Supplementary Information for:

Role of Ligand-Ligand vs. Core-Core

Interactions in Gold Nanoclusters

Karolina Z. Milowska* and Jacek K. Stolarczyk*

*Photonics and Optoelectronics Group, Department of Physics and Center for NanoScience
(CeNS), Ludwig-Maximilians-Universität München, Amalienstr. 54, 80799 Munich,
Germany*

Nanosystems Initiative Munich (NIM), Schellingstr. 4, 80799 Munich, Germany

E-mail: Karolina.Milowska@physik.uni-muenchen.de; Jacek.Stolarczyk@physik.uni-muenchen.de

Details of the colloidal approach

The van der Waals attraction for two spherical gold nanoparticles (AuNPs) of the same size is calculated using the Hamaker-formalism[1,2] with no retardation taken into account due to the small size - and hence small center-to-center distances relevant for the nanoparticle-nanoparticle interaction.

$$\Phi_{vdW} = -\frac{A_{psp}}{6} \left(\frac{2R^2}{r^2-4R^2} + \frac{2R^2}{r^2} + ln \left(\frac{r^2-4R^2}{r^2} \right) \right),$$

(1)

where R is the radius of the gold cores (2.94 Å, 4.44 Å, 8.31 Å for Au_{11}, Au_{38}, and Au_{144}, respectively), r is distance between them, and A_{psp} is a Hamaker constant for those two gold particles p interacting through the medium s. A_{psp}, the combined Hamaker constant, can be calculated from the individual Hamaker constants of both materials as:[3-6] $A_{psp} = \left(\sqrt{A_p} - \sqrt{A_s} \right)^2$, ($A_p = 2 \cdot 10^{-19}$ J for ultra-small AuNPs, $A_s = 5.4 \cdot 10^{-20}$ J for toluene[7]). The van der Waals interaction in studied system could be considered as constant for the whole relevant temperature and surface separation range.

To describe steric interaction Φ_{steric} we have chosen approach derived from the theory of polymer mixing introduced by Meier,[8] Napper[9-11] and Vincent[12,13] and developed for nanoparticles covered by alkylthiol monolayers by Shah et al.[3] The steric interaction can be described in terms of osmotic and elastic repulsions and both are inherently short range interactions.

The osmotic repulsion Φ_{osm} results from the interdigitation of ligand chains at sufficiently small distances between the nanoparticles ($r < (2R + 2l)$). Consequently, the volumes they are assumed to occupy start to overlap, forcing the exclusion of the solvent molecules. The potential needed to balance the osmotic pressure difference, and hence prevent the influx of solvent particles into the region with a reduced solvent concentration, effectively constitutes an additional repulsive term. Therefore one needs to consider two regimes. In the first regime ($(2R + l) \leq r < (2R + 2l)$) only interpenetration is described, whereas in second

one $(r < (2R + l))$ interpenetration is taken into account with compression. The expression of osmotic interaction potential between two nanoparticles of the same size R is given by formula:

$$
\Phi_{osm} =
\begin{cases}
\frac{4\pi R k_B T N_A}{V_s} \phi^2 \left(\frac{1}{2} - \chi\right) \left(l - \frac{r-2R}{2}\right)^2, & for \quad (2R + l) \leq r < (2R + 2l), \\[3mm]
\frac{4\pi R k_B T N_A}{V_s} \phi^2 \left(\frac{1}{2} - \chi\right) l^2 \left(\left(\frac{r-2R}{2l}\right) - \frac{1}{4} - ln\left(\frac{r-2R}{l}\right)\right), & for \quad r < (2R + l), \\[3mm]
0, & for \quad r \geq (2R + 2l),
\end{cases}
\tag{2}
$$

where k_B is the Boltzman constant, N_A is Avogadro constant, and T is temperature (298.15 K). l, the ligand length was taken from DFT (GGA) calculations as a distance between sulfur atom and most distant carbon atom form a core (1.83 Å, 2.87 Å, 3.10 Å, 5.31 Å, 6.48 Å, 7.89 Å, 8.61 Å, and 10.03 Å for -SCH$_3$,.., -SC$_8$H$_{17}$). χ is the Flory-Huggins interaction parameter quantifying the affinity between the ligand and the solvent and is given by the equation: $\chi = \frac{V_s}{RT}(\delta_s - \delta_l)^2$, where δ_s and δ_l are the Hildebrand solubility parameters of the solvent and ligand, respectively ($1.82 \cdot 10^4$ Pa$^{0.5}$ for toluene[7,14] and $1.62 \cdot 10^4$ Pa$^{0.5}$ for alkane chain[7,14]). Only alkane chains are assumed to take part into the interaction. The total value of χ for thiol protected AuNPs in toluene is 0.2, which indicates strong osmotic effects. V$_s$, the molar volume of solvent is equal to $\frac{M_s}{\rho_s}$, where M_s is molar mass of solvent ($9.214 \cdot 10^{-2}$ kg/mol for toluene), and ρ_s is density of solvent (890 kg/m^3 for toluene at room temperature). ϕ, the surface coverage fraction by the stabilizing ligand is defined as:

