Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2016

Supporting Information

Atomic Structure of Peptide Coated Gold Nanocluster Identified by Theoretical and Experimental Studies

Hui Wang[$, a], Xu Li[$, a, b], Liang Gao[a], Jiao Zhai[a], Ru Liu[a], Xueyun Gao[a], Dongqi Wang[a], Lina Zhao[*, a]

[a] Multidisciplinary Initiative Center, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, China.

[b] Department of Mechanical and Electrical Engineering, North China Institute of Science and Technology, Hebei 065201, China

* E-mail: linazhao@ihep.ac.cn
$ These authors contributed equally to this work.

1. The MALDI-TOF-MS identification of $Au_{24}Peptide_8$.

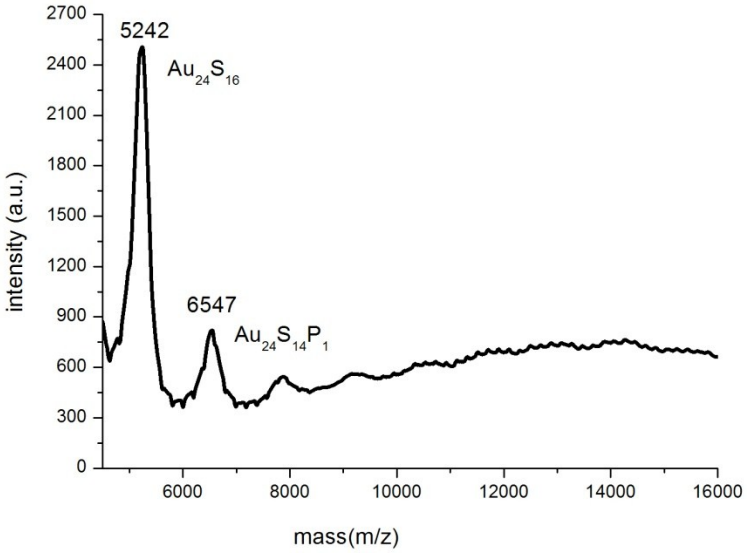


Figure S1. The MALDI-TOF-MS of peptide coated Au cluster, there two strong peaks located at about m/z ~5242 and m/z ~6547, respectively. Note that the two peaks are very close to the $Au_{24}S_{16}$ (m/z ~5240) and $Au_{24}S_{14}P_1$ (m/z ~6547) when consider the experimental deviation.

In the MALDI-TOF-MS spectra (Figure S1), the strongest peak locating at m/z ~5242 represents the fragment of Au_xP_y which represents the peptide coated Au cluster is composed of X gold atoms and Y peptide molecules. When laser is applied to the sample in MALDI-TOF-MS studies, the S-C bond will be broken and S still bind to Au cluster, but peptide chain will leave the Au cluster. If we

assign the m/z ~5242 to $Au_{24}S_{16}$ fragment, we can speculate the peptide coated Au cluster as $Au_{24}Peptide_8$ because each peptide is with two Cysteine, e.g. eight peptides are with 16 S atoms. And if we further assign the m/z ~6547 to $Au_{24}S_{14}Peptide_1$ fragment, we also can speculate the peptide coated Au cluster as $Au_{24}Peptide_8$ because each peptide is with two Cysteine. Thus the two peaks assignments are match to each other and they both could be the different fragments of $Au_{24}Peptide_8$. So the MALDI-TOF-MS study can imply that peptide coated Au cluster may be $Au_{24}Peptide_8$.

