

Supporting Information for

## Structure and Bonding in the Ubiquitous Icosahedral Metallic Gold

### Cluster Au<sub>144</sub>(SR)<sub>60</sub>

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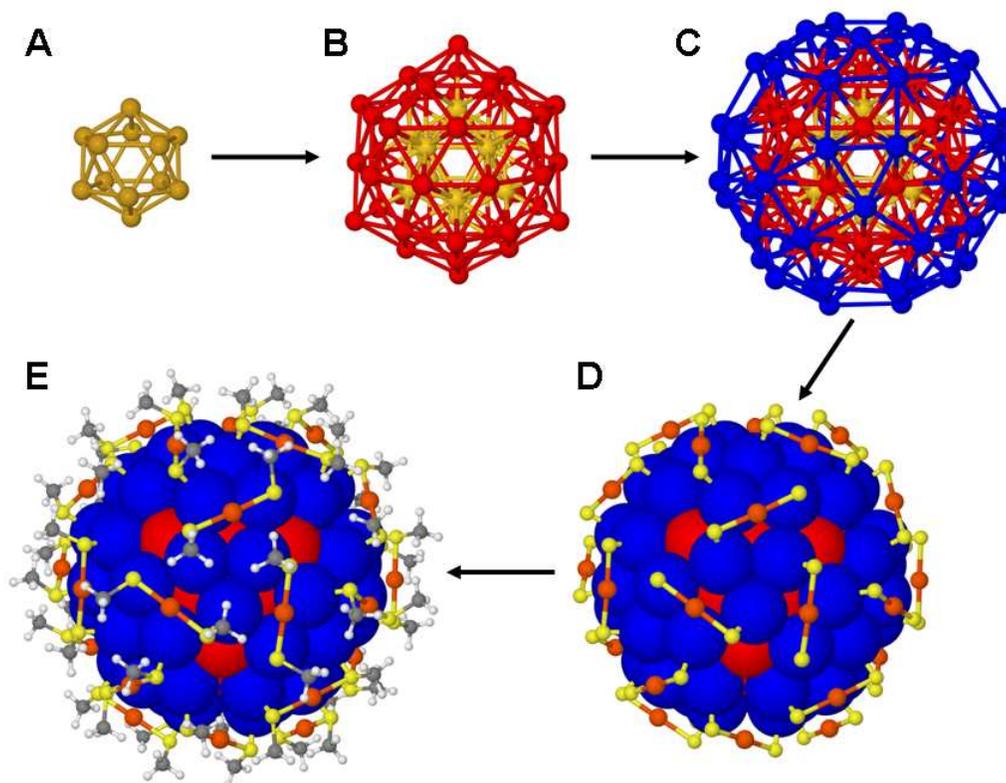
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### 1. Computational methods: GPAW

