Supporting Information:

Structural Prediction of Thiolate-Protected Au_{38}: A Face-Fused Bi-icosahedral Au Core

Yong Pei, Yi Gao, and Xiao Cheng Zeng*
Department of Chemistry and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, Nebraska, 68588

Part I. Computational details.

Part II. **Figure S1.** Isomers structures, **Is1** ~ **Is6**, and their relative energies.

Part III. **Figure S2**. A comparison of computed UV-vis spectra of **Is1** and **Is2** with the experimental spectrum.

Part IV. Coordinate of isomer **Is1**.

Part I. Computational details:

The density functional theory (DFT) computation is performed using DMol3 program package [S1]. Optimizations of the $Au_{38}(RS)_{24}$ cluster is performed using the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) functional [S2]. The *d*-polarization included basis set (DND) is used. The effective core potential (ECP) approximation with partial consideration of scalar relativity is used for the Au element [S3,S4]. All-electron calculations are otherwise applied for H, C, and S elements.

The theoretical X-ray diffraction (XRD) pattern is calculated using the Debye formula following Reference 5b:

$$I(s) = \sum_i \sum_{j \neq i} \frac{\cos\theta}{(1+\alpha\cos 2\theta)} \exp(-\frac{Bs^2}{2}) f_i f_j \frac{\sin(2\pi d_{ij})}{2\pi d_{ij}}$$

where *s* is the diffraction vector length, satisfying $s = 2\sin\theta / \lambda$. The λ and α is determined by the experimental set-up and is set to 0.1051967 nm and 1.01, respectively. *B* is the damping factor, which reflects thermal vibrations, and is set to 0.03 nm^2. The corresponding atomic numbers are used for the scattering factors f_i. d_{ij} is the distance between atoms *i* and *j*. It is found that the ECP basis set overestimates the Au-Au bond length. The computed Au-Au dimer bond length using the ECP basis set is 2.62 Å, longer than the experimental value of 2.47 Å by 0.15 Å (6.0%). In calculations of the XRD pattern, the $Au_{38}(RS)_{24}$ cluster is re-optimized using the all-electron relativitistic basis set, implemented in DMol3. The optimized Au-Au dimer length with the all-electron relativitistic basis set is 2.48 Å, closer to the experimental value. Finally, the time-dependent DFT computation of optical absorption spectrum is performed at the PBE/TZVP level of theory, implemented in the ADF program package [S5].

[S1] Delley, B. *J. Chem. Phys.* **1990**, *92*, 508; *J. Chem. Phys.* **2003**, *113*, 7756. $DMol^3$ is available from Accelrys.

[S2] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

[S3] Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.*, **86**, 866 (1987).

[S4] Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.*, **80**, 1431 (1993).

[S5] ADF 2007.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands (http://www.scm.com).

Part II.

