

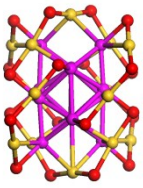
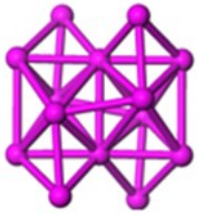
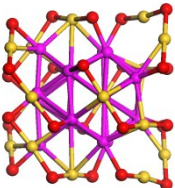
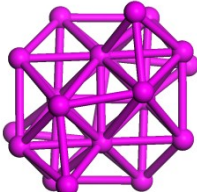
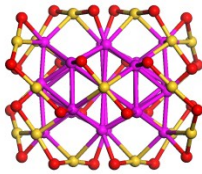
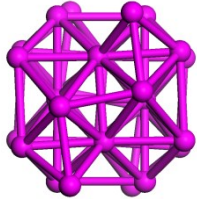
**Structure, Electronic Structure and Optical Adsorption  
Properties of One-Dimensional Thiolate-Protected Gold  
Clusters Containing Quasi-Face-Centered-Cubic (quasi-*fcc*)  
Au-core: A Density-Functional Theory Study**

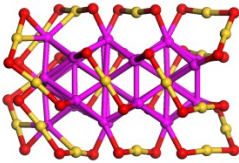
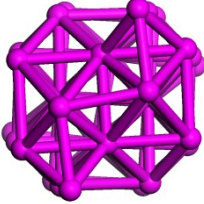
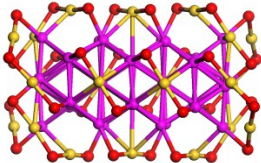
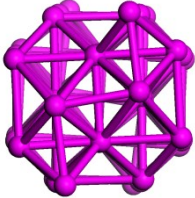
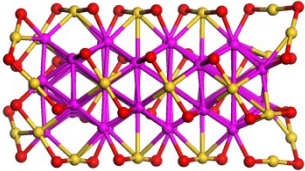
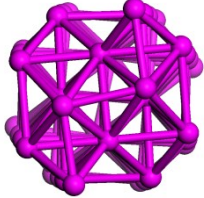
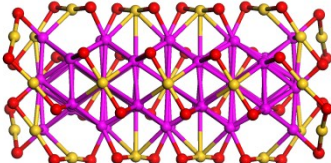
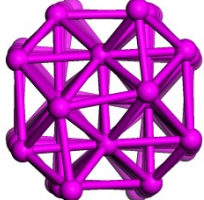
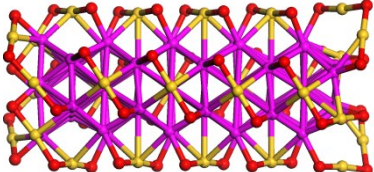
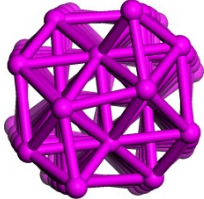
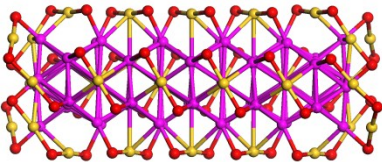
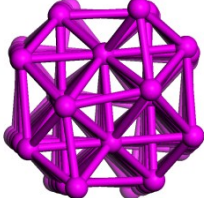
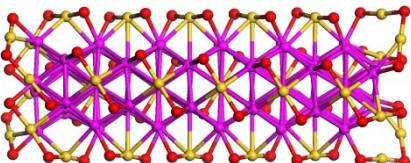
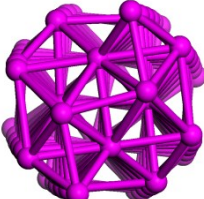
Zhongyun Ma, Pu Wang and Yong Pei\*

