>(2e) elementary blocks and two blue-colored Au<sub>3</sub>(2e) elementary blocks as the kernel. Through the proper alignments of the core and the outer ligands, both Au<sub>22</sub>(SR)<sub>16</sub> and Au<sub>21</sub>(SR)<sub>15</sub> have one Au<sub>12</sub>(SR)<sub>9</sub> part, which is made up of a Au<sub>4</sub> block in green background and Au<sub>8</sub>(SR)<sub>9</sub> ligand. Upon removing this Au<sub>12</sub>(SR)<sub>9</sub> part from Au<sub>21</sub>(SR)<sub>15</sub>, a Au<sub>9</sub>(SR)<sub>6</sub> cage can be seen, as shown in Fig. 1(a). Similarly, for  $Au_{22}(SR)_{16}$ , a  $Au_{10}(SR)_7$  cage can be observed, as given in Fig. 1(b). Therefore, Fig. 1 shows that the main structural difference between crystallized  $Au_{22}(SR)_{16}$ and Au<sub>21</sub>(SR)<sub>15</sub> lies in the aforementioned two different sized cages, i.e. Au<sub>9</sub>(SR)<sub>6</sub> cage for Au<sub>21</sub>(SR)<sub>15</sub> vs. Au<sub>10</sub>(SR)<sub>7</sub> cage for Au22(SR)16.

With the Ring model, further analysis of the main structural difference between the Au<sub>9</sub>(SR)<sub>6</sub> cage and the Au<sub>10</sub>(SR)<sub>7</sub> cage was performed, as shown in Fig. 2. The Au<sub>9</sub>(SR)<sub>6</sub> cage can be viewed as three rings [Au<sub>7</sub>(SR)<sub>5</sub>], [Au<sub>6</sub>(SR)<sub>4</sub>], and [Au<sub>5</sub>(SR)<sub>3</sub>] fusing together (Fig. 2(a)). The Au<sub>10</sub>(SR)<sub>7</sub> cage can be viewed as three rings [Au<sub>8</sub>(SR)<sub>6</sub>], [Au<sub>7</sub>(SR)<sub>5</sub>], and [Au<sub>5</sub>(SR)<sub>3</sub>] fusing together (Fig. 2(b)). Therefore, the difference between the  $Au_9(SR)_6$  cage of  $Au_{21}(SR)_{15}$  and the  $Au_{10}(SR)_7$  cage of  $Au_{22}(SR)_{16}$ can be ascribed to the different rings fusing together.

With the increment of the radii of the ring, the Ring model suggests that the ring should properly match with the structures of the within this ring to maximize the interaction between the central structure and the outer ring.<sup>27</sup> Summarized from the available crystal structures, the Ring model suggests that there should be one gold atom in the centre of the  $[Au_5(SR)_a]$  (1  $\leq q < 5$ ) ring.<sup>27</sup> For the  $[Au_6(SR)_a]$  (0  $\leq q \leq 6$ ) ring, one gold atom or one triangular Au<sub>3</sub> should locate at the

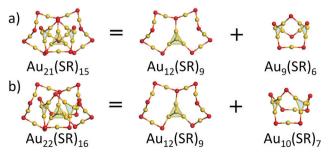


Fig. 1 Geometric decompositions of (a) Au<sub>21</sub>(SR)<sub>15</sub> and (b) Au<sub>22</sub>(SR)<sub>16</sub> (R = SAdm). Au: yellow; S: red. The R groups are omitted for clarity.

