Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Material

Is the largest aqueous gold cluster a superatom complex? Electronic structure & optical response of the structurally determined $Au_{146}(pMBA)_{57}$.

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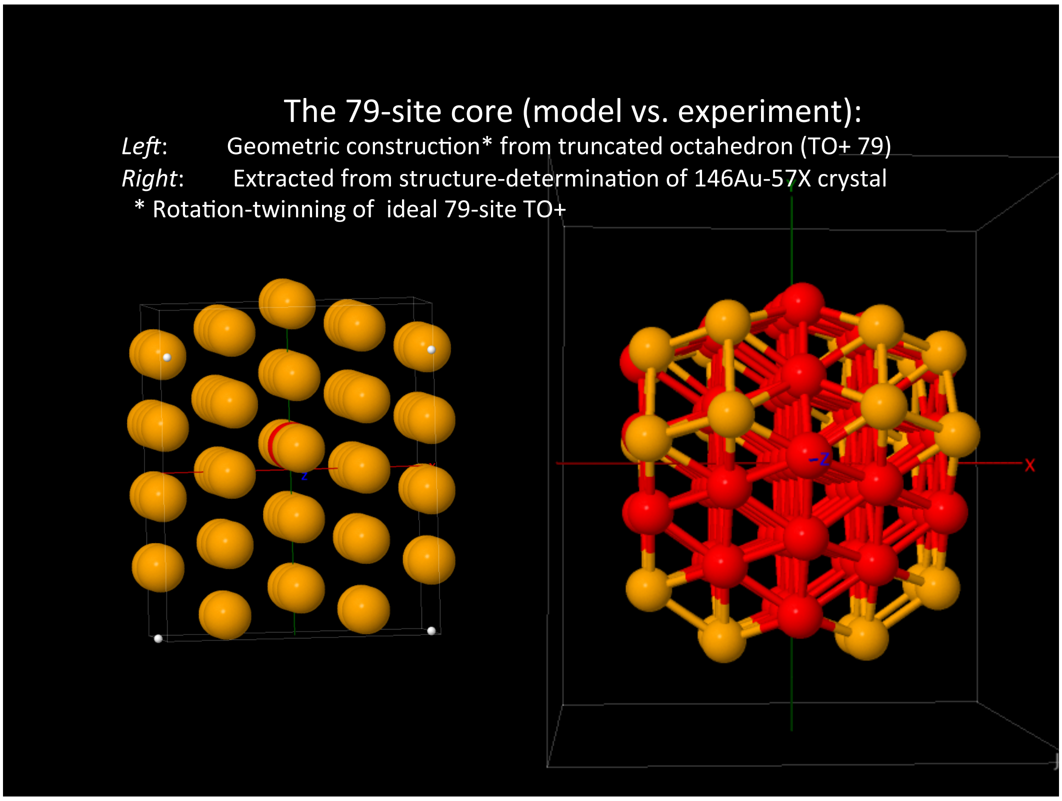


The 79-site core (model vs. experiment):

Left: Geometric construction* from truncated octahedron (TO+ 79)

Right: Extracted from structure-determination of 146Au-57X crystal

* Rotation-twinning of ideal 79-site TO+

Figure S1. Visualization of the 79-site core that shows the twinned 79-atom truncated octohedron.

