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SUPPORTING INFORMATION

Far infrared spectra of well-defined thiolate-protected gold clusters

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Experimental

General remarks. Brief description of $Au_{144}(2\text{-}PET)_{60}$, $Au_{40}(2\text{-}PET)_{24}$, $Au_{38}(2\text{-}PET)_{24}$, $Au_{25}(2\text{-}PET)_{18}$ preparation.

Gold nanoclusters Au_{40} (2-PET) $_{24}$ and Au_{38} (2-PET) $_{24}$ were prepared and purified as it was described in previous reports.[1,2] In the first step, glutathione stabilized gold clusters were prepared by reduction of tetrachloroauric acid in presence of glutathione with sodium borohydride in an ice-cooled acetone solution. Following, the solvent was decanted and ethanol, toluene and an excess amount of 2-phenylethanethiol (2-PET) were added to the black precipitate. After etching at 80 °C for 3 h the 2-PET stabilized clusters were purified as described before[1,2] and size separated on a gel permeation column (BioBeads S-X1). The clusters of $Au_{144}(2\text{-}PET)_{60}$ and $Au_{25}(2\text{-}PET)_{18}$ sizes were prepared as it was reported by Qian.[3] Tetrachloroauric acid trihydrate and tetraoctylammonium bromide (TOAB) were dissolved in methanol and stirred 20 minutes before an excess amount of 2-PET was added. To this intensely stirred white dispersion, sodium borohydride dissolved in water was added and the mixture was allowed to react 5 h at room temperature. The clusters were washed with methanol to remove free thiol. The separation of products was based on the different solubility of Au_{25} (2-PET) $_{18}$ and Au_{144} (2-PET) $_{60}$ in acetone. Further, we have improved purification of the clusters in our synthesis using a gel permeation column which also allows to separate the differently charged $Au_{25}(2\text{-}PET)_{18}$ clusters.

$Au_{144}(2\text{-}PET)_{60}$ was obtained as major product and $Au_{25}(2\text{-}PET)_{18}$ as a side product.

All clusters were characterized using UV-Vis and MALDI mass spectroscopy.