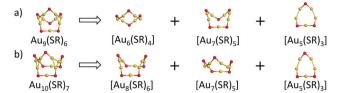


Fig. 2 Ring model-driven structural decomposition of (a) the [Au<sub>9</sub>(SR)<sub>6</sub>] ring of Au<sub>21</sub>(SR)<sub>15</sub> and (b) [Au<sub>10</sub>(SR)<sub>7</sub>] ring of Au<sub>22</sub>(SR)<sub>16</sub> into different rings. Au: yellow; S: red. The R groups are omitted for clarity.

centre of the ring.<sup>27</sup> For the  $[Au_7(SR)_q]$  (q = 4 and 5) ring, there is one tetrahedral Au<sub>4</sub> located at the centre of the ring.<sup>27</sup> For the  $[Au_8(SR)_a]$  (q = 4 and 8) ring, there should be two tetrahedral  $Au_4$ located at the centre of the rings.<sup>27</sup>

Based on the structural analysis of Fig. 1 and 2, special attention should be paid to the structural configurations of the  $Au_9(SR)_6$  cage of  $Au_{21}(SR)_{15}$  and  $Au_{10}(SR)_7$  cage of  $Au_{22}(SR)_{16}$ with the ring model. As given in Fig. 3, it can be found that the Au<sub>9</sub>(SR)<sub>6</sub> cage of the Au<sub>21</sub>(SR)<sub>15</sub> cluster one gold atom is located at the centre of [Au<sub>6</sub>(SR)<sub>4</sub>] ring, which satisfies the ring model. However, for the  $Au_{10}(SR)_7$  cage of the  $Au_{22}(SR)_{16}$  cluster, there is only one tetrahedral Au4 located at the centre of the [Au<sub>8</sub>(SR)<sub>6</sub>] ring, which conflicts with the Ring model, namely, two  $Au_4$  should exist within  $[Au_8(SR)_8]$  ring, as given in Table 1. Therefore, the experimental result could be ascribed to the confliction with the Ring model for the structural configuration in  $Au_{22}(SR)_{16}$ . For the  $[Au_7(SR)_5]$  ring and  $[Au_5(SR)_3]$  ring of both clusters, there is one tetrahedral Au<sub>4</sub> located at the centre of the [Au<sub>7</sub>(SR)<sub>5</sub>] ring and one gold atom located below the centre of the [Au<sub>5</sub>(SR)<sub>3</sub>] ring, as given in Fig. S2 (ESI†), which is in accordance with the Ring model.

In addition, the average distance between the gold atoms in tetrahedral Au4 and the gold atoms of three rings in the  $Au_9(SR)_6$  cage in  $Au_{21}(SR)_{15}$  (Fig. 2a) and the  $Au_{10}(SR)_7$  cage in  $Au_{22}(SR)_{16}$  (Fig. 2b) are also presented in Table 2. It can be found that the average Au-Au distances between Au4 and  $Au_{10}(SR)_7$  cage in  $Au_{22}(SR)_{16}$  are larger than those between Au<sub>4</sub> and Au<sub>9</sub>(SR)<sub>6</sub> cage in Au<sub>21</sub>(SR)<sub>15</sub>, which shows the weaker aurophilic interaction in Au<sub>22</sub>(SR)<sub>16</sub> over that in Au<sub>21</sub>(SR)<sub>15</sub>. This also suggests the less thermostability of Au<sub>22</sub>(SR)<sub>16</sub> than  $Au_{21}(SR)_{15}$ .

#### Structural prediction of more stable isomers of Au<sub>22</sub>(SR)<sub>16</sub>

Based on the Ring model, we have obtained the structural insights into the less thermostability of Au<sub>22</sub>(SAdm)<sub>16</sub>

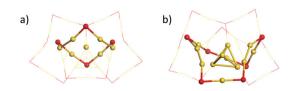


Fig. 3 The structure locates at the centre of (a) the [Au<sub>6</sub>(SR)<sub>4</sub>] ring in the Au<sub>21</sub>(SR)<sub>15</sub> cluster and (b) the [Au<sub>8</sub>(SR)<sub>6</sub>] ring in the Au<sub>22</sub>(SR)<sub>16</sub> cluster. Au: yellow; S: red. The R groups are omitted for clarity.