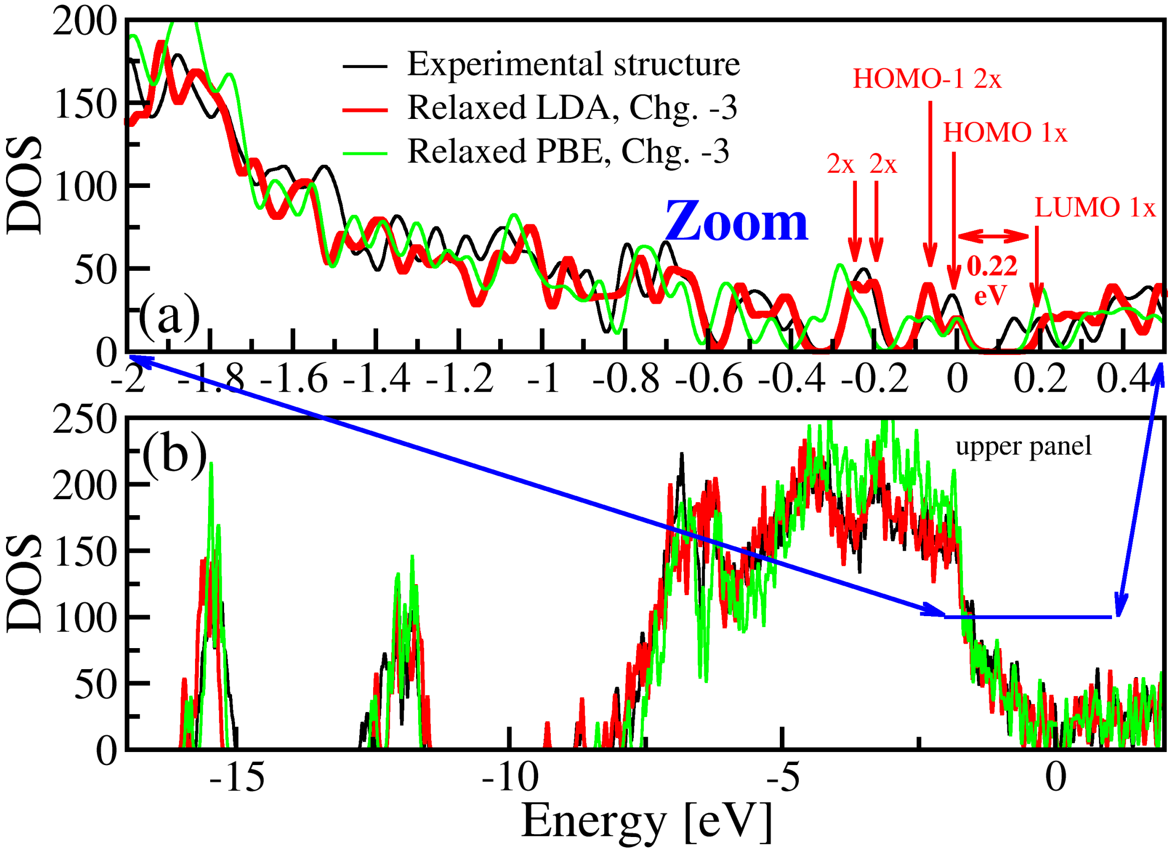


Figure S2. Comparison of density of states of the R=CH_3 calculations. We compare the unrelaxed structure from experiment *as is*, the structure after relaxation using the LDA functional, and the GGA functional PBE. The respective HOMO-LUMO gaps are 0.14 eV (unrel), 0.22 (LDA), and 0.20 eV (PBE).

Projection of orbitals onto spherical harmonics to obtain the angular-momentum-projected density of states (pDOS)

To obtain the angular-momentum-projected DOS, we follow Ref. 1 and calculate the projection coefficients

$$w_{i,l} = \sum_{m=-l}^{l} \int \rho^2 d\rho \left| \int d\Omega \, Y_{l,m}[\Omega] \, \psi(\mathbf{r}) \right|^2 = \sum_{m=-l}^{l} \sum_{n} |c_{nlm}|^2 \tag{1}$$

where ψ_i are the Kohn-Sham wave functions from the octopus ground-state calculation, $Y_{l,m}$ the spherical harmonics, and the c_{nlm} are the expansion coefficients

$$\psi(\rho, \phi, \theta) = \sum_{nlm} c_{nlm} R_{nlm}(\rho) Y_{lm}(\phi, \theta) \tag{2}$$

The integration was done up to a radius R_{cut}. For the present system, the result was found to be very insentitive to the choice of R_{cut}.

