# Supplementary information
# The wavelength-dependent non-linear absorption and refraction of $Au_{25}$ and $Au_{38}$ monolayer-protected clusters

Zhicheng Su,[1] Matias Bejide,[1] Piero Ferrari,[1,*] Kevin Anthony Kaw,[1] Michèle Moris,[2], Koen Clays,[2] Stefan Knoppe,[3] Peter Lievens,[1] Ewald Janssens[1,*]

1 Quantum Solid-State Physics, KU Leuven, 3001 Leuven, Belgium
2 Molecular Imaging and Photonics, KU Leuven, 3001 Leuven, Belgium
3 Institute for Physical Chemistry, University of Stuttgart, 70147 Stuttgart, Germany

## 1. Reported nonlinear cross section values for $Au_{25}$ clusters

**Table S1:** Reported nonlinear cross section values for $Au_{25}$ clusters protected using different ligands. Measurements are performed using different wavelengths and laser pulse durations. For comparison, our results measured at 630 nm are provided.

| Cluster[i] | Absorption cross section ($\delta_A$) [$10^4$ GM] | Refraction cross section ($\delta_R$) [$10^4$ GM] | Excitation wavelength [nm] | Laser pulse width | Ref. |
|---|---|---|---|---|---|
| **$Au_{25}(Capt)_{18}$** | 2.4<br>0.085<br>0.15 | -4.0 | 550<br>800<br>900 | < 120 fs | [1] |
| **$Au_{25}(Capt)_{18}$** | $3.85\cdot10^{-6}$ | - | 800 | 100 fs | [2] |
| **PAAM-$Au_{25}(Capt)_{18}$** | $4.97\cdot10^{-6}$ | - | 800 | 100 fs | [2] |
| **$Au_{25}(Capt)_{18}$** | 0.199 | - | 875 | < 130 fs | [3] |
| **$Au_{25}(Capt)_{18}$** | 0.108 | - | 875 | < 130 fs | [3] |
| **$Au_{25}(Capt)_{18}$** | 0.095 | - | 875 | < 130 fs | [3] |
| **$Au_{25}(SG)_{18}$** | $4.99\cdot10^{-4}$ | - | 755 | 140 fs | [4] |
| **$Au_{25}(SG)_{18}$** | 69.9 | - | 810 | 110 fs | [5] |
| **$Au_{25}(SR)_{18}$** | 42.7 | - | 500 | < 50 fs | [6] |
| **$Au_{25}(SR)_{18}$** | 0.27 | - | 1290 | 100 fs | [7] |
| **$Au_{25}Ag_6(SR)_{18}$** | 88.8 | - | 500 | < 50 fs | [6] |
| **$Au_{25}(SH)_{18}^-$** | 43<br>0.27 | - | 400<br>646 | -Computational study | [8] |
| **$Au_{25}(SH)_{18}^-$ (DFT)** | 62 | - | 785 | -Computational study | [8] |
| **$Au_{25}(GSH)_{18}$ film** | 19 | - | 800 | 30 fs | [9] |
| **$Au_{25}(C_6S)_{18}$ film** | 150-1050[ii] | - | 800 | 30 fs | [9] |
| **$Au_{25}(GSH)_{18}$ in water** | 19 | - | 800 | ~ 200 fs | [10] |
| **$Au_{25}(C6)_{18}$ in hexane** | 42.7 | - | 800 | 100 fs | [7] |
| **$Au_{25}(DDT)_{18}$** | 2200 | -2800 | 630 | 6 ns | This work |
| **$Au_{38}(DDT)_{24}$** | 31000 | 14000 | 630 | 6 ns | This work |

[i] SR = $SCH_2CH_2Ph$, SG = $C_{10}H_{17}N_3O_6S$, SG = glutathione, Capt = captopril (Capt), PAAM = Polyacrylamide, GSH = glutathione.
[ii] Range for varying concentrations.
[iii] In Ref. [11], nonlinear absorption coefficients (β) of $Au_{25}(SR)_{18}$ and $Au_{38}(SR)_{24}$ clusters, measured at 532 nm with pulses of 4 ns are $2\cdot10^{-10}$ and $3.5\cdot10^{-10}$ m/W, respectively. These numbers are of similar magnitude as our results at 532 nm, however, values cannot be compared directly because no particle concentrations were given in ref. [11].