2. The structural divisions of $Au_{24}(Cys\text{-}Cys)_8$ obtained based on the "divide and protect" approach.

According to the proposed expanded structural formula, for $Au_{24}(Cys\text{-}Cys)_8$, it is $Au_{a+a'}[Au(Cys\text{-}Cys)]_b[Au_3(Cys\text{-}Cys)_2]_c+[Au_5(Cys\text{-}Cys)_3]_d...$, where $Au_{a+a'}$ represents the Au core, and b and d denote the number of level-1, -3 and -5 staple motifs with increasing length. The total number of Au and S is 24 and 16, respectively, thus a, a′, b, c, and d satisfy Equations (1) and (2)

$a+a'+b+3c+5d=24$…….(1)

$2b+4c+6d=16$…….(2)

The subtraction of (2) from (1) gives Equation (3):

$a+a'-(b+c+d)=8$…..(3)

The total number of S-terminals must equal the number of Au atom on the core surface, i.e.,

$a'=2(b+c+d)$……(4)

Put Equation (4) into Equation (3), Equation (5) is obtained:

$a'/2+a=8$……..(5)

If a′=2, then a=7 and b+c+d=1, the Equation(2) can't be established.

If a′=4, then a=6 and b+c+d=2 , the Equation (2) also can't be established.

If a′=6, then a=5, the division is $\mathbf{Au_{11}[Au_3(Cys\text{-}Cys)_2][Au_5(Cys\text{-}Cys)_3]_2}$.

If a′=8, then a=4, the divisions are $\mathbf{Au_{12}[Au(Cys\text{-}Cys)]_2[Au_5(Cys\text{-}Cys)_3]_2}$ and $\mathbf{Au_{12}[Au_3(Cys\text{-}Cys)_2]_4}$.

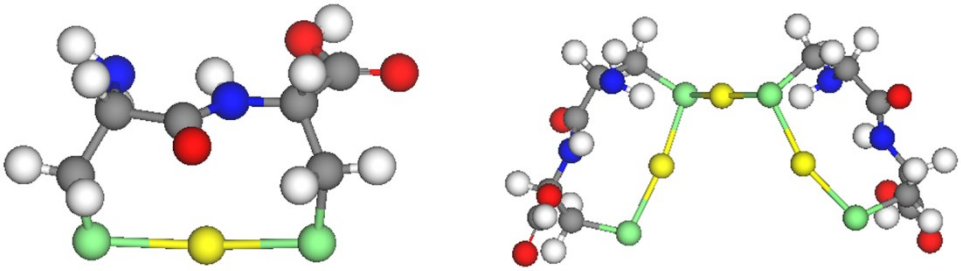
If a′=10, then a=3, the division is $\mathbf{Au_{13}[Au(Cys\text{-}Cys)]_2\ [Au_3(Cys\text{-}Cys)_2]_3}$.

If a′=12, then a=2, the divisions are $\mathbf{Au_{14}[Au(Cys\text{-}Cys)]_5[Au_5(Cys\text{-}Cys)_3]}$ and $\mathbf{Au_{14}[Au(Cys\text{-}Cys)]_4[Au_3(Cys\text{-}Cys)_2]_2}$.

If a′=14, then a=1, the division is $\mathbf{Au_{15}[Au(Cys\text{-}Cys)]_6[Au_3(Cys\text{-}Cys)_2]}$.

If a′=16, then a=0, the division is $\mathbf{Au_{16}[Au(Cys\text{-}Cys)]_8}$.

3. The atomic structures of staple motifs



Level-1 Au(Cys-Cys) **Level-3** $Au_3(Cys\text{-}Cys)_2$

Figure S2. The structures of staple motifs Au (Cys-Cys) and $Au_3(Cys\text{-}Cys)_2$