$$
\phi = \frac{2lC}{r-2R}, \quad C = \frac{N_l A_l}{A_{core}},
\tag{3}
$$

where C is a coverage of core by ligands, N_l is number of ligands (10, 24, and 60 for Au_{11}, Au_{38}, and Au_{144}, respectively), A_l is the area occupied by the one thiol on the particle surface (15.2 Å^2 for ultra-small AuNPs[15,16]), A_{core} is the area of core calculated using YASARA

program[17] as van der Waals surface of AuNPs core (242.3 Å^2, 449.2 Å^2, and 1292.7 Å^2 for Au_{11}, Au_{38}, and Au_{144}, respectively).

The elastic interactions Φ_{els} arise because of loss of configurational entropy of the ligand chains when the particles are at very close distances so that their ability to move freely is restricted. In other words elastic term describes mechanical compression of ligands preventing contact of cores. This interaction potential was derived by Napper[9,11] and Vincent[13] in a similar manner to the osmotic interactions:

$$\Phi_{els}=\begin{cases}\frac{2\pi Rk_BTN_AC}{M_l}l^2\phi\rho_l\left(\left(\frac{r-2R}{l}\right)\ln\left(\left(\frac{r-2R}{l}\right)\left(\frac{3l-r+2R}{2l}\right)^2\right)-6\ln\left(\frac{3l-r+2R}{2l}\right)+\\ \\ \qquad\qquad\qquad +3\left(\frac{l-r+2R}{l}\right)\right),\quad for\quad r<(2R+l),\\ \\ \\ 0,\quad for\quad r\geq(2R+l),\end{cases}\qquad(4)$$

