

## Electronic Supplementary Information (ESI)

### **Electronic and geometric structures of Au<sub>30</sub> clusters: A network of 2e-superatom Au cores protected by tridentate protecting motifs with $u_3$ -S**

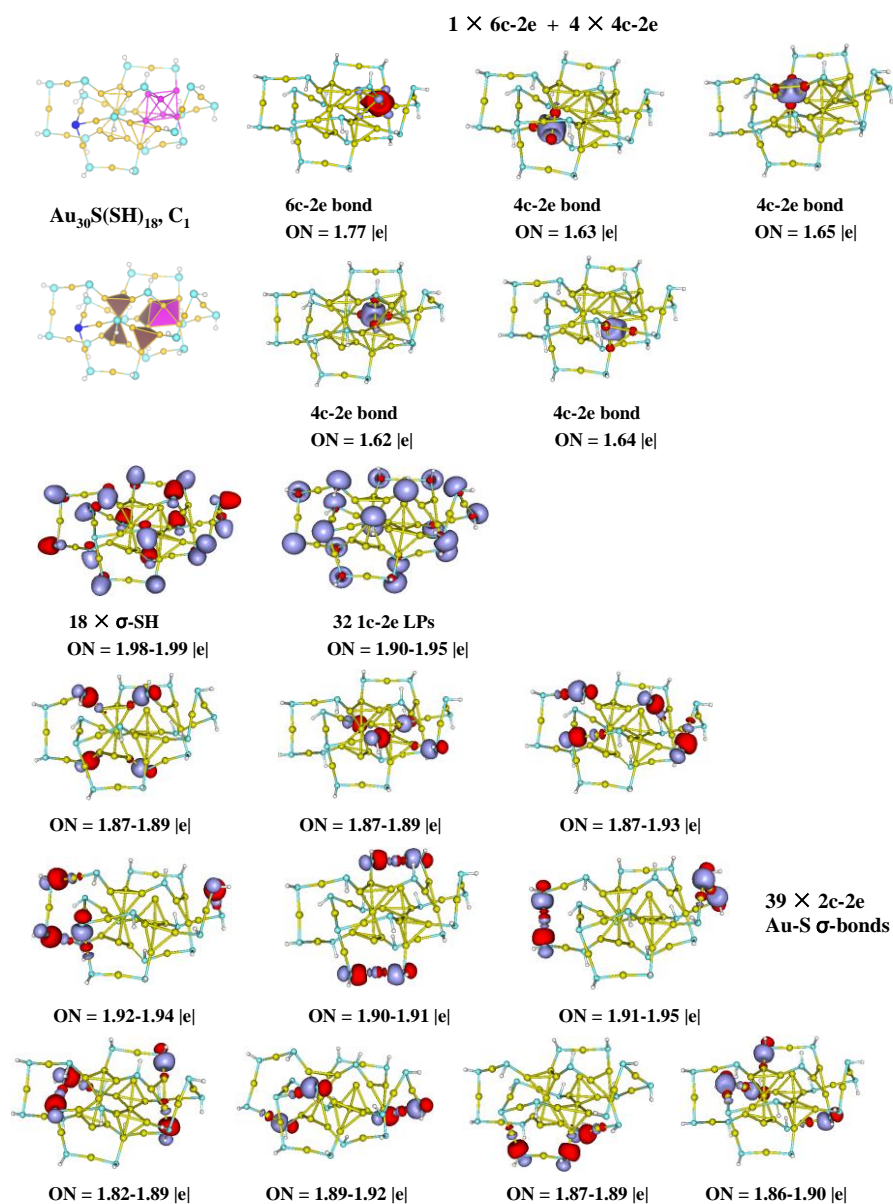
By

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