4. Relative energies of all stable isomers of $Au_{24}(Cys\text{-}Cys)_8$

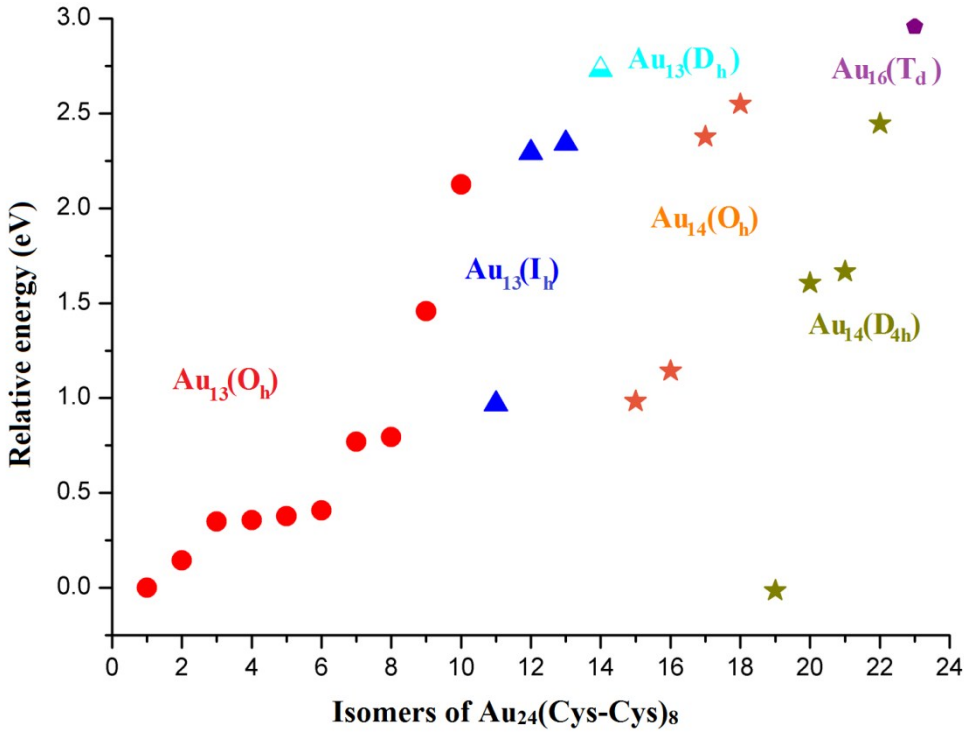


Figure S3. Relative energies of isomers of $Au_{24}(Cys\text{-}Cys)_8$ at the PBE/GGA level of theory. Red, blue, cyan, orange, dark yellow and violet points represent the relative energies of isomers based on the core of $Au_{13}(O_h)$, $Au_{13}(I_h)$, $Au_{13}(D_h)$, $Au_{14}(O_h)$, $Au_{14}(D_{4h})$ and $Au_{16}(T_d)$, respectively.