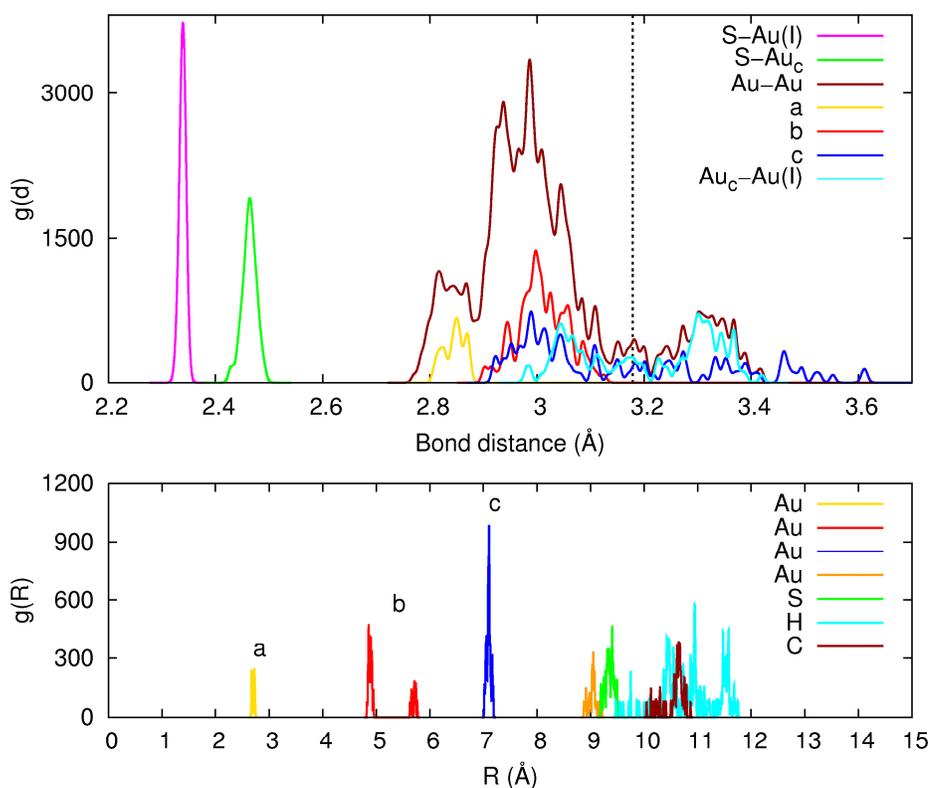
The structural relaxation, solution to the Kohn-Sham problem, and the electronic structure analysis of Au<sub>144</sub>(SR)<sub>60</sub> and Au<sub>145</sub>(SR)<sub>60</sub> clusters (R = Me) were performed using the GPAW code [1]. In this code, the projector augmented wave (PAW) method [2] has been implemented in a real space grid as described in ref. [3]. In the PAW method the all-electron Kohn-Sham wave functions are divided into a smooth part and a highly oscillatory part. The oscillatory part is localized inside an atom-centered sphere, where it can be expanded effectively by atom-centered orbital basis functions. The PAW method solves the equivalent Kohn-Sham equation for a transformed auxiliary wave function that are suitably smooth in the atom-centered sphere. Using this transformation it is possible then to take advantage of coarse grids while the all-electron density is still accessible. The inner electrons were treated in the frozen core approximation, leaving the Au(5d<sup>10</sup>6s<sup>1</sup>), C(2s<sup>2</sup>2p<sup>2</sup>), H(1s), and S(3s<sup>2</sup>3p<sup>4</sup>) as valence electrons. The PAW setup for gold includes scalar-relativistic corrections. Convergence was achieved for a grid spacing of 0.1 Å for the smooth electron density, corresponding to a 69 Ry plane wave cut-off. Structure relaxations were done without any symmetry constraints and deemed converged when the residual forces were smaller than 0.05 eV/Å. The exchange-correlation energy and potential were evaluated using the generalized gradient approximation as derived by Perdew, Burke and Ernzerhof (PBE-functional) [4]. Due to the large number of valence electrons (close to 2400) the spin degree of freedom was not explicitly considered. The calculations to determine the cohesive energy of *fcc* bulk gold were done with 10x10x10 k-point mesh.

## 2. Shell-by-shell visualization of $\text{Au}_{144}(\text{SR})_{60}$



**Fig. S1.** (A) – (C) show the concentric 12-atom (hollow), 42-atom and 60-atom Au shells of the 114-atom gold core, respectively. (D) shows the S-Au-S arrangement of the 30 RS-Au-SR units covering the surface (blue) of the 114-atom gold core and (E) shows all the atoms. Color code in (D), (E): S: yellow, Au(I): orange, C: gray, H: white. Note the sphericity of the 60-atom gold rhombicosidodecahedron shell in (C). A closely related Archimedean solid is the snub dodecahedron (SD), which features only pentagons and equilateral triangles at the surface. Although the surface of a 114-atom core of this symmetry has also 60 gold atoms, it is not possible to cover it with 30 RS-Au-SR units in a manner shown above. The computed XRD pattern of the SD structure differs clearly from the rhombicosidodecahedron and does not agree with the experimental data. Furthermore, by performing restricted-basis-set DFT calculations (DMOL package: B. Delley, *J. Chem. Phys.* 113, 7756 (2000)) for the gold core we found that the snub dodecahedron geometry of the 60-atom layer is not stable but spontaneously relaxes to the rhombicosidodecahedron.