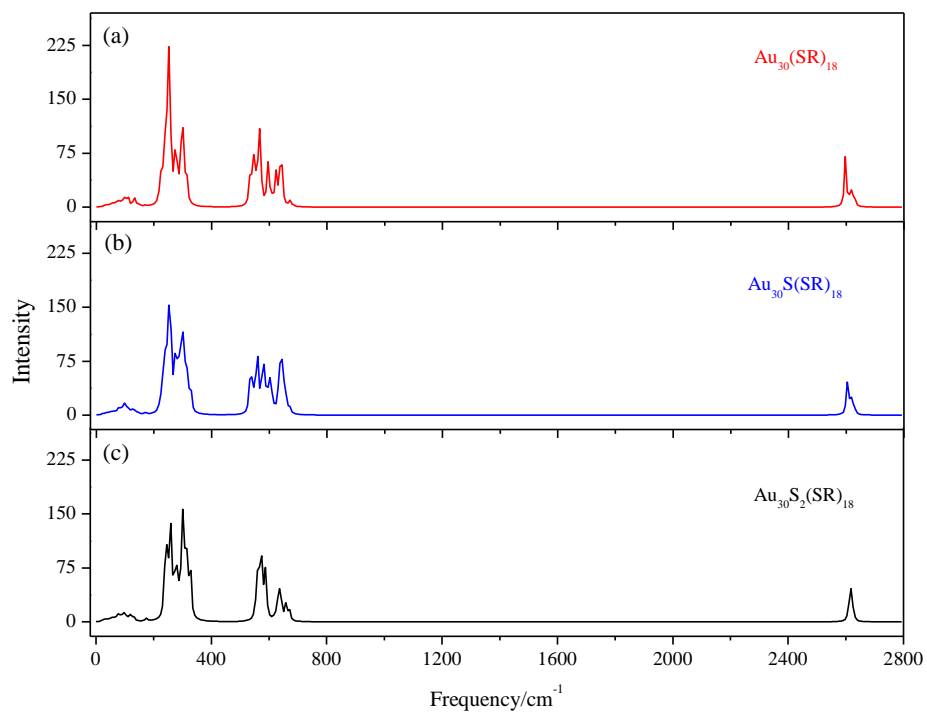
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<sup>b</sup>School of Chemistry and Materials Engineering, Fuyang Teachers College, Fuyang, Anhui, 236037, China.

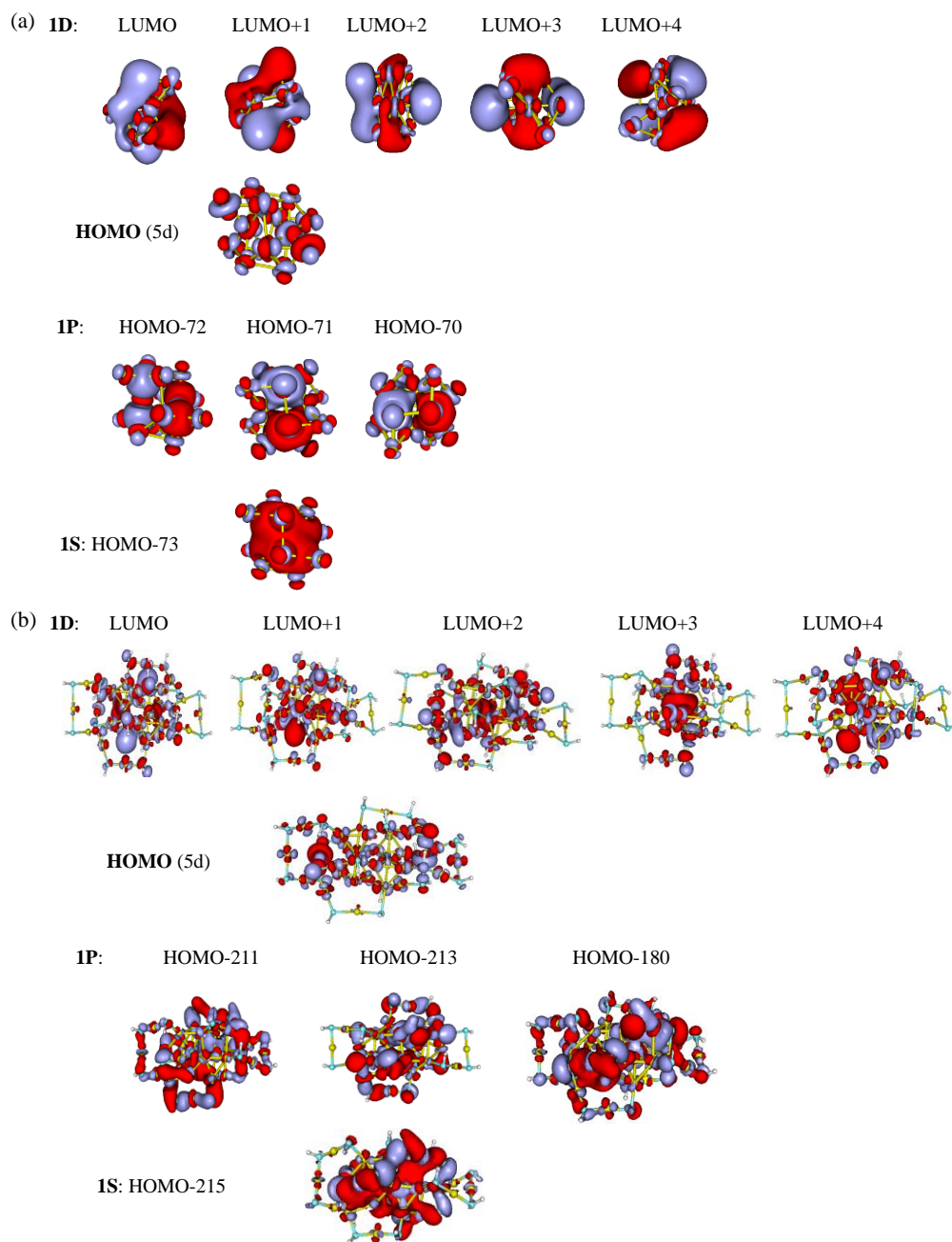
\*Corresponding author. E-mail: clj@ustc.edu