5. Orbital components of Iso1 of $Au_{24}(Cys\text{-}Cys)_8$.

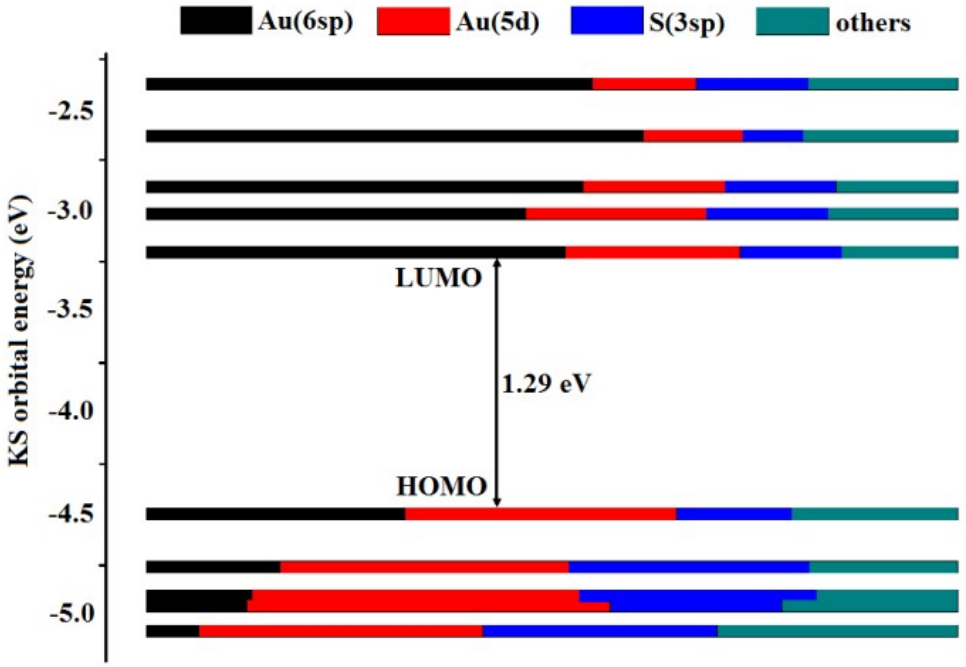


Figure S4. Kohn-Sham orbital energy levels and components of Iso**1** of $Au_{24}(Cys\text{-}Cys)_8$.

6. Comparison between $Au_{24}(Cys\text{-}Cys)_8$ and $Au_{24}(SR)_{20}$.

The coordinates of $Au_{24}(SR)_{20}$ were from Pei's work[1]. We optimized the structure at the level of PBE/LANL2DZ (for Au)/6-31G(d)(for S, C, H). The HOMO and LUMO were obtained at the same level.

Table S1. The core and HOMO-LUMO gap of $Au_{24}(Cys\text{-}Cys)_8$ and $Au_{24}(SR)_{20}$

RS-AuNCs	Au core	H-L gap (eV)
$Au_{24}(Cys\text{-}Cys)_8$	Au_{13}	1.29
$Au_{24}(SR)_{20}$	Au_8	2.10

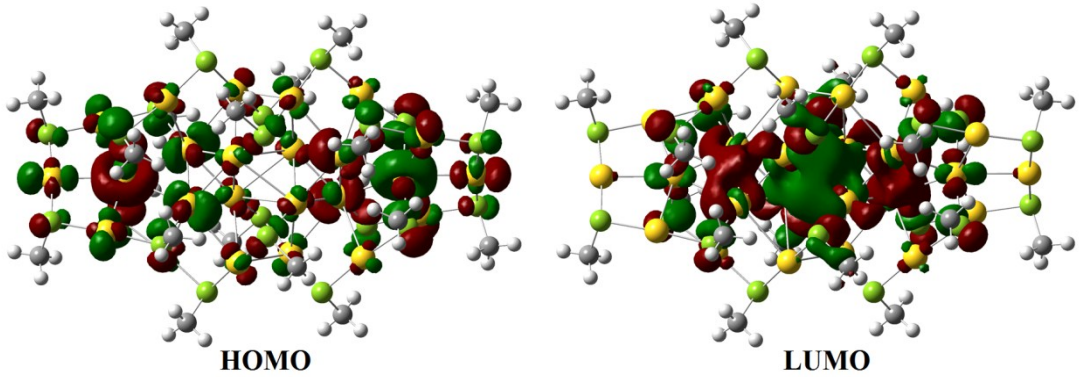


Figure S5. Schematic diagram of HOMO and LUMO of $Au_{24}(SR)_{20}$ at the level of PBE/LANL2DZ /6-31G(d).

7. XYZ coordinates of Iso1.

H1	0.316	-1.888	-7.086
H2	1.224	-3.788	-6.343
N3	-0.244	-2.291	-6.330
H4	-4.381	-0.805	-6.036
H5	-3.790	0.883	-5.951
H6	-0.476	-1.517	-5.691
C7	0.531	-3.317	-5.623
H8	3.117	3.134	-5.490
H9	4.781	2.442	-5.419
H10	-6.150	0.767	-5.368
C11	-4.155	0.031	-5.354
H12	-2.770	-5.964	-5.266
H13	-2.021	-3.298	-5.254
O14	-4.203	-3.507	-5.188
C15	-0.371	-4.494	-5.178
O16	0.081	-5.657	-5.043
H17	-5.047	-2.993	-4.958
N18	-1.671	-4.210	-4.939
H19	2.264	-2.202	-4.899
C20	3.927	2.798	-4.823
H21	4.823	4.695	-4.813
C22	-5.430	0.436	-4.593
O23	-6.250	-1.886	-4.551
C24	-2.655	-5.191	-4.475
C25	1.433	-2.781	-4.461
H26	1.472	-6.045	-4.417
O27	6.949	2.621	-4.391
S28	-2.709	-0.559	-4.348
C29	-4.033	-4.517	-4.319
H30	-5.295	2.439	-4.089
C31	4.412	4.027	-4.021
S32	3.276	1.274	-3.992
C33	-6.117	-0.797	-3.944
O34	2.153	4.935	-3.873
H35	1.859	-3.602	-3.865
O36	2.327	-6.116	-3.856
N37	-5.291	1.524	-3.627
O38	-4.866	-4.901	-3.508
H39	-1.294	-6.481	-3.386
C40	3.268	4.839	-3.384
S41	0.510	-1.579	-3.382
C42	6.623	3.116	-3.303
C43	-2.259	-5.987	-3.212