### 3.Radial atomic shells of Au<sub>144</sub>(SR)<sub>60</sub> and distribution of Au-Au and Au-S bonds



**Fig.S2** Top: Atom-atom distance distributions, Bottom: radial atomic shells. In the top figure, labels a-c refer to Au-Au distance distributions within the three shells a-c, shown at the bottom. Au(I) refers to the aurous Au atom in the RS-Au-SR unit and Au<sub>c</sub> is the surface atom of the core. The vertical dashed line is the ideal Au-Au distance in the 60-atom surface shell (label c) of a perfect rhombicosi-dodecahedron with radius of 7.1 Å. Note the two distinct S-Au bonds in the top panel.

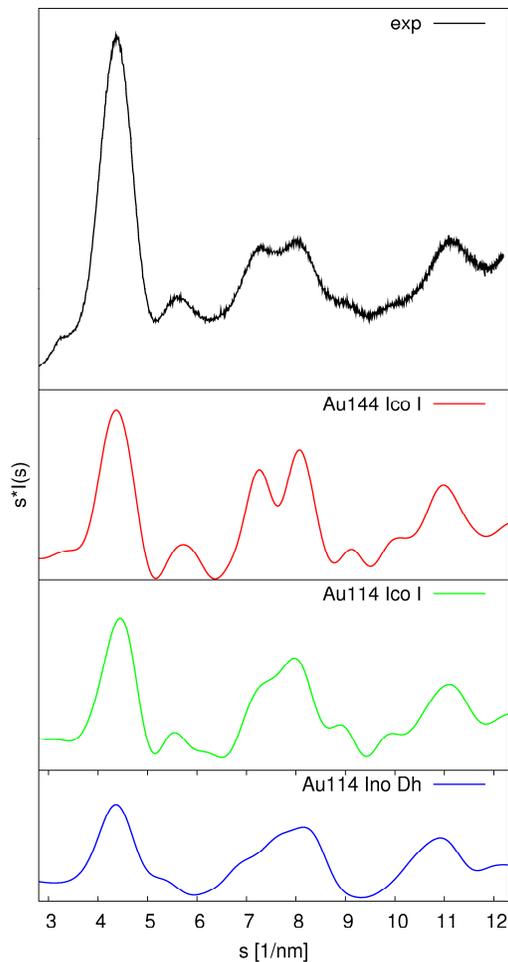
Au shell label in Fig2	Distance to center of mass for gold atoms (Å)	Mean and standard deviation of radius (Å)
a	2.0<r<4.0	2.706 (0.024)
b	4.0<r<5.2	4.886 (0.030)
b	5.2<r<6.2	5.704 (0.039)
c	6.2<r<8.0	7.099 (0.039)
	8.0<r	9.039 (0.080)

**Table 1.** Radial distribution of gold atoms, the table values correspond to the first five peaks in Fig 2. (bottom). The standard deviation shows the nearly perfect spherical distribution of the metallic core ( $r < 8.0$  Å).

Bonds	Shell label, gold radial distance (Å)	Mean and standard deviation of bond distances (Å)
Au-Au	a: 2.0<r<4.0	2.845 (0.019)
Au-Au	b: 4.0<r<6.2	3.010 (0.047)
Au-Au	c: 6.2<r<8.0	3.154 (0.187)
Au-S	$r > 8.0$ (Au in ligand shell)	2.339 (0.004)
Au-S	6.2<r<8.0 (Au in core)	2.463 (0.013)