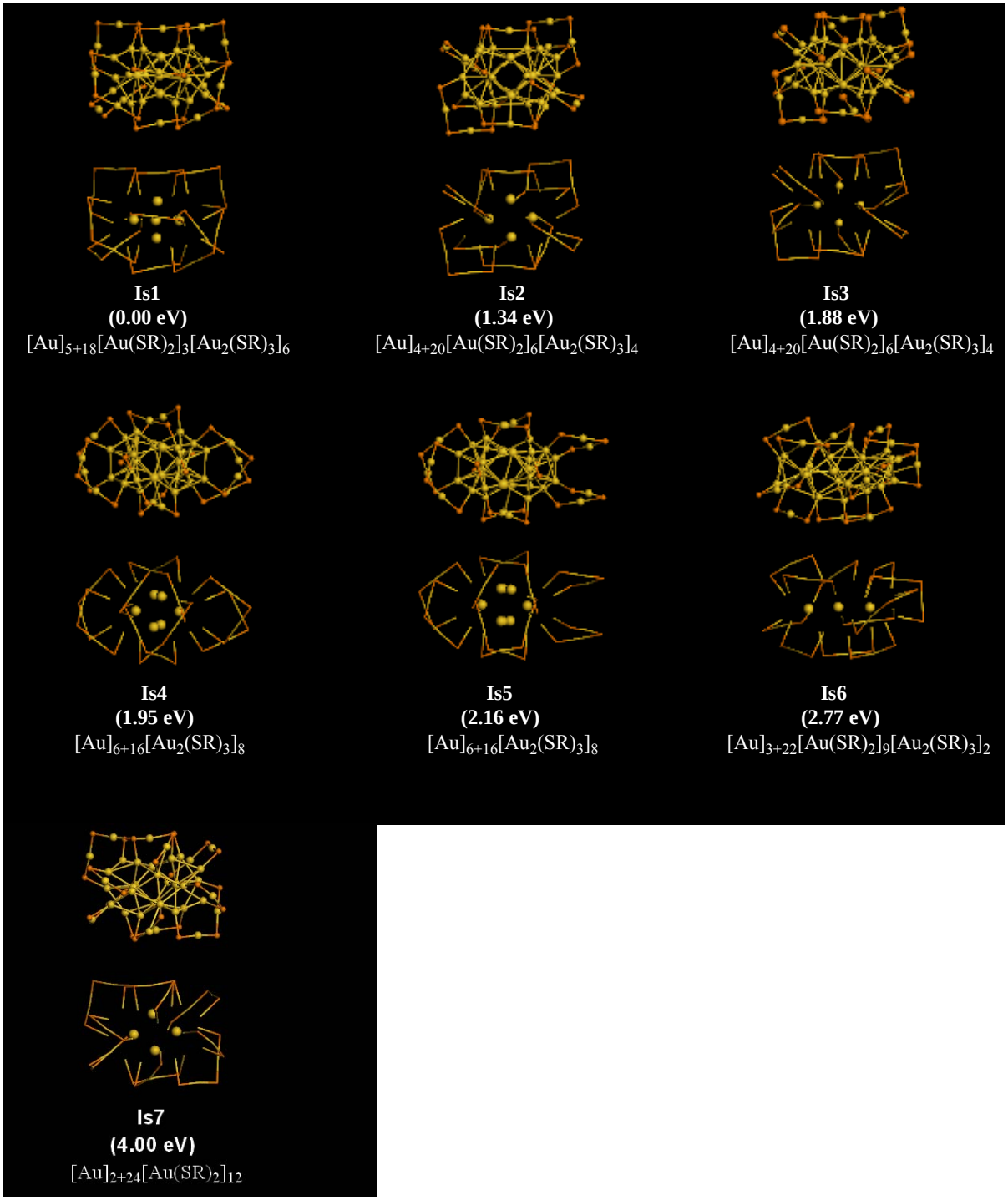
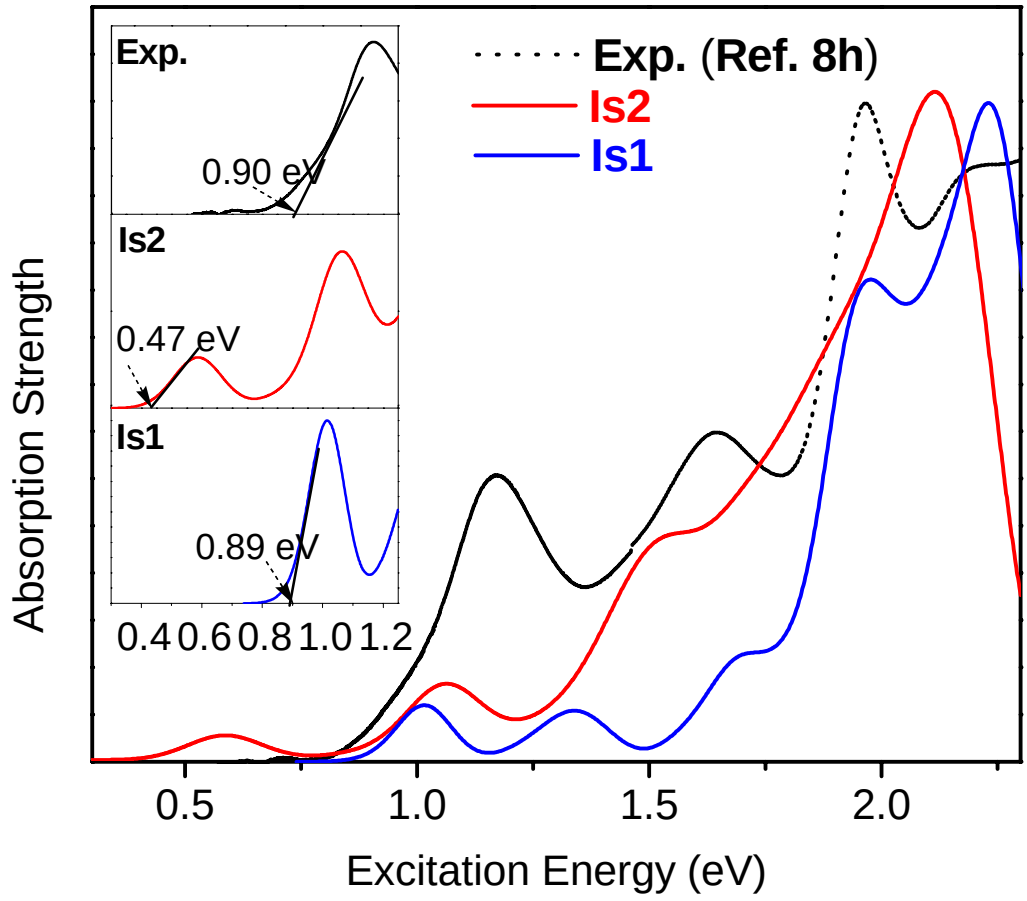