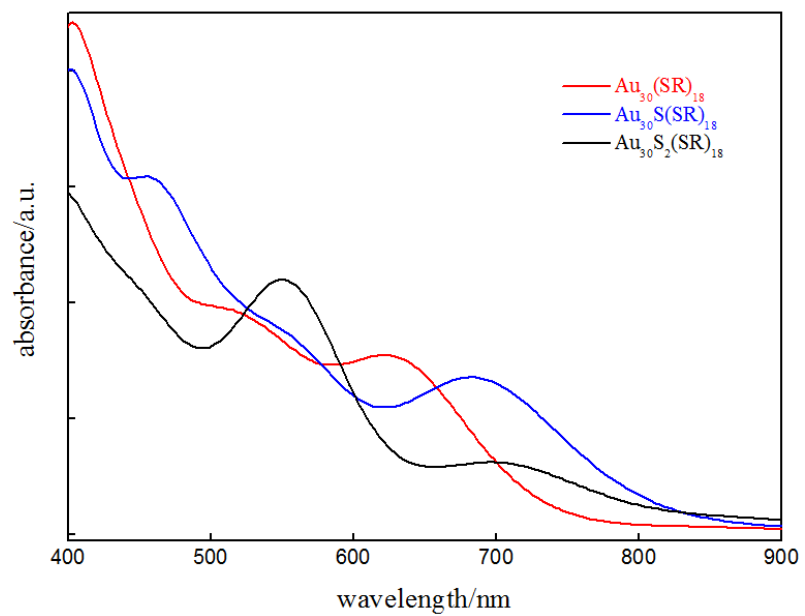
**Fig. S1** Geometry (Au yellow, S baby blue and blue, H white) and AdNDP localized natural bonding orbitals (red-grey) of Au<sub>30</sub>S(SH)<sub>18</sub> cluster. The 5d lone pairs of Au atoms with ONs = 1.83-2.00 |e| are not included.



**Fig. S2** IR spectra of (a)  $\text{Au}_{30}(\text{SR})_{18}$ , (b)  $\text{Au}_{30}\text{S}(\text{SR})_{18}$  and (c)  $\text{Au}_{30}\text{S}_2(\text{SR})_{18}$  clusters, R = CH<sub>3</sub>.



**Fig. S3** (a) The superatomic orbitals of  $\text{Au}_{14}^{6+}$  cluster, and (b) the superatomic orbitals of  $\text{Au}_{30}\text{S}_2(\text{SH})_{18}$  cluster.



**Fig. S4** Calculated optical absorption spectra of  $\text{Au}_{30}(\text{SR})_{18}$ ,  $\text{Au}_{30}\text{S}(\text{SR})_{18}$  and  $\text{Au}_{30}\text{S}_2(\text{SR})_{18}$  clusters,  $\text{R} = \text{CH}_3$ .

The xyz coordinates (in Å) of Au<sub>30</sub>S(SCH<sub>3</sub>)<sub>18</sub>, Au<sub>30</sub>(SCH<sub>3</sub>)<sub>18</sub> and Au<sub>30</sub>S<sub>2</sub>(SCH<sub>3</sub>)<sub>18</sub> clusters optimized at the TPSS/Lanl2dz basis set for Au and 6-31G\* basis set for S and H level of theory.