Au44	-1.547	1.161	-3.153
H45	-4.391	1.448	-3.131
N46	5.453	3.764	-3.046
H47	-3.037	-6.748	-3.046
C48	2.139	-6.976	-2.845
H49	8.397	1.205	-2.834
H50	5.150	-2.362	-2.812
Au51	1.264	1.793	-2.764
N52	-6.636	-0.554	-2.722
O53	1.172	-7.719	-2.712
H54	-8.138	-1.985	-2.565
H55	3.616	-4.932	-2.539
Au56	-0.657	3.677	-2.456
S57	-1.825	5.845	-2.399
H58	8.464	3.621	-2.393
H59	-6.235	-3.385	-2.361
H60	-6.460	0.394	-2.357
Au61	4.892	0.749	-2.334
N62	4.688	-3.143	-2.330
O63	3.685	5.484	-2.269
Au64	-3.598	-1.397	-2.268
Au65	-0.945	-3.100	-2.260
H66	6.556	-4.060	-2.228
H67	4.038	-7.721	-2.202
H68	5.410	4.249	-2.142
C69	7.569	3.053	-2.071
C70	-7.337	-1.550	-1.931
N71	3.970	-5.656	-1.904
C72	3.316	-6.948	-1.856
C73	8.083	1.608	-1.856
H74	2.927	5.953	-1.829
H75	4.012	-2.703	-1.686
Au76	-3.455	4.240	-1.650
S77	-2.190	-5.042	-1.602
C78	5.668	-3.934	-1.578
C79	-6.500	-2.774	-1.485
H80	-2.780	10.174	-1.335
C81	5.169	-5.383	-1.316
Au82	1.562	-0.851	-1.263
H83	8.949	1.612	-1.172
S84	6.922	0.327	-1.156
H85	-5.921	5.261	-1.017
O86	-3.061	9.283	-1.016
N87	7.004	3.757	-0.917

H88	-0.257	6.806	-0.848
H89	-7.129	-3.371	-0.804
O90	-8.048	0.443	-0.771
C91	-8.053	-0.918	-0.732
C92	-1.244	6.340	-0.708
O93	5.820	-6.193	-0.642
H94	-4.228	7.034	-0.619
Au95	-0.114	-5.722	-0.613
Au96	-0.492	1.529	-0.595
S97	-4.904	-2.503	-0.592
H98	2.360	-8.386	-0.569
S99	-5.024	2.853	-0.566
H100	6.794	-2.427	-0.461
C101	2.900	-7.433	-0.452
C102	-1.975	8.727	-0.447
O103	-0.888	9.306	-0.380
H104	6.401	3.119	-0.372
O105	2.236	7.156	-0.295
Au106	-3.312	1.028	-0.289
H107	7.747	4.057	-0.277
C108	6.203	-3.335	-0.261
N109	-6.062	5.866	-0.195
H110	-1.111	5.436	-0.092
Au111	-1.484	-1.064	-0.030
H112	-7.068	5.861	0.002
H113	-8.489	0.736	0.059
C114	-2.184	7.315	0.065
S115	1.961	4.000	0.077
Au116	2.514	1.578	0.123
N117	-3.561	6.877	0.142
O118	-8.605	-1.565	0.143
H119	3.811	-7.589	0.146
H120	6.843	-4.090	0.226
Au121	3.839	-0.772	0.358
Au122	0.481	-3.071	0.376
H123	0.483	8.511	0.595
S124	1.813	-6.373	0.616
Au125	3.157	-4.406	0.754
H126	3.901	5.246	0.766
C127	1.821	7.127	0.861
C128	-5.320	5.318	0.947
Au129	6.285	1.131	0.988
S130	4.951	-2.843	1.020
Au131	-5.262	-0.851	1.051