Figure S1. Isomers structures, **Is1** ~ **Is6**, and their relative energies. **Is2**/**Is3** and **Is4**/**Is5** are different from each other by different arrangement of the exterior staple motifs.

Part III. **Figure S2**. A comparison of computed UV-vis spectra of **Is1** and **Is2** with the experimental spectrum.



Part IV. Coordinate for **Is1**.

S	-4.7686	-2.6080	-1.8251
S	1.4133	-2.4711	-6.1941
Au	-3.6579	-3.5926	-3.6632
S	-2.6430	-4.7434	-5.4553
Au	-0.6140	-3.5624	-5.6966
S	0.4808	4.9359	-2.2820
S	-2.8857	-0.4303	-6.2676
Au	-1.2409	4.4971	-3.8397
S	-3.0405	4.1880	-5.3292
Au	-2.8772	1.8536	-5.6851
S	4.4000	-2.8114	-1.6088
S	1.1595	2.2193	-6.2651
Au	4.6518	-1.5628	-3.5958
S	5.0727	-0.2998	-5.5408
Au	3.1018	0.9835	-5.7515
S	4.6498	-1.7625	2.2747
S	0.0182	2.7221	6.4689
Au	4.3970	-0.3780	4.1723
S	4.3313	0.8512	6.1918
Au	2.1595	1.7680	6.1560
S	-4.0277	-3.6456	1.8738
S	1.7424	-2.0538	6.6112
Au	-2.8766	-4.1481	3.8663
S	-2.0133	-4.8157	5.9554
Au	-0.1054	-3.4445	6.1380
S	-1.5995	4.8373	1.7746
S	-3.1292	-0.9772	6.4200
Au	-2.8935	4.0284	3.5770
S	-4.4157	3.4047	5.2707
Au	-3.6932	1.2108	5.7554
S	-4.3503	2.9174	-2.1748
S	-5.3290	1.4654	2.1847
Au	-4.7499	2.0736	-0.0142
S	0.3343	-5.3323	-2.2359
S	0.6641	-5.3079	2.4509
Au	0.4956	-5.1308	0.1097
S	4.4456	2.3636	-2.0774
S	3.8412	3.1383	2.5237
Au	3.9962	2.7063	0.2089
C	-3.8254	4.3352	6.7521
H	-4.4707	4.0591	7.5978
H	-2.7831	4.0866	6.9838

H	-3.9284	5.4091	6.5443
C	-0.5579	6.1399	2.5607
H	-1.2164	6.9644	2.8684
H	-0.0166	5.7497	3.4283
H	0.1576	6.5036	1.8114
C	-1.9661	-0.6870	7.8220
H	-2.5482	-0.3187	8.6784
H	-1.5000	-1.6522	8.0696
H	-1.1914	0.0386	7.5530
C	0.3040	4.5143	6.1461
H	0.8061	4.9484	7.0221
H	0.9217	4.6563	5.2535
H	-0.6719	4.9975	5.9970
C	5.4440	2.2824	5.8626
H	5.3698	2.9725	6.7146
H	6.4695	1.8962	5.7838
H	5.1584	2.7867	4.9306
C	2.4844	-5.3754	2.7416
H	2.8730	-6.2973	2.2880
H	2.9861	-4.5000	2.3129
H	2.6459	-5.4044	3.8276
C	2.6696	-3.8052	-6.0078
H	2.5549	-4.5058	-6.8474
H	3.6626	-3.3368	-6.0406
H	2.5412	-4.3348	-5.0578
C	-1.6310	-0.4979	-7.6181
H	-2.0777	-0.0537	-8.5185
H	-0.7213	0.0472	-7.3407
H	-1.3863	-1.5544	-7.7972
C	-2.4727	4.8791	-6.9428
H	-3.2600	4.6945	-7.6864
H	-2.3296	5.9605	-6.8158
H	-1.5378	4.4090	-7.2683
C	-5.8565	2.5031	-3.1507
H	-6.1498	1.4568	-3.0194
H	-6.6685	3.1656	-2.8188
H	-5.6250	2.6972	-4.2070
C	-6.0842	-0.2101	2.0308
H	-5.4928	-0.8612	1.3774
H	-6.1324	-0.6461	3.0377
H	-7.1009	-0.0915	1.6304
C	1.6746	3.9796	-6.0925
H	2.3624	4.2189	-6.9156
H	0.7706	4.6010	-6.1581