Au<sub>30</sub>S(SCH<sub>3</sub>)<sub>18</sub> cluster:

Au	2.029198	2.212240	0.563530
Au	-1.545704	0.805764	-0.202273
Au	1.277294	-0.351783	-0.048013
Au	0.641314	1.954852	-1.829840
Au	-0.732482	3.347585	0.446880
Au	-0.340442	-1.729319	1.841068
Au	-2.758463	3.004849	-2.006904
Au	3.207937	0.849029	-1.629897
Au	4.847283	2.499007	0.470042
Au	-0.166161	1.200632	2.194859
Au	-2.034443	-1.871421	-0.520712
Au	-2.796308	2.094691	1.910844
Au	4.728821	-1.074358	0.117143
Au	-0.396006	-0.672571	-2.436289
Au	0.601729	-2.931952	-0.557130
Au	2.545145	-1.946868	-2.664242
Au	2.291812	4.992650	-0.110071
Au	3.055330	0.619160	2.783437
Au	-3.383946	-0.806627	1.770363
Au	2.394056	-2.205948	1.606548
Au	-4.666173	0.850105	0.010938
Au	6.468188	0.996299	-1.751707
Au	-3.108367	-0.028231	-2.352735
Au	-4.833469	-1.820313	-0.434035
Au	-2.593006	-4.538228	-1.196303
Au	-5.462897	0.691272	3.267879
Au	7.888723	-1.290858	0.296574
Au	-6.410671	-0.158640	-2.495332
Au	-7.277545	-0.763181	0.909164
Au	5.645885	-3.529457	1.938817
S	4.572245	4.590666	-0.680747
S	5.206680	0.566891	1.795022
S	-2.061346	-1.868040	3.556846
S	1.040910	-1.193666	-4.363110
S	4.831824	0.945118	-3.475562
S	1.122444	0.712429	4.196940
S	0.042709	5.648892	0.298909
S	-0.271551	-5.078930	-1.355353
S	4.299184	-2.911487	-1.381694

S	-4.979280	3.043517	-1.101616
S	-0.757061	3.350567	-3.275417
S	-4.724466	-0.006500	-4.171266
S	-4.422298	2.806842	3.595424
S	8.271462	1.008062	-0.187845
S	-4.949457	-4.147739	-1.241112
S	-6.560682	-1.424733	3.092081
S	7.701883	-3.613862	0.750203
S	-8.362295	-0.199462	-1.127285
S	3.614545	-3.648119	3.149133
C	1.313066	2.365824	5.020187
C	4.742959	2.683349	-4.112543
C	-3.487418	2.570191	5.180933
C	-4.949143	4.417382	0.141496
C	9.786291	0.972201	-1.262062
C	-2.639743	-3.628437	3.493939
C	0.047431	6.194962	2.071746
C	0.302522	-2.764431	-5.020825
C	5.502145	5.790674	0.384880
C	-4.628309	-1.730954	-4.849943
C	5.705964	-2.888917	-2.592624
C	-1.038974	2.352292	-4.810558
C	-5.577543	-5.040410	0.257848
C	0.027968	-6.178617	0.108411
C	-8.096020	-1.265598	4.127880
C	8.968134	-3.911659	2.073083
C	-8.740952	1.607143	-0.943415
C	3.921875	-2.575245	4.629672
H	-8.754649	-2.106058	3.883422
H	-8.603268	-0.318711	3.928972
H	-7.796400	-1.320074	5.180204
H	-4.207456	2.584764	6.006077
H	-2.788583	3.407805	5.281167
H	-2.942025	1.623086	5.170979
H	-9.501875	1.712628	-0.163180
H	-9.134437	1.960656	-1.902242
H	-7.838061	2.164520	-0.680376
H	-5.523266	-1.906607	-5.456279
H	-4.567414	-2.466170	-4.044312
H	-3.733613	-1.787260	-5.479076
H	-5.446589	-6.116267	0.102015
H	-6.641972	-4.801424	0.351703
H	-5.046346	-4.713941	1.155228
H	-5.817794	4.301152	0.798197