C132	-5.203	3.764	1.058
C133	-3.919	5.959	1.092
H134	-1.805	7.306	1.105
C135	3.006	4.910	1.316
O136	0.881	7.964	1.339
Au137	0.093	3.490	1.452
H138	-6.127	3.347	1.493
Au139	1.270	-0.656	1.560
H140	-4.365	3.506	1.723
H141	-5.844	5.635	1.868
C142	2.317	6.142	1.941
Au143	-1.560	0.804	2.010
O144	-3.190	5.662	2.049
H145	3.305	4.229	2.126
H146	3.118	6.670	2.506
Au147	-0.867	-2.140	2.612
H148	6.119	-0.686	2.785
N149	1.219	5.827	2.847
H150	0.391	6.438	2.870
S151	-5.652	0.599	2.931
S152	5.750	2.251	3.005
S153	-1.608	3.034	3.062
H154	-7.475	-1.034	3.112
Au155	3.552	1.391	3.180
H156	2.790	-4.192	3.442
H157	7.528	-1.176	3.493
H158	-1.682	5.545	3.534
N159	6.530	-1.020	3.670
H160	-3.704	-3.654	3.677
Au161	-3.685	-0.554	3.721
S162	1.450	0.493	3.756
C163	-7.072	-0.272	3.797
C164	1.269	4.940	3.895
O165	3.227	-3.430	3.896
H166	-7.825	0.522	3.944
O167	-6.229	-3.008	3.959
H168	4.623	-1.804	4.163
O169	2.260	4.276	4.220
H170	7.694	1.580	4.246
N171	-1.022	5.881	4.252
C172	6.617	1.437	4.436
C173	-0.627	3.368	4.611
C174	-3.153	-3.606	4.627
C175	-0.084	4.827	4.660

S176	-2.117	-2.064	4.673
H177	0.198	2.644	4.697
H178	-2.463	-4.461	4.705
C179	2.326	-2.859	4.731
C180	6.325	-0.053	4.742
N181	4.174	-1.221	4.878
C182	-5.982	-2.267	4.919
O183	1.221	-3.320	4.969
H184	-1.585	6.191	5.049
C185	-6.748	-0.935	5.150
H186	6.322	2.036	5.314
C187	1.788	-0.452	5.314
C188	2.858	-1.573	5.372
C189	4.927	-0.213	5.404
H190	-1.339	3.208	5.440
H191	7.033	-0.313	5.554
H192	-7.727	-1.241	5.571
H193	-4.764	-4.592	5.604
H194	0.826	-0.899	5.615
H195	0.200	5.003	5.714
H196	-5.295	0.391	5.733
C197	-4.166	-3.680	5.804
N198	-5.066	-2.548	5.891
H199	2.080	0.324	6.038
N200	-6.086	-0.108	6.166
O201	4.574	0.507	6.349
H202	2.934	-1.794	6.458
H203	-6.732	0.604	6.525
H204	-4.944	-1.836	6.618
C205	-3.412	-3.930	7.109
O206	-2.653	-4.868	7.278
O207	-3.662	-2.986	8.060
H208	-3.099	-3.239	8.830

Reference

1 Y. Pei, R. Pal, C. Liu, Y. Gao, Z. Zhang, X. C. Zeng, *J. Am. Chem. Soc.* 2012, **134**, 3015.