H	2.1583	4.1572	-5.1262
C	6.3524	0.9111	-5.0004
H	6.4760	1.6513	-5.8030
H	6.0485	1.4038	-4.0684
H	7.2935	0.3639	-4.8514
C	2.9851	4.7699	2.5547
H	2.0570	4.7303	1.9731
H	2.7581	5.0068	3.6030
H	3.6649	5.5310	2.1452
C	-1.3165	-6.4873	5.6071
H	-0.8069	-6.8353	6.5158
H	-2.1547	-7.1578	5.3732
H	-0.6169	-6.4514	4.7617
C	5.6105	-0.6937	1.1227
H	5.7265	-1.2481	0.1827
H	5.0914	0.2554	0.9361
H	6.5939	-0.5050	1.5763
C	-5.7459	-1.2390	-2.5761
H	-6.6280	-1.6659	-3.0730
H	-6.0557	-0.5755	-1.7568
H	-5.1356	-0.6761	-3.2919
C	4.2645	4.0360	-2.8272
H	5.0726	4.6791	-2.4501
H	4.3660	3.9165	-3.9152
H	3.2874	4.4760	-2.5904
C	-3.3988	-4.9216	0.7036
H	-3.7665	-4.6599	-0.2974
H	-2.3014	-4.9531	0.6998
H	-3.8084	-5.8945	1.0106
C	3.2062	-3.1303	6.3021
H	3.1511	-3.6037	5.3170
H	4.1031	-2.4968	6.3531
H	3.2399	-3.8950	7.0917
C	3.9749	-4.5310	-2.1063
H	4.8782	-5.0135	-2.5039
H	3.6342	-5.0552	-1.2031
H	3.1749	-4.5473	-2.8537
C	-1.1693	-6.3739	-2.4550
H	-2.0537	-5.8816	-2.0364
H	-1.3114	-6.5265	-3.5330
H	-1.0004	-7.3388	-1.9573
C	-3.6287	-4.1839	-6.9112
H	-3.1393	-4.5617	-7.8188
H	-4.6346	-4.6174	-6.8241

H	-3.6901	-3.0883	-6.9358
C	-0.2011	6.3166	-1.2705
H	-1.1200	6.0107	-0.7584
H	0.5650	6.5896	-0.5322
H	-0.3971	7.1740	-1.9291
Au	-1.7293	-1.2347	4.4544
Au	-0.7219	1.7741	4.3608
Au	1.3321	-0.8457	4.5364
Au	2.0493	1.5094	2.9734
Au	-0.2567	-0.1008	2.2739
Au	1.5114	0.9073	0.1795
Au	-1.9253	0.7902	0.0899
Au	-0.1292	2.7169	-1.3853
Au	-0.0021	1.6384	-4.2147
Au	-0.1294	-0.1471	-1.9712
Au	1.4993	-1.1609	-4.1494
Au	-1.6842	-1.0181	-4.2256
Au	-2.4929	1.4189	-2.6832
Au	-0.3460	2.7383	1.6109
Au	-2.9722	1.0029	2.7530
Au	-2.5523	-1.7131	1.6110
Au	-0.0686	-2.1152	0.1711
Au	-2.5748	-1.5694	-1.4358
Au	2.2845	-1.4254	1.7629
Au	-0.0213	-3.0061	2.9469
Au	-0.2910	-3.0090	-2.6051
Au	2.3099	-1.5794	-1.3428
Au	2.4363	1.1069	-2.5931