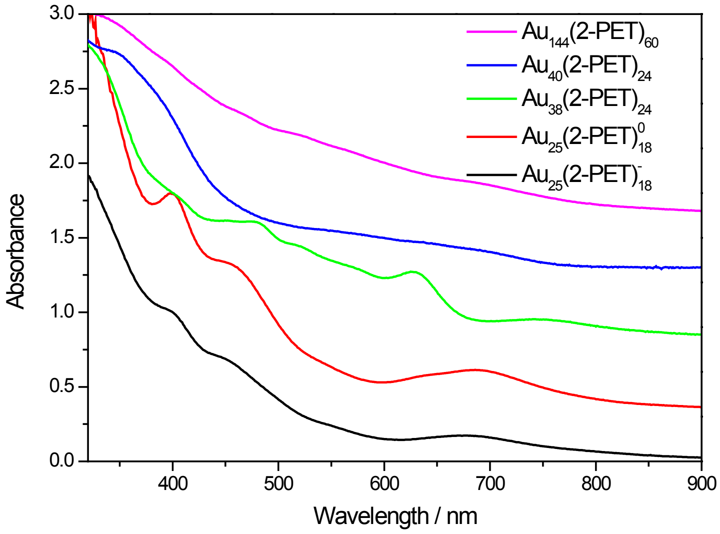
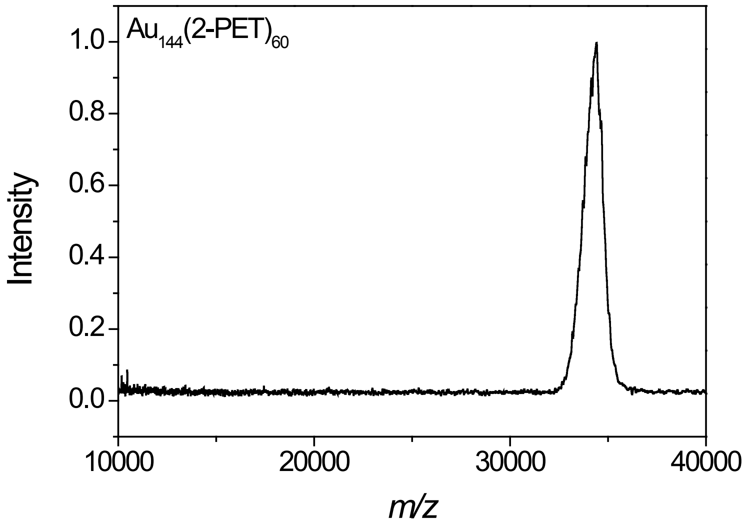
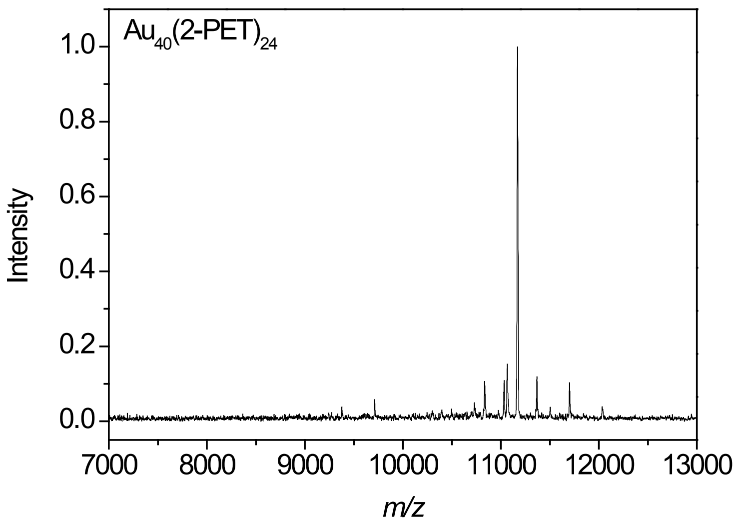
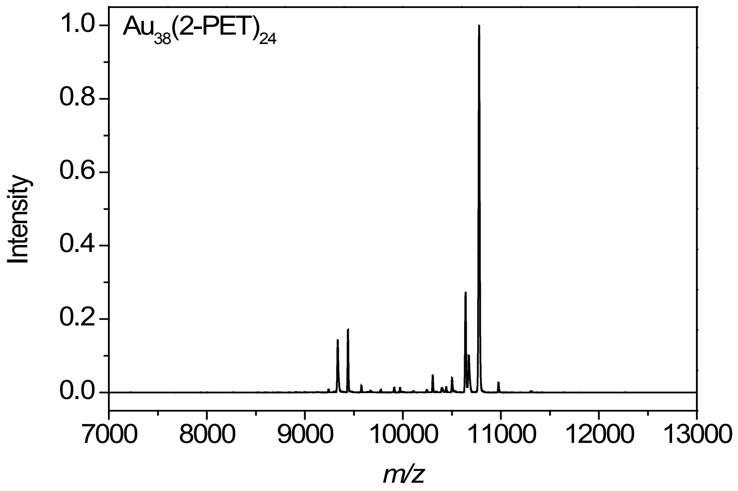


Figure S-1. UV-Vis spectra of size selected gold nanoclusters.




$Au_{40}(2\text{-}PET)_{24}$
Intensity
1.0
0.8
0.6
0.4
0.2
0.0
7000
8000
9000
10000
11000
12000
13000
m/z


$Au_{38}(2\text{-}PET)_{24}$
Intensity
1.0
0.8
0.6
0.4
0.2
0.0
7000
8000
9000
10000
11000
12000
13000
m/z

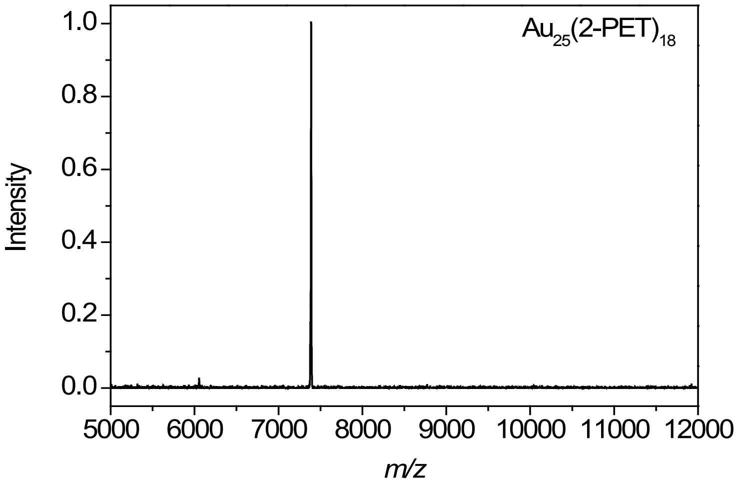

$Au_{25}(2\text{-}PET)_{18}$
Intensity
1.0
0.8
0.6
0.4
0.2
0.0
5000
6000
7000
8000
9000
10000
11000
12000
m/z