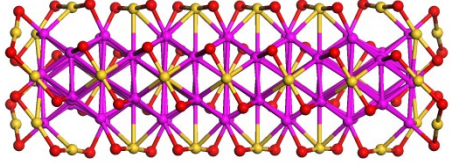
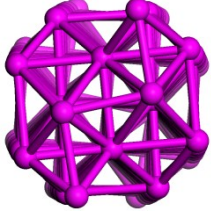
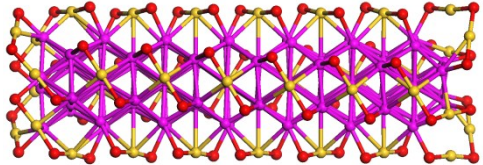
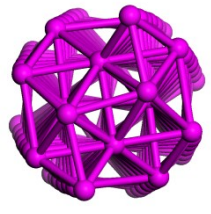
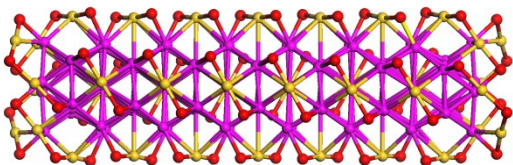
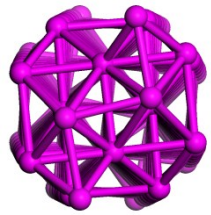
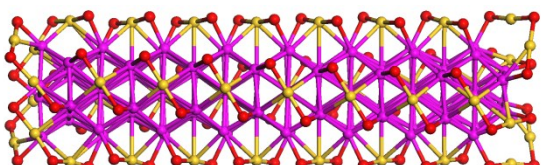
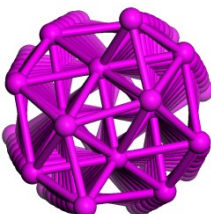
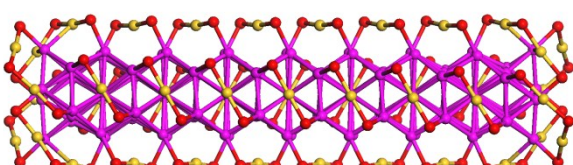
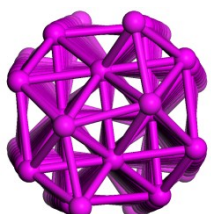
*Department of Chemistry, Key Laboratory of Environmentally Friendly Chemistry  
and Applications of Ministry of Education, Xiangtan University, Hunan Province,  
Xiangtan 411105, P. R. China*