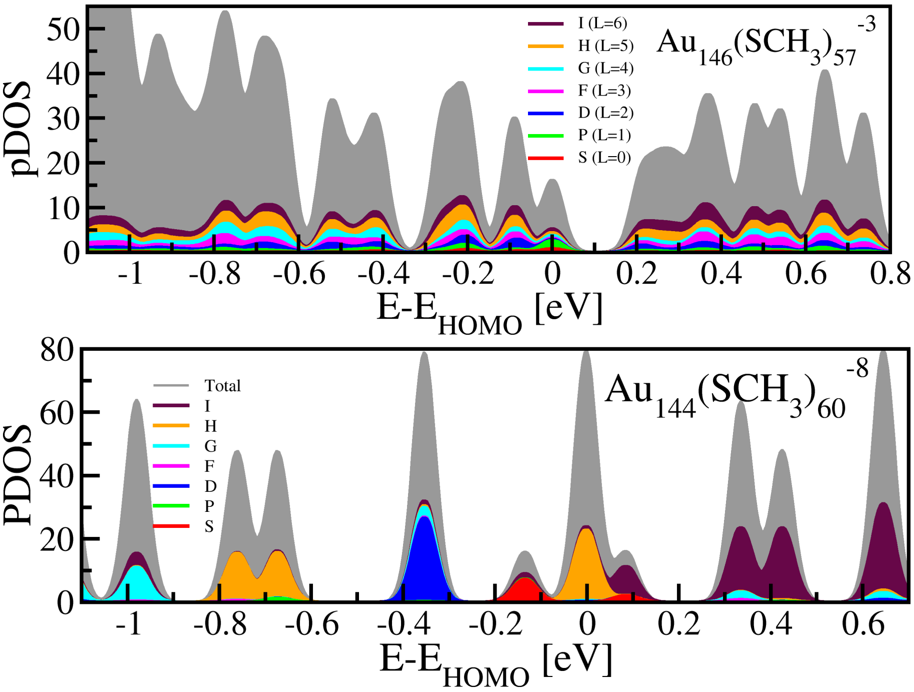


Figure S3. Complement to Fig. 3 of the article, showing the total DOS in addition to the projected DOS.

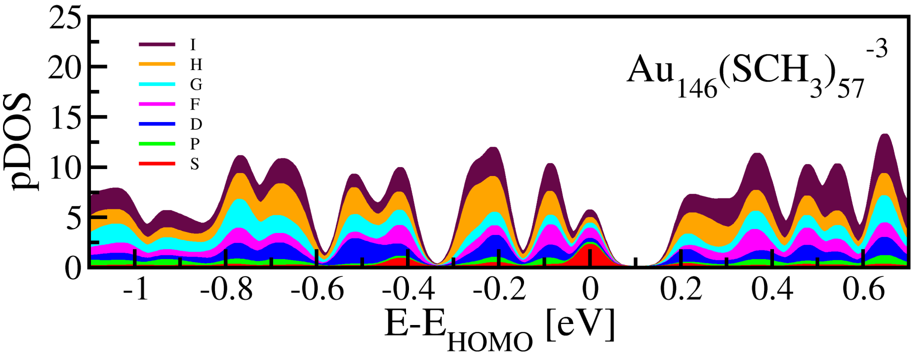


Figure S4. The projection of the pDOS shown in the article was done using the central atom of the cluster as origin. The present figure shows a test using instead the center of mass. Clearly, this did not produce significant differences.