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Table 1 Inner structure of Au<sub>9</sub>(SR)<sub>6</sub> cage in Au<sub>21</sub>(SR)<sub>15</sub> and Au<sub>10</sub>(SR)<sub>7</sub> cage in Au<sub>22</sub>(SR)<sub>16</sub> via the Ring model

	$[\mathrm{Au}_5(\mathrm{SR})_3]$	[Au <sub>6</sub> (SR) <sub>4</sub> ]	[Au <sub>7</sub> (SR) <sub>5</sub> ]	[Au <sub>8</sub> (SR) <sub>6</sub> ]
Au <sub>9</sub> (SR) <sub>6</sub> cage	Au	Au	Au <sub>4</sub>	—
Au <sub>10</sub> (SR) <sub>7</sub> cage	Au	—	Au <sub>4</sub>	Au <sub>4</sub>
Ring model	Au	Au/Au <sub>4</sub>	Au <sub>4</sub>	2Au <sub>4</sub>

Table 2 The average distance between the gold atoms in tetrahedral  $Au_4$ and the gold atoms of the surrounded rings.  $d_1$ ,  $d_2$  and  $d_3$  denote the average distance between the gold atoms in tetrahedral Au<sub>4</sub> and the gold atoms of [Au<sub>7</sub>(SR)<sub>5</sub>], [Au<sub>6</sub>(SR)<sub>4</sub>], and [Au<sub>5</sub>(SR)<sub>3</sub>] rings in the Au<sub>9</sub>(SR)<sub>6</sub> cage in  $Au_{21}(SR)_{15}$ , respectively.  $d_1^*$ ,  $d_2^*$  and  $d_3^*$  denote the average distances between the gold atoms in tetrahedral Au<sub>4</sub> and the gold atoms of  $[Au_8(SR)_6]$ ,  $[Au_7(SR)_5]$ , and  $[Au_5(SR)_3]$  rings in the  $Au_9(SR)_6$  cage in  $Au_{21}(SR)_{15}$ , respectively. R is simplified as CH<sub>3</sub>

$Au_{21}(SR)_{15}$			Au <sub>22</sub> (SR) <sub>16</sub>			
$d_1$ (Å)	$d_2$ (Å)	$d_3$ (Å)	$d_1^*$ (Å)	$d_2^*$ (Å)	$d_3^*$ (Å)	
2.980	3.030	2.762	3.368	3.223	2.949	

compared with Au<sub>21</sub>(SR)<sub>15</sub>, one may question if there exist more stable isomers of Au<sub>22</sub>(SR)<sub>16</sub> with respect to the available crystallized structure (referred as Iso1 hereafter).

Recently, the GUM and Ring model have been used widely to predict the atomic structures of thiolate-protected gold nanoclusters, i.e.,  $Au_{28+4n}(SR)_{20+2n}$  (n = 0-8) nanoclusters and Au<sub>15</sub>(SR)<sub>13</sub> nanocluster with a new type of ligand [Au<sub>7</sub>(SR)<sub>7</sub>] ring. 29,30 Here, the GUM together with the Ring model was employed to the structural predictions for Au<sub>22</sub>(SR)<sub>16</sub>. Based on GUM, two new Au<sub>11</sub> and Au<sub>10</sub> cores can be constructed by three packing or fusing tetrahedral Au<sub>4</sub> units, as shown in Fig. 4. The Au<sub>11</sub> core can be viewed as one bi-tetrahedron Au<sub>7</sub> and one tetrahedron Au<sub>4</sub> packing together, while the Au<sub>10</sub> core can be viewed as three tetrahedron Au<sub>4</sub> fusing together by sharing two