**Supporting Information**

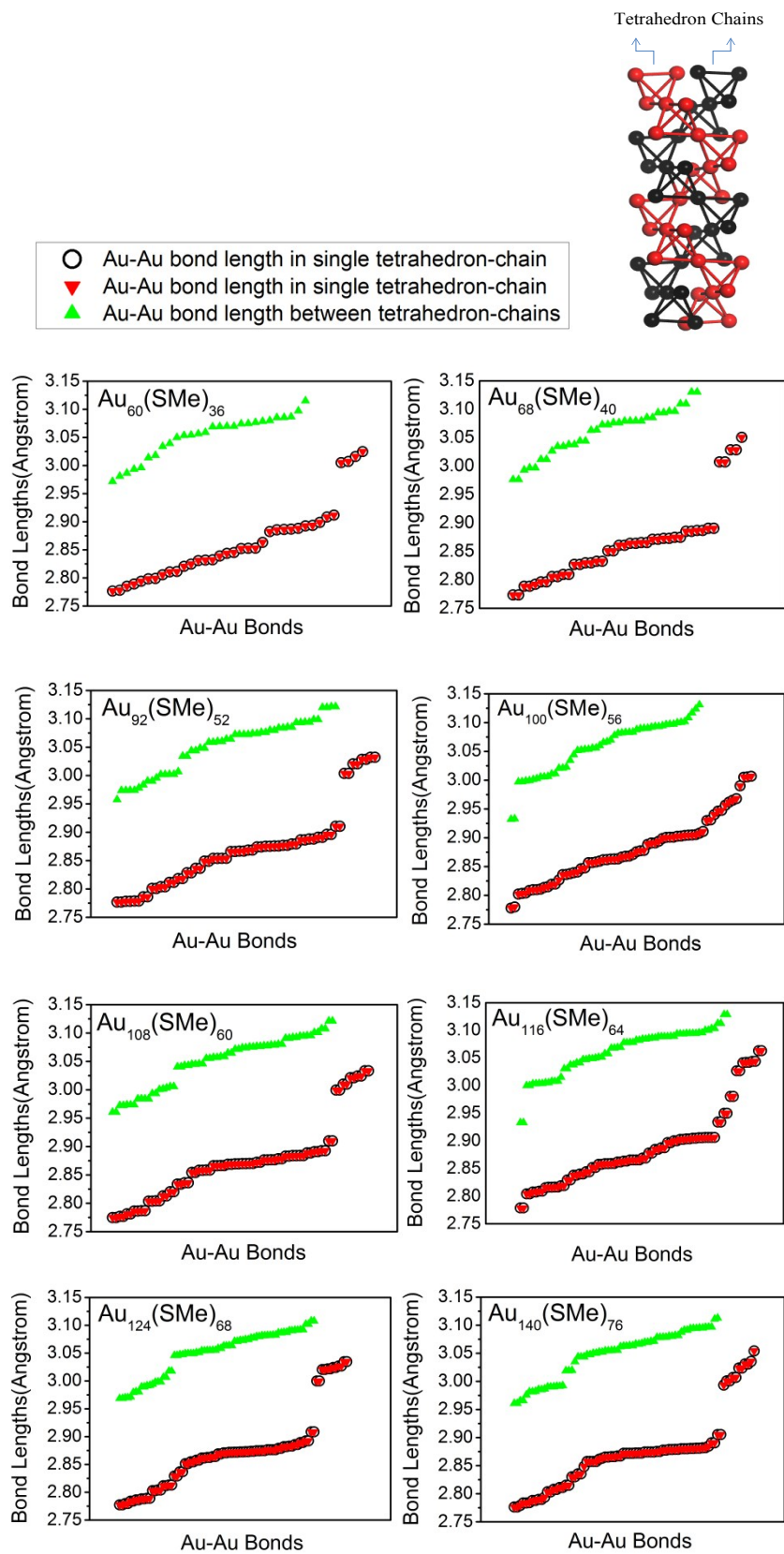
**Figure S1. Optimized geometric structures of  $\text{Au}_{20+8N}(\text{SR})_{16+4N}$ .**

$\text{Au}_{20+8N}(\text{SR})_{16+4N}$	N	Side view	Top view
$\text{Au}_{28}(\text{SR})_{20}$	1		
$\text{Au}_{36}(\text{SR})_{24}$	2		
$\text{Au}_{44}(\text{SR})_{28}$	3		

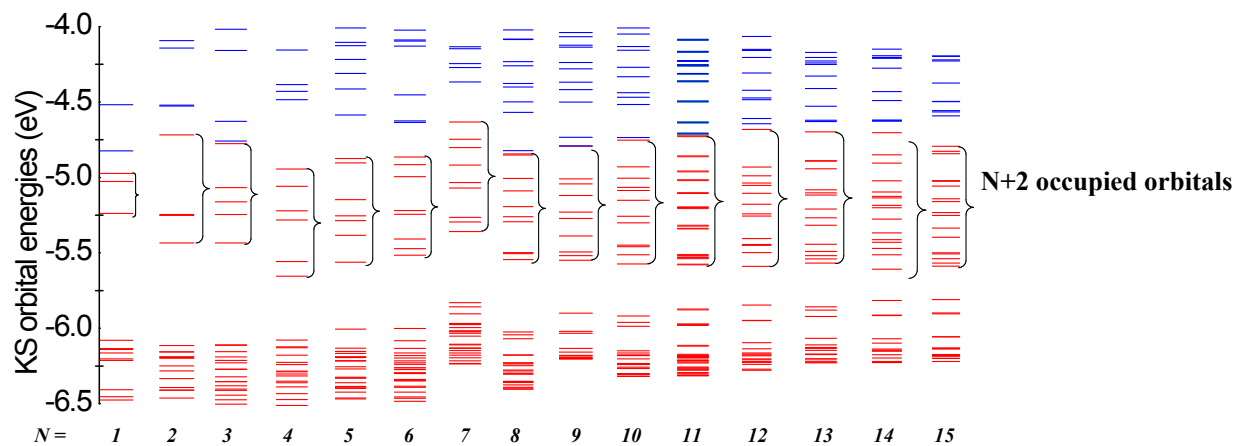
$\text{Au}_{52}(\text{SR})_{32}$	4		
$\text{Au}_{60}(\text{SR})_{36}$	5		
$\text{Au}_{68}(\text{SR})_{40}$	6		
$\text{Au}_{76}(\text{SR})_{44}$	7		
$\text{Au}_{84}(\text{SR})_{48}$	8		
$\text{Au}_{92}(\text{SR})_{52}$	9		
$\text{Au}_{100}(\text{SR})_{56}$	10		