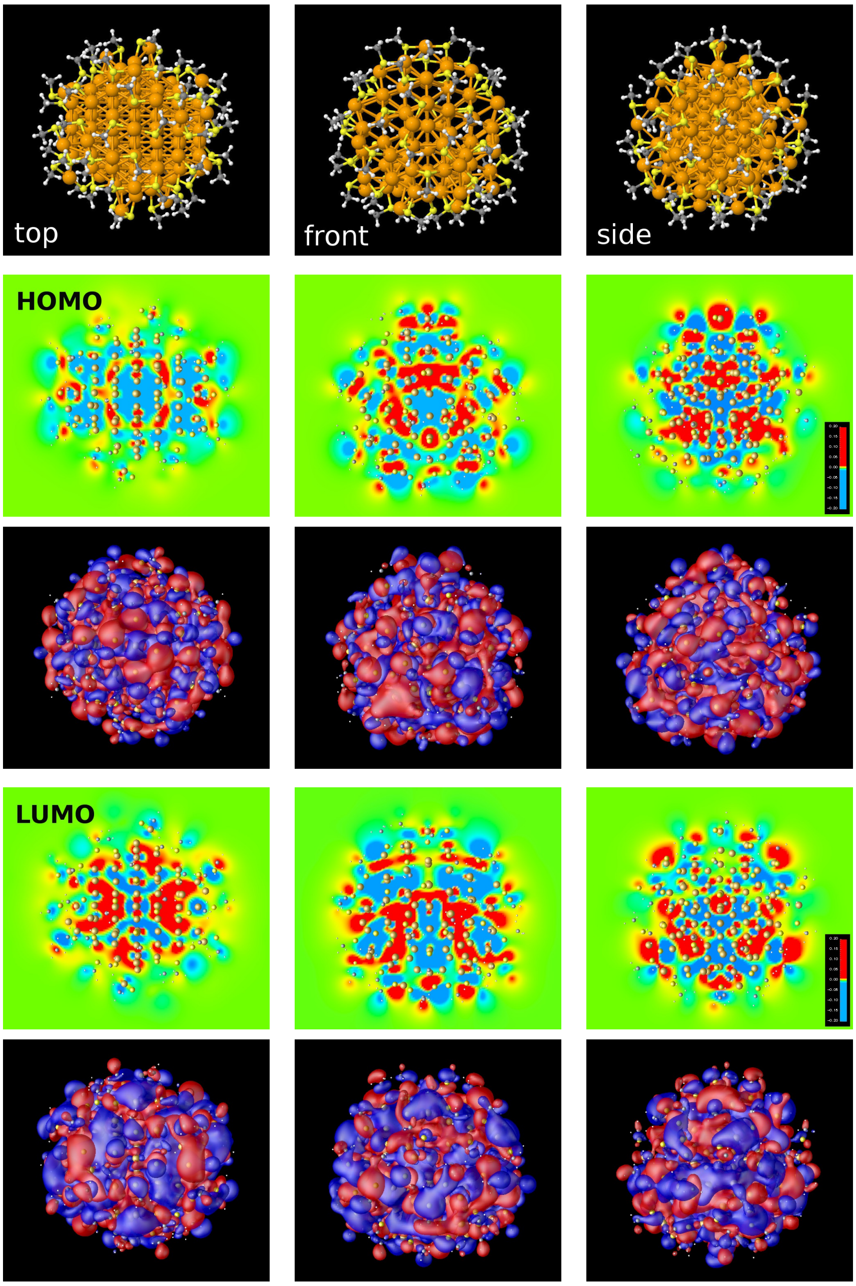


Figure S5: Frontier orbitals of the $Au_{146}(SCH_3)_{57}$ cluster along with the geometry of the $R{=}CH_3$ model used in the calculation. We show the geometry from the three different perspectives (top, front, side) which are then used for the presentation of the states. These are slice representations, cutting through the center of the cluster (blue – negative, red – positive), as well as isosurfaces of the same states (iso value $0.005\,\text{Å}^{-3}$). Note that the top isosurface view of HOMO and LUMO concerns the same states as shown in Fig. 2 of the article; the visual difference comes from the different iso values used. Slice representations of the full series of states around the HOMO-LUMO gap are shown in Fig. S7 of the the ESI.