gold atoms. Then, in accordance with the Ring model, the outer ligands were added to protect the newly constructed cores. For the Au<sub>11</sub> core, two Au(SR)<sub>2</sub>, one Au<sub>2</sub>(SR)<sub>3</sub>, one Au<sub>3</sub>(SR)<sub>4</sub>, and one Au<sub>4</sub>(SR)<sub>5</sub> ligands were added to surround the Au<sub>11</sub> core via the formation of two [Au<sub>4</sub>(SR)<sub>2</sub>], one [Au<sub>4</sub>(SR)<sub>3</sub>], one [Au<sub>6</sub>(SR)<sub>4</sub>], and one [Au<sub>6</sub>(SR)<sub>5</sub>] rings (filled with green color in Fig. 4), which ultimately forms the whole structure of a new Au<sub>22</sub>(SR)<sub>16</sub> isomer (referred as Iso2 hereafter). Following the same way, two Au(SR)<sub>2</sub>, two Au<sub>2</sub>(SR)<sub>3</sub>, and one Au<sub>6</sub>(SR)<sub>6</sub> ligands can be added on the  $Au_{10}$  core *via* the formation of two  $[Au_4(SR)_2]$ , one  $[Au_4(SR)_3]$ , one  $[Au_6(SR)_3]$ , and one  $[Au_6(SR)_6]$  rings (filled with green color in Fig. 4) to form the whole structure of another new Au<sub>22</sub>(SR)<sub>16</sub> isomer (referred as Iso3). It should be noted that the [Au<sub>6</sub>(SR)<sub>6</sub>] ring has been confirmed in crystallized Au<sub>28</sub>(SR)<sub>22</sub> nanoclusters. 31

#### Further analysis on three Au<sub>22</sub>(SR)<sub>18</sub> isomers via density functional theory calculations

To show the advantages of these two newly constructed isomers, density functional theory (DFT) calculations were performed to obtain the electronic properties of three Au<sub>22</sub>(SR)<sub>16</sub> isomers with the Perdew-Burke-Ernzerhof (PBE) functional and the all-electron basis set 6-31G(d) for C, H, and S, pseudopotential basis set LANL2DZ for Au. In addition, Tao-Perdew-Staroverov-Scuseria functional (TPSS) and Becke's three parameter hybrid functional with the Lee-Yang-Parr correlation functional (B3LYP) were also employed to check the stabilities of Au<sub>22</sub>(SR)<sub>16</sub> isomers. -CH<sub>3</sub> was used as the outer organic ligand. All calculations were performed using the Orca package.<sup>32</sup> Super-fast approximate TD-DFT implemented in the Orca package by Grimme et al. was used to obtain the UV-abs spectrum.<sup>33</sup> As shown in Table 3, calculations using the three functionals (PBE, TPSS, and B3LYP) confirmed that both Iso2 and Iso3 had lower relative energies and larger HOMO-LUMO gaps (HL gaps) than the crystallized Iso1 with R = CH<sub>3</sub>.

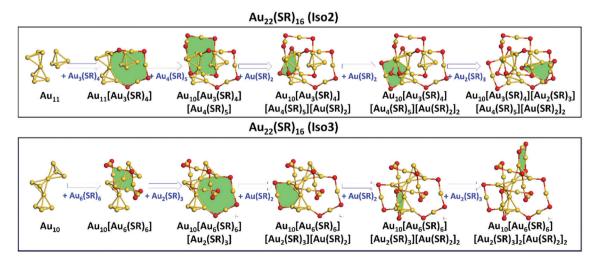


Fig. 4 The structural predictions of two Au<sub>22</sub>(SR)<sub>16</sub> isomers Iso2 (upper panel) and Iso3 (lower panel). Au: yellow; S: red. The rings were filled with green color. The R groups are omitted for clarity.