$\text{Au}_{108}(\text{SR})_{60}$	11		
$\text{Au}_{116}(\text{SR})_{64}$	12		
$\text{Au}_{124}(\text{SR})_{68}$	13		
$\text{Au}_{132}(\text{SR})_{72}$	14		
$\text{Au}_{140}(\text{SR})_{76}$	15		

**Figure S2. Bond lengths of Au-Au in the Au-cores of  $\text{Au}_{20+8N}(\text{SR})_{16+4N}$  clusters.**

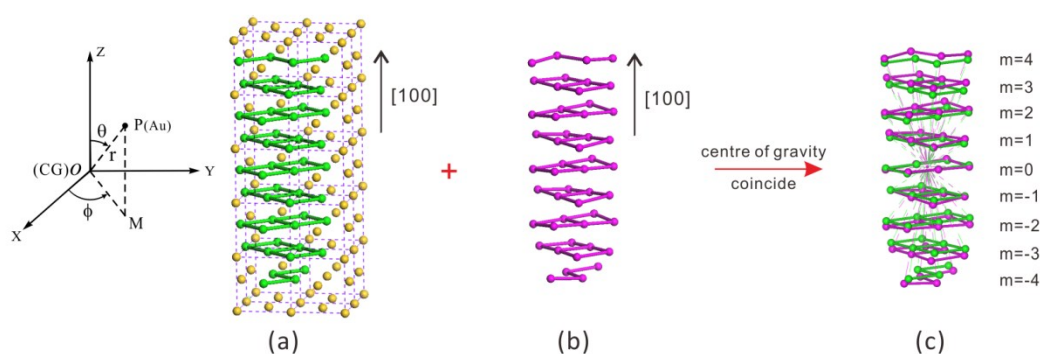


**Figure S3. Kohn-Sham (KS) orbital energy level of  $Au_{6N+8}$ -cores. Red lines: occupied energy levels; Blue: Unoccupied energy levels.**



## Definition and calculations of mean deviation (MD) for various gold clusters

A geometric parameter termed by mean deviation (MD) is defined to describe the average distortion of Au-atoms in Au-cores in comparison to the bulk gold crystal structure. The MD value of each Au-core is calculated from the arithmetic mean of relative coordinate displacement (in unit of angstrom (Å)) and twist angle (in unit of degree) of each Au atom, as described by the following eq. s1-s5.



**Figure S4.** A schematic diagram for calculating the mean deviation value (MD) of Au-cores in  $\text{Au}_{20+8n}(\text{SR})_{16+4n}$  clusters. (a)  $\text{Au}_{50}$ -unit in bulk Au crystal structure. (b)  $\text{Au}_{50}$ -core structure of optimized  $\text{Au}_{76}(\text{SR})_{44}$  cluster. To determine the coordinate position of each Au atom, we make YOZ plane of Cartesian coordinates be parallel to the surface of the paper with z-axis aligning the [100] crystal orientation. The original point O locates at the centre of gravity (CG). (c) Overlap of  $\text{Au}_{50}$ -core of  $\text{Au}_{76}(\text{SR})_{44}$  cluster and  $\text{Au}_{50}$ -unit in bulk Au crystal structure. The CGs of them are forced to coincide. The layer index “m” for each layer is listed. For odd- $N$  cluster, the layer “m=0” is the most middle layer. For even- $N$  cluster, the layer “m=0” chooses one of the two layers near the CG.