Note that due to the symmetry, the top views of the slice representations have an *approximate* mirror symmetry at the center (representing the symmetry of the core), which is, however, broken in the periphery so that only the screw-like symmetry (180-degree rotation) remains, in accordance with the C_2 symmetry of the full system where the chiral character is introduced in the peripheral Au layer and the ligands. The front and side views for the slices through the center, by contrast, are mirror symmetric. However, this holds only for the slice views cutting through the center. Seen from outside, the system is not symmetric except for the two-fold rotation axis, as it is clearly seen in the isosurfaces.

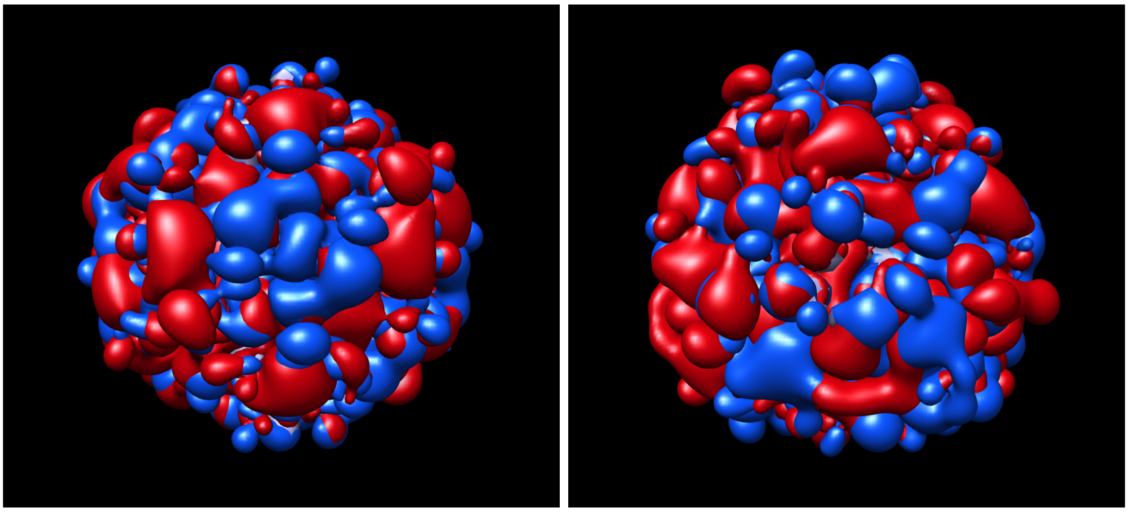
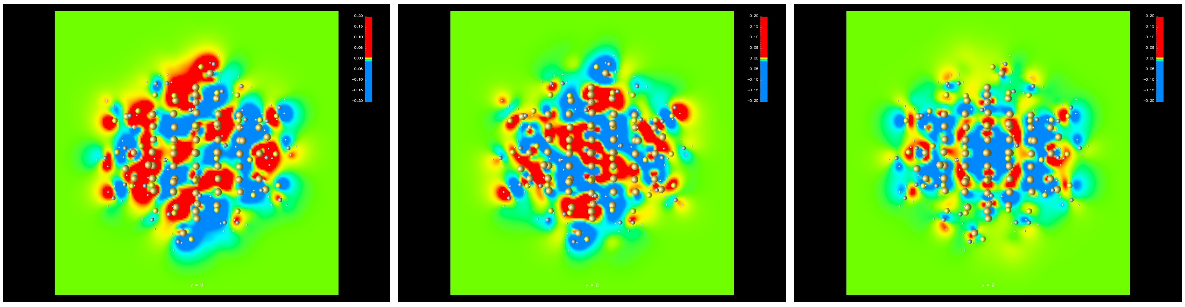
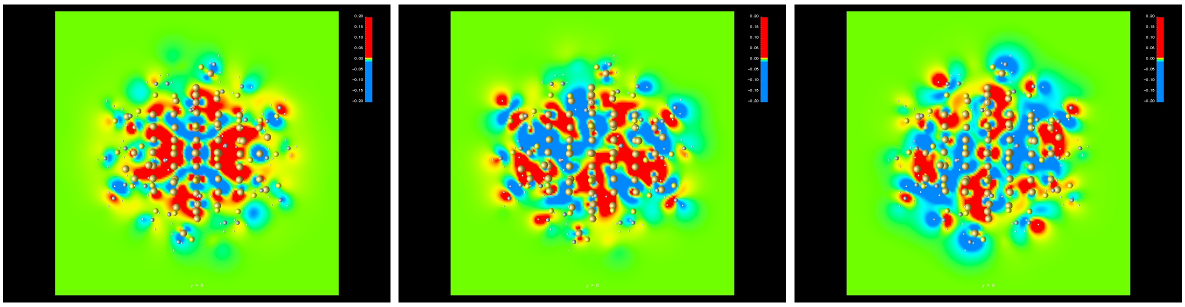


