Supporting Information for

The Role of the Anchor Atom in the Ligand of the Monolayer-Protected $Au_{25}(XR)_{18}^-$ Nanocluster

Emmi Pohjolainen[1], Hannu Häkkinen[1,2], Andre Clayborne[2]*

[1]Department of Physics, Nanoscience Center, University of Jyväskylä, Jyväskylä, Finland, FI-40014

[2]Department of Chemistry, Nanoscience Center, University of Jyväskylä, Jyväskylä, Finland, FI-40014

*To whom correspondence should be addressed: andre.clayborne@jyu.fi

Supporting Information Contents:

Figures of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for Au $(XCH_3)^-$ (X = S, Se, and Te), and comparisons of previously reported bond lengths and optical absorption peaks to the current work.

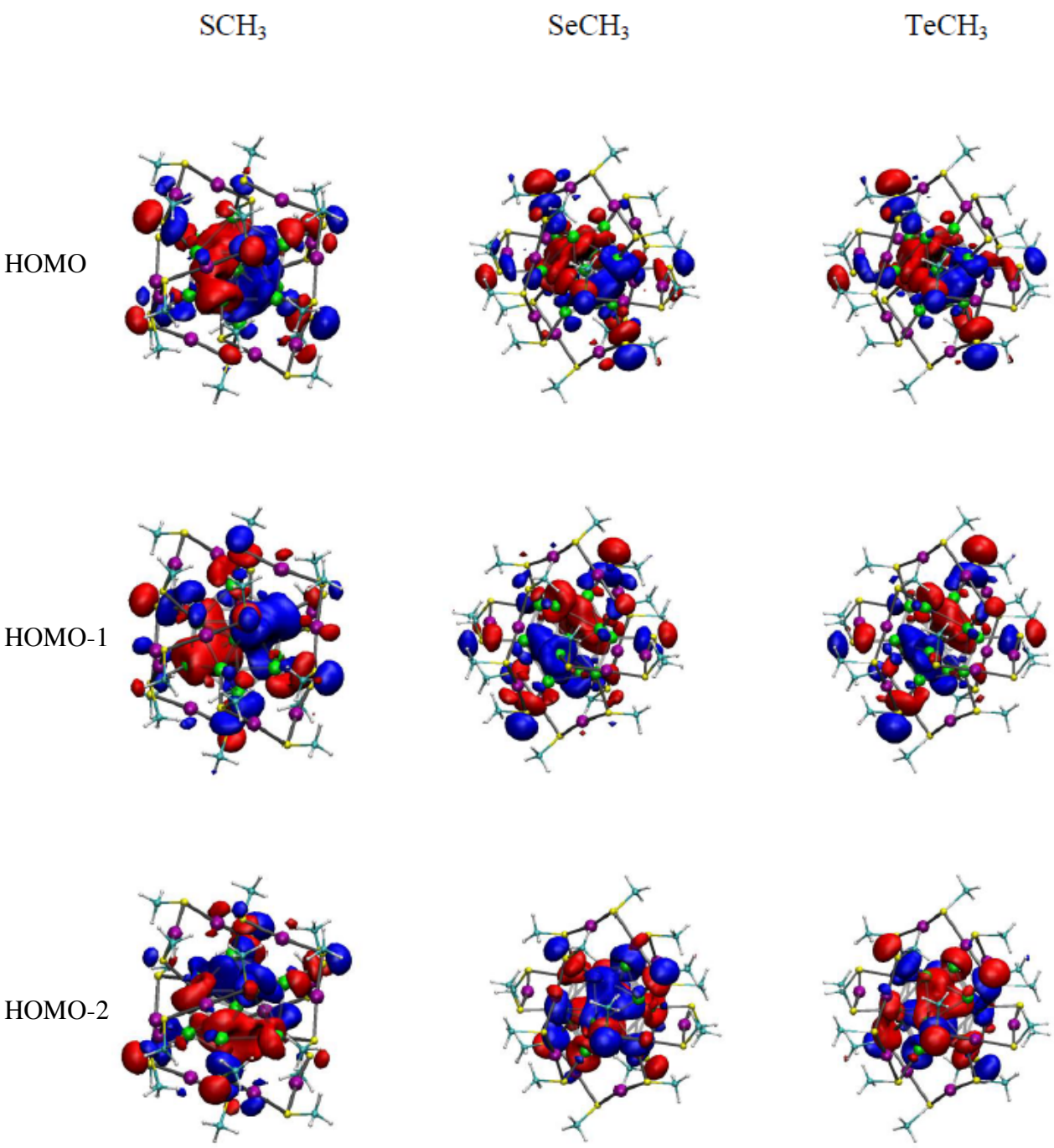

Figure S1. Molecular orbitals for the three uppermost highest occupied molecular orbitals (HOMO) for $Au_{25}(XCH_3)_{18}^-$ nanoclusters.