Figure S-2. MALDI mass spectra of $Au_{144}(2\text{-PET})_{60}$, $Au_{40}(2\text{-PET})_{24}$, $Au_{38}(2\text{-PET})_{24}$, $Au_{25}(2\text{-PET})_{18}$.

DFT calculations

In order to help the assignment of 2-phenylethethanethiol (2-PET) bands DFT calculations were performed using the Gaussian09 suite of programs.[4] Two types of calculations were performed. In the first one isolated 2-PET was considered in trans and gauche conformations. These calculations were performed at the DFT level using the B3PW91 functional and a 6-311+g(2d,2p) basis set. The molecule was first completely relaxed before calculating the IR spectrum. In a second type of calculation monomeric and dimeric staples were calculated (Fig. S3). For this the experimental structure of $Au_{38}(2\text{-PET})_{24}$ served as the model. The geometry of one staple was taken from the crystal structure of $Au_{38}(2\text{-PET})_{24}$, including three Au core atoms. The latter were fixed and the staple relaxed before calculating the normal modes. These calculations were done using the B3LYP functional and a LanL2DZ basis set (D95V for H and C).

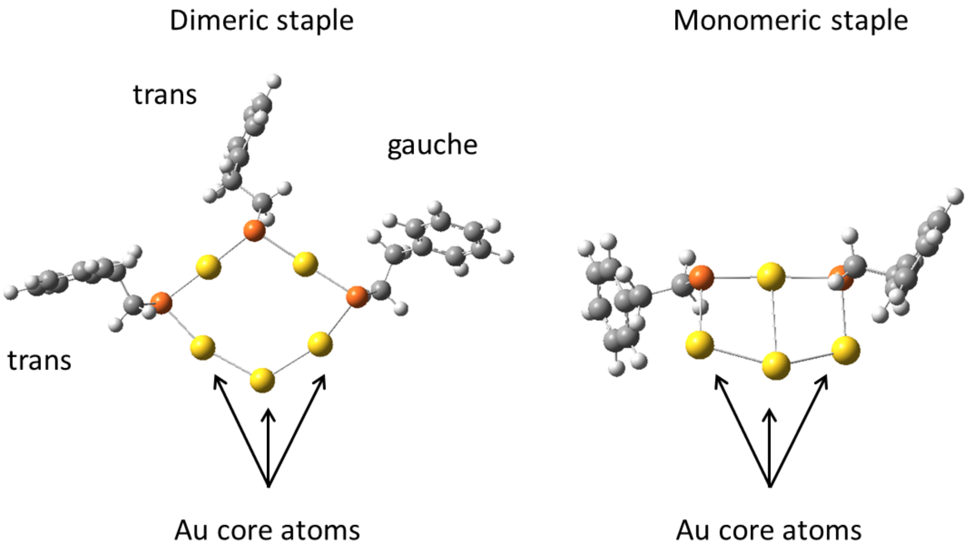


Figure S3: Dimeric and monomeric staple unit used for the calculation.

1. Knoppe, S., et al., *Ligand Exchange Reactions on Au(38) and Au(40) Clusters: A Combined Circular Dichroism and Mass Spectrometry Study. Journal of the American Chemical Society*, 2010. **132**(47): p. 16783-16789.
2. Knoppe, S., et al., *Size Exclusion Chromatography for Semipreparative Scale Separation of Au(38)(SR)(24) and Au(40)(SR)(24) and Larger Clusters. Analytical Chemistry*, 2011. **83**(13): p. 5056-5061.
3. Qian, H.F. and R.C. Jin, *Ambient Synthesis of Au-144(SR)(60) Nanoclusters in Methanol. Chemistry of Materials*, 2011. **23**(8): p. 2209-2217.

4. Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.