The MD value is calculated as follows. Taking  $\text{Au}_{76}(\text{SR})_{44}$  cluster as the example. We first cut an  $\text{Au}_{50}$ -unit (denoted as “Au-crystal”, balls with green color in Figure S4a) from a bulk Au-crystal structure, which is regarded as a reference standard of zero-distortion. Then, we calculated the mass centre of this  $\text{Au}_{50}$ -unit and the  $\text{Au}_{50}$ -core (denoted as “Au-core”, pink color in Figure S4b) in the Au-cores of

Au<sub>76</sub>(SR)<sub>44</sub> cluster. The two kinds of Au<sub>50</sub> structures are then put into the same coordinate system and their mass centers are kept overlap (Figure S4c). Consequently, one-to-one relationship between Au-crystal and Au-core has been established.

Based on the Cartesian coordinates, we defined four parameters to measure the atomic positions deviation. The MD values of the coordinate positions for all Au-core atoms in each cluster (MD<sub>p-total</sub>) are calculated using eq. s1, where N is the number of Au atoms in Au-core or Au-crystal. In order to analyze more clearly the variation tendency of MD as the cluster length increased, MD<sub>p-total</sub> is decomposed into two components, i. e. the MD values of atomic positions along the direction parallel to the central axis (MD<sub>p-total</sub>(||), i. e. the longitudinal MD), and that in the plane perpendicular to the central axis (MD<sub>p-total</sub>(⊥), i. e. the transversal MD), as described by eq. s2 and s3, respectively. After then, the MD values of coordinate positions for Au<sub>6</sub>-unit in every layer (MD<sub>p-layer-m</sub>, “m” is the layer index) is calculated using eq. s4. The same as MD<sub>p-total</sub>(⊥), the deviation in z-axis is not included in MD<sub>p-layer-m</sub>.

MD<sub>p-total</sub> =

$$\frac{\sum_{j=1}^N \sqrt{[(x_{\text{core}}(j) - x_{\text{crystal}}(j))^2 + (y_{\text{core}}(j) - y_{\text{crystal}}(j))^2 + (z_{\text{core}}(j) - z_{\text{crystal}}(j))^2]}{N} \quad (\text{s1})$$

$$\text{MD}_{\text{p-total}}(\parallel) = \frac{\sum_{j=1}^N |z_{\text{core}}(j) - z_{\text{crystal}}(j)|}{N} \quad (\text{s2})$$

$$\text{MD}_{\text{p-total}}(\perp) = \frac{\sum_{j=1}^N \sqrt{[(x_{\text{core-m}}(j) - x_{\text{crystal-m}}(j))^2 + (y_{\text{core-m}}(j) - y_{\text{crystal-m}}(j))^2]}{N} \quad (\text{s3})$$

$$\text{MD}_{\text{p-layer-m}} = \frac{\sum_{j=1}^6 \sqrt{[(x_{\text{core-m}}(j) - x_{\text{crystal-m}}(j))^2 + (y_{\text{core-m}}(j) - y_{\text{crystal-m}}(j))^2]}{6} \quad (\text{s4})$$