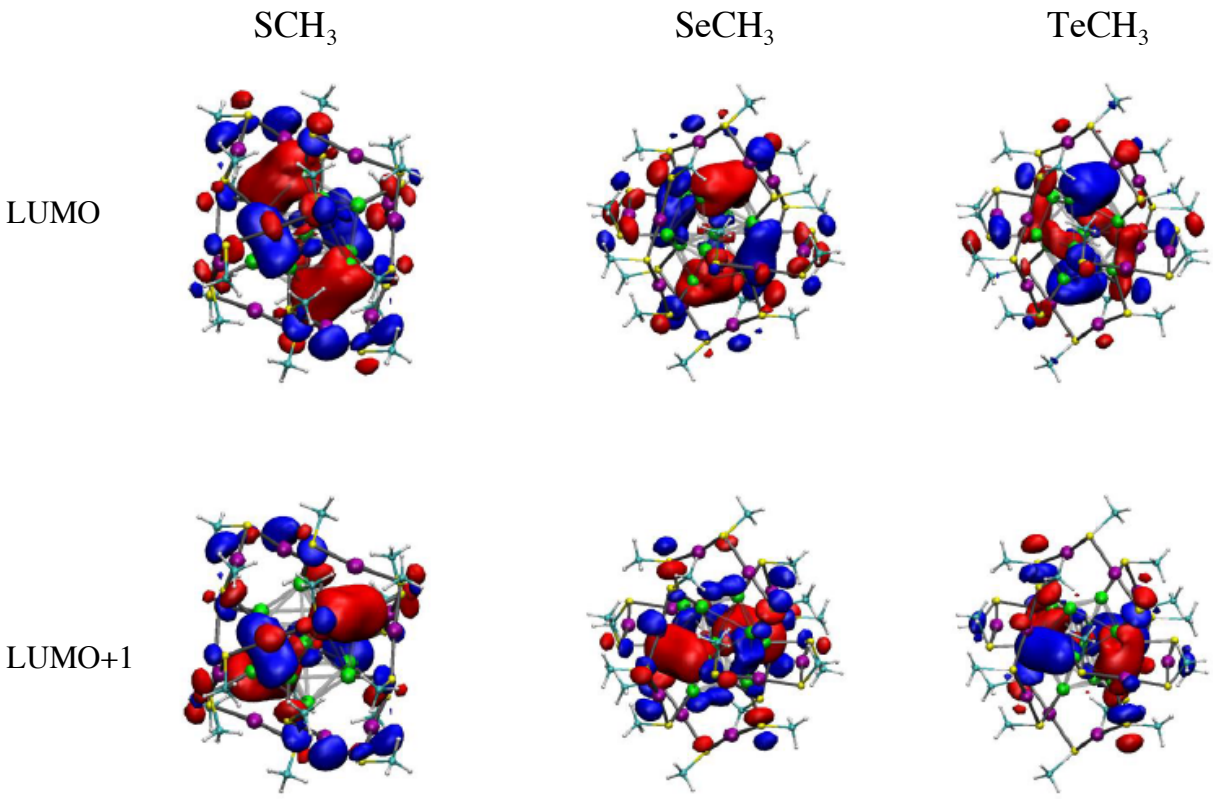

Figure S2. Molecular orbitals for the two lowermost unoccupied molecular orbitals (LUMO) for $Au_{25}(XCH_3)_{18}^-$ nanoclusters.

Table S1. Comparison of average bond lengths (Å) to previous reports.

System	Au_S-X	Au_L-X	Au_S-Au_S	Au_S-Au_L	Au_S-Au_C
SCH_3	2.43	2.34	3.01	3.40	2.85
theory[a]	2.45	2.36	2.98	3.30	
previous[b]	2.40	2.40	2.99		2.84
previous[c]			2.99	3.32	2.84
$SeCH_3$	2.54	2.46	2.99	3.42	2.84
previous[b]	2.50	2.50	2.99		2.85
$TeCH_3$	2.66	2.62	3.00	3.57	2.85
previous[c]			3.00	3.54	2.85

a) Reference 1 b) Reference 2 c) Reference 3

Table S2. Comparison of calculated (LDA) spectral peaks (eV) to experimental peak positions.

System	1	2	3	4
SH	1.49	2.28	2.64	2.88
SCH_3	1.36	2.09	2.52	2.71
$S(CH_2)_2Ph$	1.38	2.12	2.43	2.54
experiment[a] (78 K)	1.67	1.90	2.57	2.87
experiment[a] (323 K)	1.81	2.79		
SeH	1.46	2.19	2.59	3.2
$SeCH_3$	1.42	2.06	2.20	2.73
$Se(CH_2)_2Ph$	1.39	2.02	2.16	2.52
experiment[b]	1.80	2.60	3.10	
TeH	1.52	2.21	2.38	2.65
$TeCH_3$	1.48	2.12	2.61	2.83
$Te(CH_2)_2Ph$	1.39	1.90	2.04	2.66
experiment[c]	1.70	2.60	3.1	

a) Reference 4
b) Reference 2
c) Averages of peak positions between the spectra reported from Reference 3

References for Supporting Information

(1) Akola, J.; Walter, M.; Whetten, R. L.; Häkkinen, H.; Grönbeck, H. On the Structure of Thiolate-Protected Au25. *J. Am. Chem. Soc.* **2008**, *130*, 3756–3757.

(2) Kurashige, W.; Yamaguchi, M.; Nobusada, K.; Negishi, Y. Ligand-Induced Stability of Gold Nanoclusters: Thiolate versus Selenolate. *J. Phys. Chem. Lett.* **2012**, *3*, 2649–2652.

(3) Kurashige, W.; Yamazoe, S.; Yamaguchi, M.; Nishido, K.; Nobusada, K.; Tsukuda, T.; Negishi, Y. Au25 Clusters Containing Unoxidized Tellurolates in the Ligand Shell. *J. Phys. Chem. Lett.* **2014**, *5*, 2072–2076.

(4) Devadas, M. S.; Bairu, S.; Qian, H.; Sinn, E.; Jin, R.; Ramakrishna, G. Temperature-Dependent Optical Absorption Properties of Monolayer-Protected Au25 and Au38 Clusters. *J. Phys. Chem. Lett.* **2011**, *2*, 2752–2758.