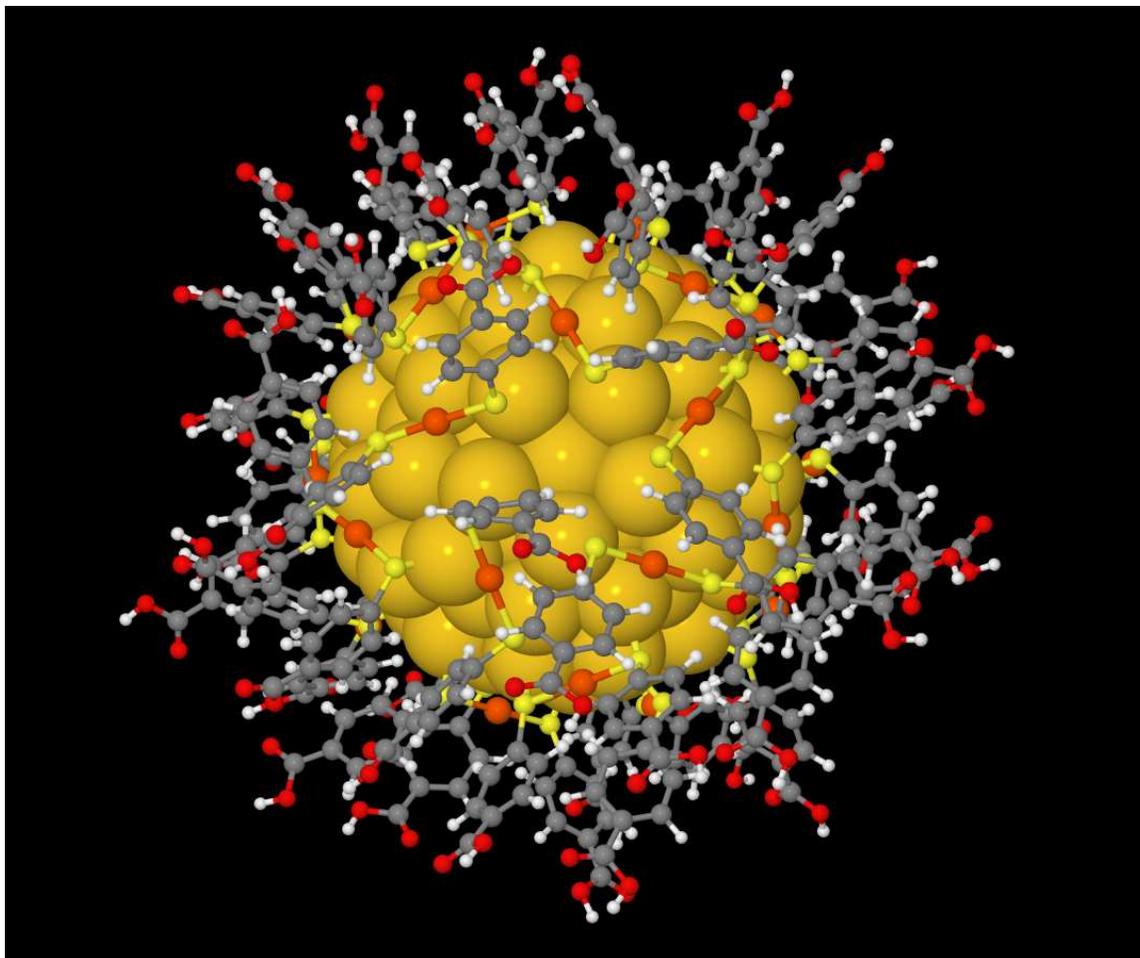
**Table 2.** Bond distance distribution of Au-S bonds and Au-Au bonds inside a given shell.

#### 4. Comparison of XRD structure factors for Au<sub>114</sub> Ino-decahedral and icosahedral cores



**Fig. S3.** From top to bottom: The experimental XRD function (ref. 19 of the main text), the theoretical structure factor for the fully relaxed Au<sub>144</sub>(SMe)<sub>60</sub>, the structure factor of the Au<sub>114</sub> core of the Au<sub>144</sub>(SMe)<sub>60</sub> particle, and the structure factor calculated for an Ino-decahedral Au<sub>114</sub> core, suggested in ref. 21 of the main text. Note that the Ino-decahedral core fails to yield the features for  $s = 9, 10 \text{ nm}^{-1}$ , present in the experiment and reproduced by our Au<sub>144</sub>(SMe)<sub>60</sub> cluster.