Moreover, we also transform the Cartesian coordinates into spherical polar coordinates to describe the twist angle of the Au atoms more directly. The coordinate position of each Au atoms is then determined by  $(r, \phi, \theta)$ ,

$$r = \sqrt{x^2 + y^2 + z^2}$$

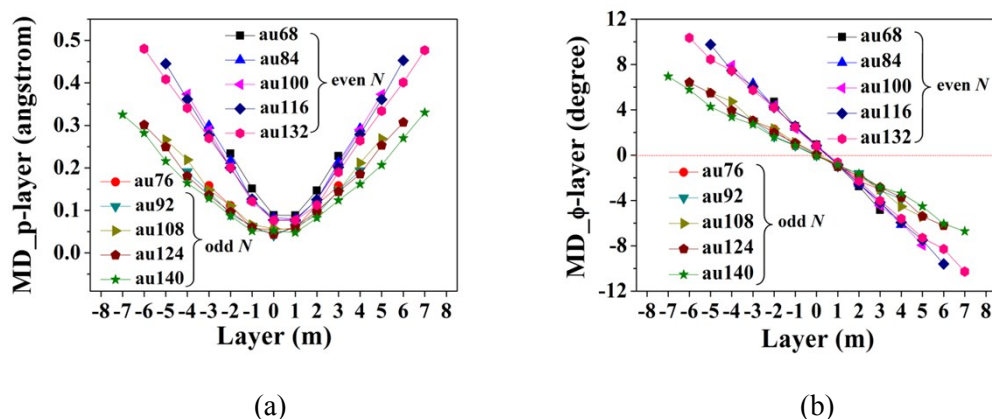
$$\phi = \arctan(y / x)$$

$$\theta = \arccos(z / r)$$

as shown in Figure S4. The initial position of each Au atom in the plane perpendicular to the central axis in Au-crystal or Au-core can be characterized by polar angle  $\phi$ . Therefore, the MD values of distortion angles for Au<sub>6</sub>-unit in every layer (MD <sub>$\phi$</sub> -layer-m) is calculated using eq. s5,

$$\text{MD}_{\phi\text{-layer-m}} = \frac{\sum_{j=1}^6 (\phi_{\text{core-m}}(j) - \phi_{\text{crystal-m}}(j))}{6} \quad (\text{s5})$$

The same scheme is applied to calculate MD <sub>$\phi$</sub> -layer-m values of two Au<sub>4</sub>-units at both ends of the Au-cores, where 6 is instead by 4 in eq. s5. The results of MD <sub>$\phi$</sub> -layer-m are shown in Figure S5.

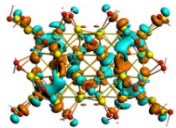
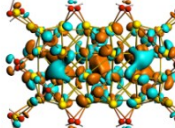
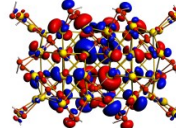
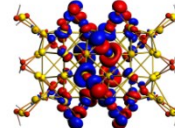
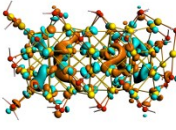
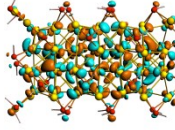
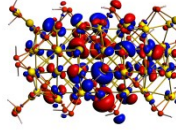
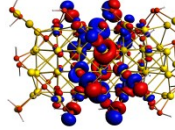
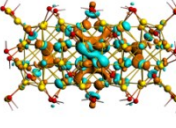
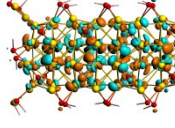
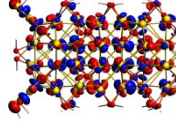
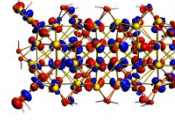
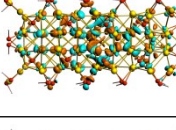
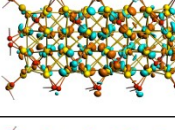
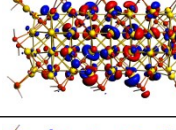
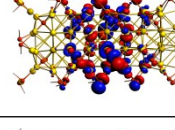
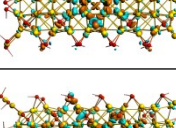
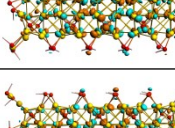
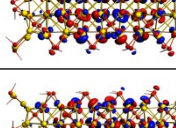
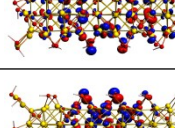
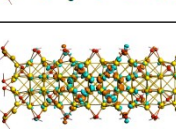
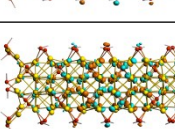
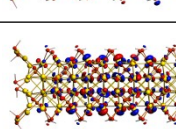
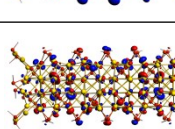
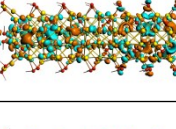
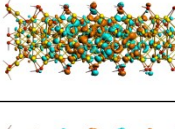
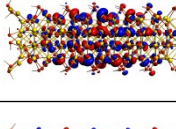
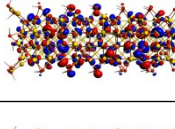
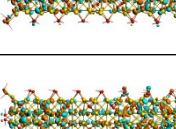
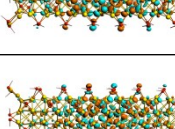
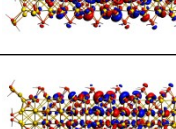
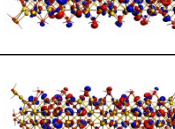
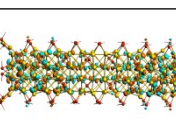
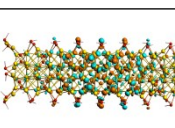
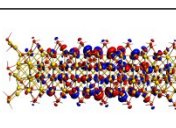
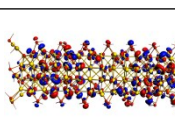