where ρ_l is density of ligand (843 kg/m^3 at room temperature for all studied thiols), and M_l is molar mass of ligand (4.710·10^{-2} kg/mol, 6.113·10^{-2} kg/mol, 7.515·10^{-2} kg/mol, 8.918·10^{-2} kg/mol, 10.321·10^{-2} kg/mol, 11.723·10^{-2} kg/mol, 13.126·10^{-2} kg/mol, 14.529·10^{-2} kg/mol, 20.140·10^{-2} kg/mol, for -SCH$_3$,.., -SC$_8$H$_{17}$, respectively).
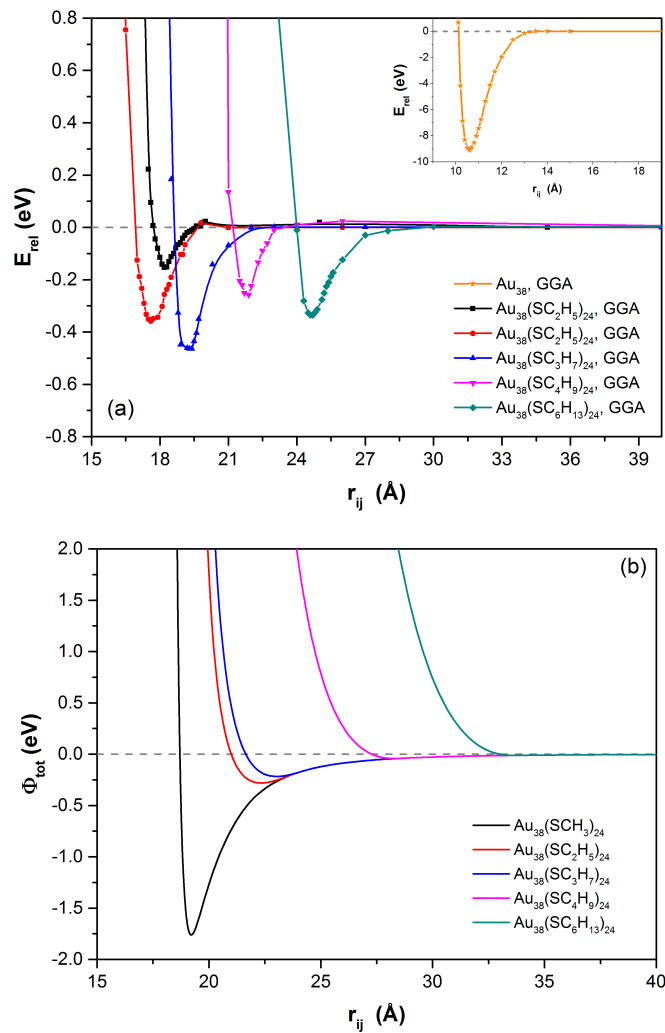
Figure S1: Interaction potential for different ligand length. Interaction potential profile calculated in (a) *ab initio* and (b) colloidal approach between two Au_{38} NCs for different lengths of ligands. r_{ij} is the distance between centres of cores. Inset: Interaction potential for bare Au_{38}
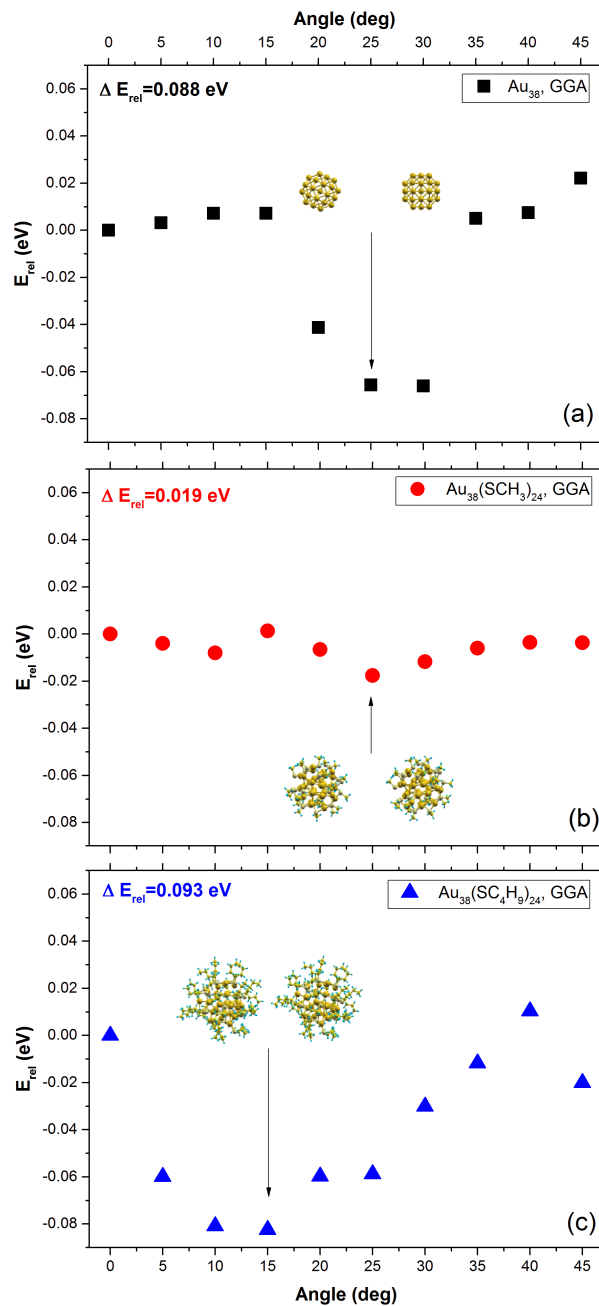
Figure S2: The influence of crystal orientation on interaction potential. The relative energy of interactions between two Au_{38} NCs (a) unprotected and protected with (b) -SCH_3 and (c)-SC_4H_9 ligands at the distance of 25Å as a function of angle between two different (100) facets.

(a)   (b)

Scale: Δ n(r)

■ -0.0870
■ -0.0580
□ -0.0290
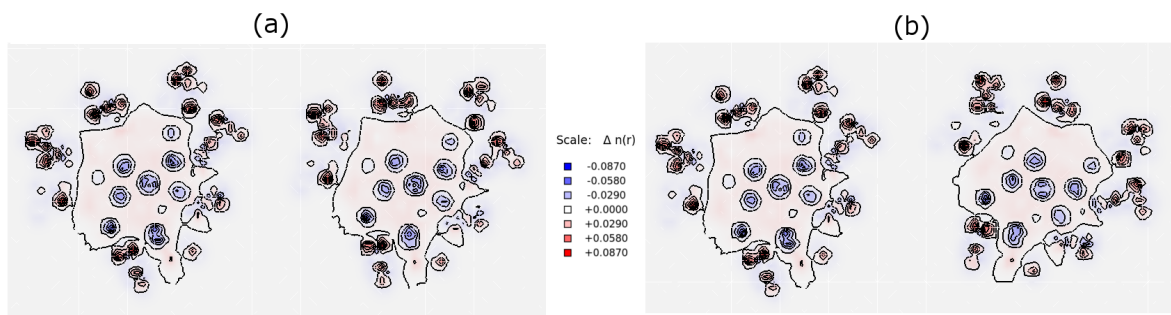□ +0.0000
■ +0.0290
■ +0.0580
■ +0.0870

Figure S3:   Changes in electronic properties related to morphology. The difference of the valence pseudocharge density and the superposition of the atomic valence pseudocharge densities (DRHO) for two $Au_{38}(SC_4H_9)_{24}$ clusters at 25Å distance. The angles between corresponding (100) facets from two clusters are equal to (a) 15° and (b) 40°, respectively. Those crystal orientations correspond to maximal and minimal differences in relative energies.

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