H	-5.015995	5.362751	-0.408185
H	-4.029841	4.386750	0.733226
H	-3.632716	-3.672235	3.954751
H	-1.933199	-4.240138	4.065984
H	-2.691709	-3.980330	2.459811
H	-0.518553	-7.114949	-0.045530
H	-0.295069	-5.690913	1.031364
H	1.104375	-6.373966	0.149715
H	-1.805496	2.860150	-5.405595
H	-1.362795	1.338965	-4.556438
H	-0.092352	2.317256	-5.360128
H	0.599808	7.138294	2.137761
H	0.508363	5.438631	2.711342
H	-0.994953	6.350922	2.368929
H	5.284172	6.802636	0.027577
H	6.568903	5.573013	0.267772
H	5.212253	5.685287	1.433192
H	10.646128	0.747322	-0.621816
H	9.904431	1.966454	-1.706140
H	9.691741	0.218202	-2.046925
H	8.820677	-4.929731	2.448590
H	8.860132	-3.189412	2.885515
H	9.958427	-3.821822	1.614399
H	5.476597	-3.616583	-3.378697
H	6.608811	-3.190526	-2.051150
H	5.837763	-1.892287	-3.021193
H	5.608485	2.847507	-4.763798
H	4.744629	3.403353	-3.291073
H	3.817373	2.772127	-4.690985
H	2.112715	2.284379	5.764333
H	0.365852	2.604932	5.515556
H	1.560514	3.138043	4.287766
H	4.578452	-3.126465	5.311762
H	2.955425	-2.385311	5.107999
H	4.384950	-1.629225	4.335968
H	1.054682	-3.264276	-5.640449
H	-0.563729	-2.493509	-5.634421
H	-0.008325	-3.420938	-4.204408



Au<sub>30</sub>(SCH<sub>3</sub>)<sub>18</sub> cluster:

Au	-1.156746	2.688136	-0.181298
Au	1.035689	1.046393	-0.213833
Au	-1.116012	0.928338	-2.348015
Au	-3.176945	0.664333	-0.146462
Au	1.272352	-0.723085	1.980596
Au	0.776474	2.985707	-2.176035
Au	-0.005137	5.217479	0.001452
Au	2.408129	4.028033	0.045653
Au	3.176945	-0.664333	-0.146462
Au	3.473783	1.608950	-2.188313
Au	-3.453606	4.284602	-0.449081
Au	0.612298	3.328466	1.989529
Au	2.950534	1.489513	1.685985
Au	1.599832	6.183143	-2.415170
Au	1.953589	7.201736	1.055706
Au	3.129576	4.533005	3.158380
Au	1.156746	-2.688136	-0.181298
Au	-1.035689	-1.046393	-0.213833
Au	1.116012	-0.928338	-2.348015
Au	-1.272352	0.723085	1.980596
Au	-0.776474	-2.985707	-2.176035
Au	0.005137	-5.217479	0.001452
Au	-2.408129	-4.028033	0.045653
Au	-3.473783	-1.608950	-2.188313
Au	3.453606	-4.284602	-0.449081
Au	-0.612298	-3.328466	1.989529
Au	-2.950534	-1.489513	1.685985
Au	-1.599832	-6.183143	-2.415170
Au	-1.953589	-7.201736	1.055706
Au	-3.129576	-4.533005	3.158380
S	-2.172635	6.297239	-0.526032
S	2.615069	0.209040	-3.928617
S	1.427132	4.443523	-4.023014
S	-0.578872	2.183868	3.811522
S	-4.885303	2.375484	-0.537223
S	4.585170	3.199899	-0.784924
S	1.814789	8.165501	-1.116110
S	2.183623	6.709500	3.374045
S	4.465676	2.559468	3.245568
S	2.172635	-6.297239	-0.526032
S	-2.615069	-0.209040	-3.928617
S	-1.427132	-4.443523	-4.023014
S	0.578872	-2.183868	3.811522