Table 3 Relative energies and HOMO-LUMO gaps of three Au<sub>22</sub>(SR)<sub>16</sub>  $(R = CH_3)$  isomers

	Relative energy (eV)			HOMO-LUMO gap (eV)		
Au <sub>22</sub> (SR) <sub>16</sub>	PBE	TPSS	B3LYP	PBE	TPSS	B3LYP
Iso1 Iso2	0.30 0.17	0.25 0.18	0.21 0.03	1.66 1.90	1.59 1.79	2.75 3.20
Iso3	0.00	0.00	0.00	1.97	1.96	3.20

Frequency calculations showed that no imagination frequency existed, which confirmed the stability of these clusters. Calculations using the PBE functional showed that Iso2 was more stable than Iso1 by 0.17 eV, while Iso3 showed further stability with respect to Iso1 by 0.30 eV, which suggested the high stabilities of the predicted Iso2 and Iso3. Similar to the relative energy, taking the PBE functional as an example, Iso2 and Iso3 showed greater HOMO-LUMO gaps by 0.24 and 0.31 eV over Iso1, respectively. All the three functionals showed that Iso3 had the lowest relative energy and the largest HOMO-LUMO gap.

The calculated absorption spectra of the three Au<sub>22</sub>(SR)<sub>16</sub> isomers are presented to compare with the experimental measurement and to obtain the optical absorption properties of the predicted isomers. PBE functional is widely known to cause a red-shift in the spectrum;34 herein, CAM-B3LYP was used to get the absorption spectra. Gaussian broadening was applied in obtaining the absorption spectra using the reorganization energy (Fig. S1, ESI†) as widths. It can be seen in Fig. 5 that the prominent absorption peaks of Iso1 (2.10, 2.53 eV) could well reproduce the experimental peaks (2.04, 2.66 eV), indicating the reliabilities of the theoretical methods employed in our simulations. In addition, the main absorption peak for Iso2 was 2.70 eV. Two absorption peaks for Iso3 included 2.81 eV and 2.97 eV.

To show the optical emission properties of the three isomers, results on photoemission are also presented here, as can be seen in Fig. 6. Experimentally, Iso1 yielded emission at 1.60 eV from its first excited state. Fig. 6 and Fig. S1 (ESI†) showed that calculations using PBE functional gave 1.23 eV,

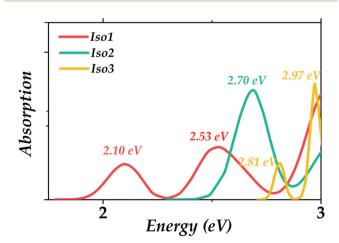


Fig. 5 Calculated optical absorption spectra for the three Au<sub>22</sub>(SR)<sub>16</sub>  $(R = CH_3)$  isomers.

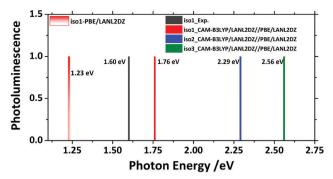


Fig. 6 Photoluminescence spectra of the three Au<sub>22</sub>(SR)<sub>16</sub> (R = CH<sub>3</sub>)

which was significantly lower than the experimental one due to the lack of exact exchange. 34 Thus, CAM-B3LYP functional was also used to rectify the emission spectrum, resulting in the emission peak (1.76 eV) that had a good agreement with the experiment (1.60 eV). Calculations showed that the emission peaks from the first excited state of Iso2 and Iso3 were 2.29 eV and 2.56 eV, respectively.

#### Conclusions

In summary, based on the recently developed Ring model, we presented new structural insights into the lower thermostability of Au<sub>22</sub>(SAdm)<sub>16</sub> than Au<sub>21</sub>(SAdm)<sub>15</sub>. The violation of the Ring Model for the rings in  $Au_{22}(SAdm)_{16}$  as well as the weaker aurophilic interactions between the Au4 core and surrounded rings in Au<sub>22</sub>(SAdm)<sub>16</sub> led to the spontaneous transformation from Au<sub>22</sub>(SAdm)<sub>16</sub> to Au<sub>21</sub>(SAdm)<sub>15</sub>. Further, with GUM and the Ring model, another two new Au<sub>22</sub>(SR)<sub>16</sub> isomers with lower relative energies and higher HOMO-LUMO gaps over the crystallized isomer were predicted.

#### Conflicts of interest

There are no conflicts to declare.

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