## 5. $\text{Au}_{144}(\text{p-MBA})_{60}$



**Fig. S4.** The structure of  $\text{Au}_{144}(\text{SR})_{60}$  with  $\text{R} = \text{p-MBA}$  (para mercapto benzoic acid). The colors are the same as in Fig. 1 on the main text. Additionally, oxygen is shown in red. The figure shows the optimized structure of the ligand shell, with the fixed Au core structure taken from  $\text{Au}_{144}(\text{SR})_{60}$  with  $\text{R} = \text{Me}$ . The cluster has 1044 atoms, 4644 valence electrons and a diameter of 3.2 nm. The optimization was done with the CP2K code [7] and the set-up has been described in ref. [8].

## 6. Calculation of the XRD intensity

The theoretical XRD intensities were calculated by use of the Debye formula following Ref. [5]:

$$I(s) = \sum_i \sum_{j \neq i} \frac{\cos \theta}{(1 + \alpha \cos^2 2\theta)} \exp\left(-\frac{Bs^2}{2}\right) f_i f_j \frac{\sin(2\pi s d_{ij})}{2\pi s d_{ij}},$$

where the double summation is over all the atom pairs of the cluster and  $s=2\sin\theta / \lambda$  is the diffraction vector length.  $\lambda$  and  $\alpha$  were determined by the experimental set-up [6] and were set to 0.15405 nm and 1.01, respectively.  $B$  is a damping factor owing to thermal vibrations and was set to  $0.01 \text{ nm}^2$ . The corresponding atomic numbers were used for the scattering factors  $f_i$ .  $d_{ij}$  is the distance between atom  $i$  and  $j$ . It is well-known that the PBE approximation to the exchange-correlation functional overestimates Au-Au bond lengths. Within the present scheme, the lattice constant of Au in fcc bulk is calculated to be 4.18 Å. This is 2.6 percent longer than the experimental value of 4.07 Å. We have taken this into consideration by scaling the theoretical bond lengths by 0.974 in the calculations of the XRD intensity.

## 7. Angular momentum analysis of Kohn-Sham wave functions

The Kohn-Sham states were analyzed with respect to the globular angular momentum. Taking the center for the expansion to be the center of mass of the cluster we calculate the coefficients

$$c_{i,l}(R_0) = \sum_m \int_0^{R_0} r^2 dr |\varphi_{i,lm}(r)|^2$$

where

$$\varphi_{i,lm}(r) = \int d\hat{r} Y_{lm}^*(\hat{r}) \psi_i(\vec{r})$$

and  $i$  is the index of the Kohn-Sham state,  $Y_{lm}$  is the spherical harmonic function with  $l$  as the angular quantum number and  $m$  as the magnetic quantum number. We consider angular momenta up to  $l=6$  (I-symmetry). The expansion is made in a sphere of radius  $R_0$ , where  $R_0$  was chosen to be 8.5 Å.

## References

1. <https://wiki.fysik.dtu.dk/gpaw>.
2. P.E. Blöchl, *Phys. Rev. B* **50**, 17953 – 17979 (1994).
3. J.J. Mortensen, L.B. Hansen, K.W. Jacobsen, *Phys. Rev. B* **71**, 035109 (2005).
4. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 – 3868 (1996).
5. C.L. Cleveland, U. Landman, M.N. Shafigullin, P.W. Stephens, R.L. Whetten, *Z. Phys. D* **40**, 503 (1997).
6. T. G. Schaaff, M. N. Shafigullin, J. T. Khoury, Igor Vezmar, and R.L. Whetten, *J. Phys. Chem. B* **105**, 8785 (2001).
7. CP2K Developers Group (2000 - 2007), <http://cp2k.berlios.de>.
8. M. Walter, J. Akola, O. Lopez-Acevedo, P. D. Jadzinsky, G. Calero, C. J. Ackerson, R. L. Whetten, H. Grönbeck, H. Häkkinen, *Proc. Natl. Acad. Sci. USA* **105**, 9157 (2008).
9. The coordinates of Au<sub>144</sub>(SMe)<sub>60</sub> are available upon request from the corresponding author.