S	4.885303	-2.375484	-0.537223
S	-4.585170	-3.199899	-0.784924
S	-1.814789	-8.165501	-1.116110
S	-2.183623	-6.709500	3.374045
S	-4.465676	-2.559468	3.245568
C	-2.615069	7.150534	1.058436
C	3.972203	-1.015403	-4.243566
C	-0.174389	4.814960	-4.884263
C	-2.076440	3.245876	4.076481
C	-5.779068	2.412171	1.087038
C	5.182237	4.463557	-2.007009
C	3.548869	8.729219	-1.459436
C	0.442306	6.451523	3.943023
C	3.980456	1.809648	4.872390
C	2.615069	-7.150534	1.058436
C	-3.972203	1.015403	-4.243566
C	0.174389	-4.814960	-4.884263
C	2.076440	-3.245876	4.076481
C	5.779068	-2.412171	1.087038
C	-5.182237	-4.463557	-2.007009
C	-3.548869	-8.729219	-1.459436
C	-0.442306	-6.451523	3.943023
C	-3.980456	-1.809648	4.872390
H	0.480024	6.037664	4.956192
H	-0.077335	5.762052	3.269186
H	-0.052917	7.428538	3.956041
H	4.399059	2.431394	5.671052
H	4.413956	0.804676	4.916387
H	2.893101	1.752412	4.966431
H	3.758149	9.579126	-0.801433
H	3.594062	9.045480	-2.507025
H	4.266182	7.925792	-1.276546
H	-0.020514	5.681776	-5.535724
H	-0.966807	5.019125	-4.160538
H	-0.430266	3.934939	-5.483706
H	5.988508	4.015462	-2.597617
H	5.570919	5.312599	-1.433448
H	4.369975	4.791693	-2.661533
H	6.444567	-3.281811	1.095097
H	5.069542	-2.463903	1.916466
H	6.364822	-1.489786	1.155213
H	3.653141	-7.492670	0.991698
H	1.944682	-8.010533	1.160242
H	2.491078	-6.478512	1.911783

H	-3.758149	-9.579126	-0.801433
H	-3.594062	-9.045480	-2.507025
H	-4.266182	-7.925792	-1.276546
H	-0.480024	-6.037664	4.956192
H	0.077335	-5.762052	3.269186
H	0.052917	-7.428538	3.956041
H	-4.399059	-2.431394	5.671052
H	-4.413956	-0.804676	4.916387
H	-2.893101	-1.752412	4.966431
H	-3.653141	7.492670	0.991698
H	-1.944682	8.010533	1.160242
H	-2.491078	6.478512	1.911783
H	-6.444567	3.281811	1.095097
H	-5.069542	2.463903	1.916466
H	-6.364822	1.489786	1.155213
H	-2.842763	2.639919	4.572297
H	-2.454814	3.624879	3.122705
H	-1.791773	4.081108	4.726378
H	1.791773	-4.081108	4.726378
H	2.842763	-2.639919	4.572297
H	2.454814	-3.624879	3.122705
H	0.020514	-5.681776	-5.535724
H	0.966807	-5.019125	-4.160538
H	0.430266	-3.934939	-5.483706
H	-5.988508	-4.015462	-2.597617
H	-5.570919	-5.312599	-1.433448
H	-4.369975	-4.791693	-2.661533
H	3.562967	-1.805082	-4.883207
H	4.343859	-1.443616	-3.309587
H	4.782182	-0.496124	-4.767356
H	-4.782182	0.496124	-4.767356
H	-3.562967	1.805082	-4.883207
H	-4.343859	1.443616	-3.309587

Au<sub>30</sub>S<sub>2</sub>(SCH<sub>3</sub>)<sub>18</sub> cluster:

Au	-0.962994	2.832165	0.189863
Au	1.115841	1.070108	0.040170
Au	-0.913489	1.147929	-2.017210
Au	-3.103632	0.781859	0.035152
Au	1.282952	-0.726730	2.177183
Au	1.044654	3.128941	-1.818750
Au	0.029155	5.483514	-0.033118
Au	3.225719	3.782119	0.094666
Au	3.103632	-0.781859	0.035152
Au	3.261596	1.086375	-2.357540
Au	-3.286825	4.196622	-0.772908
Au	0.655669	3.365206	2.593155
Au	3.053197	1.422510	1.929382
Au	2.341337	6.120020	-2.078086
Au	4.840306	6.508859	0.133957
Au	5.644417	3.735056	2.191154
Au	0.962994	-2.832165	0.189863
Au	-1.115841	-1.070108	0.040170
Au	0.913489	-1.147929	-2.017210
Au	-1.282952	0.726730	2.177183
Au	-1.044654	-3.128941	-1.818750
Au	-0.029155	-5.483514	-0.033118
Au	-3.225719	-3.782119	0.094666
Au	-3.261596	-1.086375	-2.357540
Au	3.286825	-4.196622	-0.772908
Au	-0.655669	-3.365206	2.593155
Au	-3.053197	-1.422510	1.929382
Au	-2.341337	-6.120020	-2.078086
Au	-4.840306	-6.508859	0.133957
Au	-5.644417	-3.735056	2.191154
S	-1.809481	-5.113574	1.489323
S	1.809481	5.113574	1.489323
S	-1.892889	6.039814	-1.366970
S	2.092440	-0.244139	-3.962184
S	1.816082	4.482129	-3.718560
S	-0.499980	1.933300	4.128872
S	-4.840306	2.436762	-0.408739
S	4.795509	2.438876	-1.139817
S	3.013470	7.856899	-0.586303
S	6.773756	5.311175	0.818363
S	4.684998	2.095987	3.605505
S	1.892889	-6.039814	-1.366970
S	-2.092440	0.244139	-3.962184