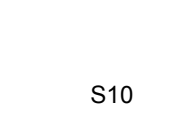








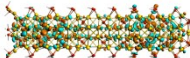
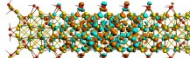
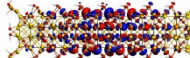
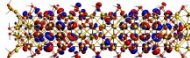
**Figure S5.** The MD values for each layer Au-atoms (MD<sub>p-layer-m</sub> and MD <sub>$\phi$</sub> -layer-m). The definition of layer Au-atoms are given in the text in this Supporting Information.



Herein, we only focus on the MD values of atomic positions in the plane perpendicular to the central axis ( $MD_{p\text{-total}}(\perp)$ ) and the MD values of distortion angles for  $Au_6$ -unit in every layer ( $MD_{\phi\text{-layer-m}}$ ). These parameters reflect the extent of the transversal structural distortion of the Au-core perpendicular to the central axis. The  $MD_{p\text{-total}}(\parallel)$  is ignored due to the stretch of cluster along the central axis direction may affect relatively slight on the stability of the structure.

Figure S6. Electronic density diagrams of HOMO–1, HOMO, LUMO and LUMO+1 of various sized  $\text{Au}_{20+8N}(\text{SR})_{16+4N}$  clusters. The isovalue used for plotting electronic density is 0.02.

$\text{Au}_{20+8N}(\text{SR})_{16+4N}$	<i>LUMO+1</i>	<i>LUMO</i>	<i>HOMO</i>	<i>HOMO–1</i>
$\text{Au}_{52}(\text{SR})_{32}$				
$\text{Au}_{60}(\text{SR})_{36}$				
$\text{Au}_{68}(\text{SR})_{40}$				
$\text{Au}_{76}(\text{SR})_{44}$				
$\text{Au}_{84}(\text{SR})_{48}$				
$\text{Au}_{92}(\text{SR})_{52}$				
$\text{Au}_{100}(\text{SR})_{56}$				
$\text{Au}_{108}(\text{SR})_{60}$				
$\text{Au}_{116}(\text{SR})_{64}$				
$\text{Au}_{124}(\text{SR})_{68}$				
$\text{Au}_{132}(\text{SR})_{72}$				

<b>Au<sub>140</sub>(SR)<sub>76</sub></b>				
<b>Au<sub>148</sub>(SR)<sub>80</sub></b>	