## **Supporting Information**

# On the Structure of Thiolate-Protected Au<sub>25</sub>

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#### **Computational methods**

The first principles calculations were performed within the density functional theory (DFT) using the generalized-gradient corrected approximation proposed by Perdew, Burke, and Ernzerhof (PBE) for the exchange-correlation energy functional [1].

The major part of the calculations were performed with the QUICKSTEP/CP2K program [2,3]. The Kohn-Sham orbitals are expanded with localized Gaussian functions and an efficient treatment of the Coulomb potential is achieved by an additional plane-wave representation of the electron density (GPW basis). In particular, a library of contracted molecularly-optimized m-DZVP basis sets [4] was used, and the complementary plane-wave cut-off was set to 320 Ry. Scalar-relativistic pseudo-potentials were used to model the interaction between the valence electrons [Au(5d<sup>10</sup>6s<sup>1</sup>), S(3s<sup>2</sup>3p<sup>4</sup>), C(2s<sup>2</sup>2p<sup>2</sup>), and H(1s)] and the atomic cores [5]. The calculations were done by using a cubic (35 Å edge) embedding geometry free from periodic boundary conditions.

The theoretical XRD patterns were calculated by use of the Debye formula following Reference [9]:

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

where  $s=2\sin\theta / \lambda$  is the diffraction vector length.  $\lambda$  and  $\alpha$  are determined by the experimental set-up and was set to 0.1051967 nm and 1.01, respectively. *B* is a damping factor owing to thermal vibrations and was set to 0.03 nm<sup>2</sup>. 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 bonds by ~3 percent. Within the present scheme, the bond length of the Au<sub>2</sub> dimer is calculated to be 2.56 Å which is 3.6 percent longer than the experimental value of 2.47 Å. We have taken this into consideration by scaling the theoretical bond lengths by 0.97 in the calculations of the XRD-pattern.

The optical spectra and the angular analysis of the Kohn-Sham states were performed with the GPAW program [6]. In this method, the projector augmented wave (PAW) method [7] has been implemented in a real space grid [8]. The core electrons are in this approach treated within the frozen core approximation. The frozen core states are obtained from calculations of isolated atoms including a scalar relativistic potential. The grid spacing was set to 0.1 Å for the smooth electron density, which corresponds to a 69 Ry plane-wave cut-off.

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

$$c_l(R_0) = \sum_m \int_0^{R_0} r^2 dr \, |\, \psi_{nlm}(r) \, |^2$$

where

$$\psi_{nlm}(r) = \int d\hat{r} Y_{lm}(\hat{r}) \psi_n(r)$$

and *n* 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 4.0 Å.

The optical spectra were calculated the linear-response time-dependent DFT formalism [10]. In brief, the weights  $F_I$  and energies  $\hbar\omega_I$  of optical transition *I*, are obtained by solving the eigenvalue problem  $\Omega F_I = \omega_I^2 F_I$ . The matrix elements of  $\Omega$  contain the energy difference of Kohn-Sham (KS) single-particle energies and the coupling matrix that mixes the KS particle-hole transition (ij) with (kl) owing to the linear response of the density on the excitation. The convergence of the spectra depends on the extent of the KS particle-hole basis and on the size of the grid representing the wave functions. The results presented here are converged up to 3.5 eV.

## **Structural analysis**

Figure S1 shows the full structure of isomer **1-3** (anions) in two views. Additional structures considered included cuboctahedral and decahedral Au<sub>13</sub> cores protected by 6 (RS-Au-RS-Au-RS) complexes. Such structures are, however, not minima on the potential energy surface.



**Figure S1**. Optimized anionic structures. Atomic color code: Orange (Au), yellow (S), grey (C) and white (H).

Mean bond distances and angles for the three isomers in the different charge states are reported in Table S1.

| Table S1. Mean bond distances (Å) and angles (°). For cases with appreciable standard |  |
|---------------------------------------------------------------------------------------|--|
| deviations, these are reported in parenthesis.                                        |  |

| Isomer      | Au-         | -Au         | Au-S |       | C-S S-Au-S |             | Au-S-Au    |             |  |  |
|-------------|-------------|-------------|------|-------|------------|-------------|------------|-------------|--|--|
| (charge)    | core        | core-       | Core | Comp- |            |             | core       | complex     |  |  |
|             |             | complex     |      | lex   |            |             |            |             |  |  |
|             |             |             |      |       |            |             |            |             |  |  |
| 1 (anion)   | 2.98 (0.10) | 3.30 (0.09) | 2.45 | 2.36  | 1.84       | 171.8 (0.9) | 90.2 (0.8) | 100.5 (0.4) |  |  |
| 1 (neutral) | 3.00 (0.15) | 3.34 (0.14) | 2.44 | 2.36  | 1.84       | 171.2 (1.4) | 91.8 (1.2) | 99.3 (0.5)  |  |  |
| 1 (cation)  | 3.00 (0.20) | 3.32 (0.20) | 2.44 | 2.36  | 1.84       | 170.8 (1.9) | 93.4 (2.1) | 98.4 (1.3)  |  |  |
|             |             |             |      |       |            |             |            |             |  |  |
| 2 (anion)   | 2.82 (0.08) | 3.19 (0.27) | -    | 2.36  | 1.84       | 173.2 (2.5) | -          | 97.1 (3.3)  |  |  |
| 2 (neutral) | 2.81 (0.04) | 3.19 (0.28) | -    | 2.36  | 1.84       | 173.3 (2.4) | -          | 97.1 (3.1)  |  |  |
| 2 (cation)  | 2.80 (0.02) | 3.18 (0.27) | -    | 2.36  | 1.84       | 173.4 (1.7) | -          | 97.5 (3.5)  |  |  |
|             |             |             |      |       |            |             |            |             |  |  |
| 3 (anion)   | 2.82 (0.08) | 3.17 (0.23) | -    | 2.40  | 1.84       | 165.1 (7.7) | -          | 88.6 (6.8)  |  |  |
| 3 (neutral) | 2.82 (0.02) | 3.18 (0.23) | -    | 2.39  | 1.84       | 166.3 (6.4) | -          | 89.0 (7.1)  |  |  |
| 3 (cation)  | 2.81 (0.02) | 3.18 (0.23) | -    | 2.38  | 1.84       | 167.4 (6.6) | -          | 89.2 (7.4)  |  |  |

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