S	-1.816082	-4.482129	-3.718560
S	0.499980	-1.933300	4.128872
S	4.840306	-2.436762	-0.408739
S	-4.795509	-2.438876	-1.139817
S	-3.013470	-7.856899	-0.586303
S	-6.773756	-5.311175	0.818363
S	-4.684998	-2.095987	3.605505
C	-2.643705	7.465056	-0.447205
C	3.327059	-1.562719	-4.391403
C	0.272736	5.087231	-4.545540
C	-1.953946	2.970846	4.635261
C	-5.530725	2.757566	1.282775
C	5.452849	3.558694	-2.465403
C	3.817058	9.106076	-1.701568
C	7.597583	6.452002	2.027452
C	3.704626	3.089155	4.826499
C	2.643705	-7.465056	-0.447205
C	-3.327059	1.562719	-4.391403
C	-0.272736	-5.087231	-4.545540
C	1.953946	-2.970846	4.635261
C	5.530725	-2.757566	1.282775
C	-5.452849	-3.558694	-2.465403
C	-3.817058	-9.106076	-1.701568
C	-7.597583	-6.452002	2.027452
C	-3.704626	-3.089155	4.826499
H	8.403466	5.892311	2.513811
H	6.883990	6.811703	2.772277
H	8.014059	7.293202	1.463442
H	4.409759	3.539186	5.533934
H	3.032248	2.401812	5.350271
H	3.124176	3.865148	4.320226
H	4.358608	9.819529	-1.071092
H	3.022793	9.624202	-2.249660
H	4.503110	8.622550	-2.400864
H	0.553817	5.885824	-5.240854
H	-0.446058	5.459761	-3.812139
H	-0.151780	4.243032	-5.099358
H	6.081382	2.951574	-3.126091
H	6.055737	4.329989	-1.974739
H	4.638405	4.018150	-3.030592
H	6.170309	-3.644843	1.230247
H	4.726716	-2.905753	2.007222
H	6.125067	-1.881060	1.560250
H	3.622863	-7.677320	-0.889224

H	1.978549	-8.324974	-0.577737
H	2.747062	-7.230553	0.615063
H	-4.358608	-9.819529	-1.071092
H	-3.022793	-9.624202	-2.249660
H	-4.503110	-8.622550	-2.400864
H	-8.403466	-5.892311	2.513811
H	-6.883990	-6.811703	2.772277
H	-8.014059	-7.293202	1.463442
H	-4.409759	-3.539186	5.533934
H	-3.032248	-2.401812	5.350271
H	-3.124176	-3.865148	4.320226
H	-3.622863	7.677320	-0.889224
H	-1.978549	8.324974	-0.577737
H	-2.747062	7.230553	0.615063
H	-6.170309	3.644843	1.230247
H	-4.726716	2.905753	2.007222
H	-6.125067	1.881060	1.560250
H	-2.683842	2.311250	5.116662
H	-2.402654	3.460713	3.767618
H	-1.600851	3.723094	5.349019
H	1.600851	-3.723094	5.349019
H	2.683842	-2.311250	5.116662
H	2.402654	-3.460713	3.767618
H	-0.553817	-5.885824	-5.240854
H	0.446058	-5.459761	-3.812139
H	0.151780	-4.243032	-5.099358
H	-6.081382	-2.951574	-3.126091
H	-6.055737	-4.329989	-1.974739
H	-4.638405	-4.018150	-3.030592
H	2.790994	-2.364518	-4.910723
H	3.809518	-1.956891	-3.493654
H	4.076192	-1.123119	-5.058839
H	-4.076192	1.123119	-5.058839
H	-2.790994	2.364518	-4.910723
H	-3.809518	1.956891	-3.493654