Figure S6. Frontier states of the R=CH_3 calculation seen from top (left panel) and front (right panel). It can be clearly seen that both functions are rather equally distributed throughout the cluster and its surface. They do not, therefore, show any very clear “complementary active sites” in the sense discussed by Reber *et al.*[2]. This means that the cluster should be expected to be unreactive [2]. However, the additional information does not allow for strong conclusions about the *stability* of the cluster and the different possible effects involved.



state 1173 state 1174 **state 1175 HOMO**



state 1176 LUMO state 1177 state 1178

Figure S7. Series of the wave functions of $Au_{146}(SCH_3)_{57}^{-3}$ around the HOMO-LUMO gap (sliced through the center (cutting through the center atom); top view, i.e., we are looking down the two-fold rotation axis.

- States 1174, 1175 = HOMO, 1176 = LUMO, and 1178 are symmetric under the 180 degree rotation around the symmetry axis, the other states (1173, 1177) are **antisymmetric**, i.e., they change sign under the two-fold rotation. The C_2 symmetry is clearly visible.

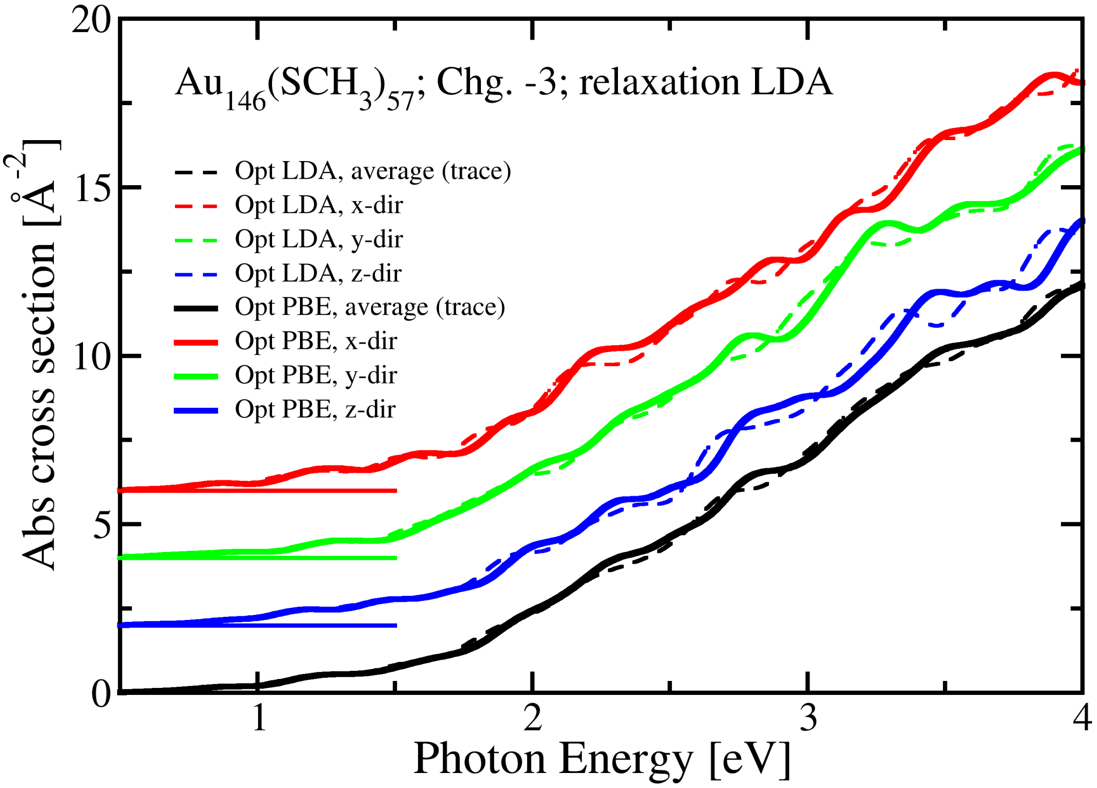


Figure S8. Comparison of spectra calculated using the LDA functional and the GGA functional PBE. Both calculations use the same structure, relaxed using LDA.

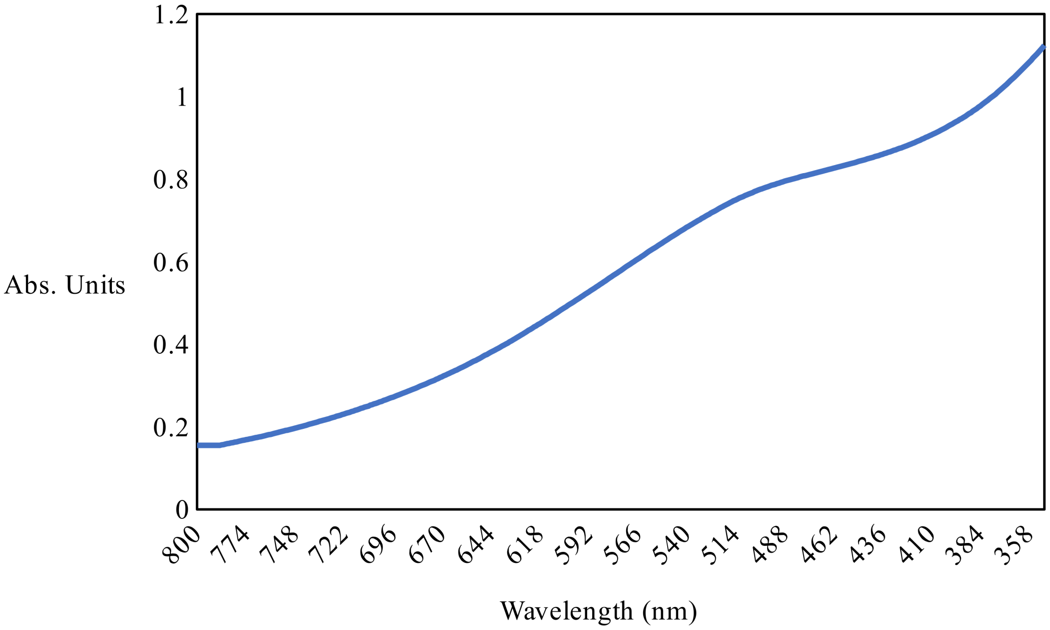


Figure S9. Absorption spectra measured in solution phase.

References

[1] Michael Walter, Jaakko Akola, Olga Lopez-Acevedo, Pablo D. Jadzinsky, Guillermo Calero, Christopher J. Ackerson, Robert L. Whetten, Henrik Grönbeck, and Hannu Häkkinen. A unified view of ligand-protected gold clusters as superatom complexes. *Proceedings of the National Academy of Sciences*, 105(27):9157–9162, 2008.

[2] Arthur C. Reber and Shiv N. Khanna. Superatoms: Electronic and geometric effects on reactivity. *Accounts of Chemical Research*, 50(2):255–263, 2017. PMID: 28182404.