## 2. Sample preparation

The synthesis of size selected MPCs follows the Brust-Schiffrin reaction and derived protocols [12]. Briefly, for the $Au_{25}$ clusters, a precursor solution composed of Au(III) tetrachloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$) and tetraoctylammonium bromide ($[CH_3(CH_2)_7]_4N(Br)$) was dissolved in THF. This solution reacts with (pro)ligand 1-dodecanethiol (DDT(-H)) to form an Au(I)-thiolate polymer. Borohydride ($NaBH_4$) dissolved in cold water is used to reduce the formed polymer and assemble the clusters. The crude $Au_{25}$ MPC were then passed over a silica gel column, using dichloromethane as eluent, to oxidize them and neutralize the created negatively charged particles to obtain pure $Au_{25}(SR)_{18}$ MPCs. For the $Au_{38}$ clusters, a methanol solution of Au(III) tetrachloroauric acid trihydrate was mixed with a water solution of glutathione. This allows obtaining glutathionate-stabilized clusters. These clusters were dissolved in a water/acetone solution and mixed with 1-dodecanethiol. The crude $Au_{38}$ MPC were then passed over a silica gel column, with dichloromethane as eluent, to remove the remaining free thiol and insoluble material. This procedure results in pure $Au_{38}(SR)_{24}$ MPCs, as was confirmed by reversed-phase high-performance liquid chromatography measurements [13]. Control over the gold:thiol ratio, solvent, temperature, thiol addition rate, steering speed and time allows the formation of a narrow size distribution of clusters. The desired cluster size can be obtained in pure form by fractionated precipitation, size-exclusion chromatography or (for water-soluble clusters) polyacrylamide gel electrophoresis. This process finally produces an atomically precise particle solution.

## References


[1] J. Olesiak-Banska, M. Waszkielewicz, K. Matczyszyn and M. Samoc, RSC Adv., 6, 98748, 2016.
[2] A. McLean, R. Wang, Y. Huo, A. Cooke, T. Hopkins, N. Potter, Q. Li, J. Isaac, J. Haidar, R. Jin and R. Kopelman, ACS Appl. Nano Mater., 3, 1420–1430, 2020.
[3] J. Olesiak-Banska, M. Waszkielewicz and M. Samoc, Phys. Chem. Chem. Phys., 20, 24523-24526, 2018.
[4] I. Russier-Antoine, F. Bertorelle, M. Vojkovic, D. Rayane, E. Salmon, C. Jonin, P. Dugourd, R. Antoine and P.-F. Brevet, Nanoscale, 6, 13572-13578, 2014.
[5] N. Abeyasinghe, S. Kumar, K. Sun, J. F. Mansfield, R. Jin and T. Goodson III, J. Am. Chem. Soc., 138, 16299–16307, 2016.
[6] R. Ho-Wu, P. Kumar Sahu, N. Wu, T. Kai Chen, C. Yu, J. Xie and T. Goodson III, J. Phys. Chem. C, 122, 24368–24379, 2018.
[7] G. Ramakrishna, O. Varnavski, J. Kim, D. Lee and T. Goodson, J. Am. Chem. Soc., 130, 5032–5033, 2008.
[8] P. N. Day, K. A. Nguyen and R. Pachter, J. Chem. Theory Comput., 6, 2809–2821, 2010.
[9] R. Ho-Wu, S. H. Yau and T. Goodson, ACS Nano, 10, 562–572, 2016.
[10] L. Polavarapu, M. Manna and Q.-H. Xu, Nanoscale, 3, 429-434, 2011.
[11] R. Philip, P. Chantharasupawong, H. Qian, R. Jin and J. Thom-as, Nano Lett., 12, 4661–4667, 2012.
[12] R. Jin, H. Qian, Z. Wu, Y. Zhu, M. Zhu, A. Mohanty and N. Garg, J. Phys. Chem. Lett., 1, 2903–2910, 2010.
[13] S. Knoppe and P. Vogt, Anal. Chem., 91, 1603–1609, 2019.