Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Ligand effects on the optical and chiroptical properties of the thiolated Au_{18} cluster

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Figures S1-S5. Comparison of Au-S framework and Au_9 inner cores of studied structures by including or not the long range interactions (DFT-D).

Figure S6. Bond lengths of all studied structures.

Figure S7. Relaxed structures by means of DFT calculations of Au_{18} clusters protected by chiral ligands.

Figure S8. Comparison of calculated absorption spectra of the Au_{18} cluster protected by S-c-C_6H_{11} ligand based on DFT and DFT-D approach with the experimental curve.

Figure S9. Comparison of CD spectra of Au_{18} cluster protected by S-c-C_6H_{11} ligands and DFT and DFT-D approaches.

Figure S10. Contribution of the atoms constituting the thiolated gold clusters to the energy levels of clusters protected by achiral ligands.

Figure S11. Comparison of CD spectra of Au_{18} cluster protected by S-c-C_6H_{11} ligands based on DFT-D and DFT calculations.

Figure S12-S16. Comparison of UV spectra of Au18 cluster protected by mainly chiral ligands.

Figures S17. C Contribution of the atoms constituting the thiolated gold clusters to the energy levels of clusters protected by mostly chiral ligands.

Section 2. Cartesian coordinates of some studied clusters.

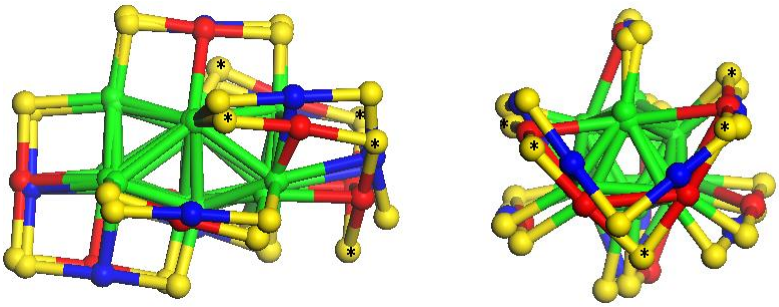


Figure S1. Comparison of cores (green balls) and Au-S framework of thiolated Au_{18} cluster protected by p-MBA ligands. Structure with Au atoms in blue corresponds with the un-corrected (DFT) compound. It is easy to note that the distortion occurs in both the Au core and the staples, but the distortion is stronger in the tetramer staple (S atoms are indicated with asterisks).

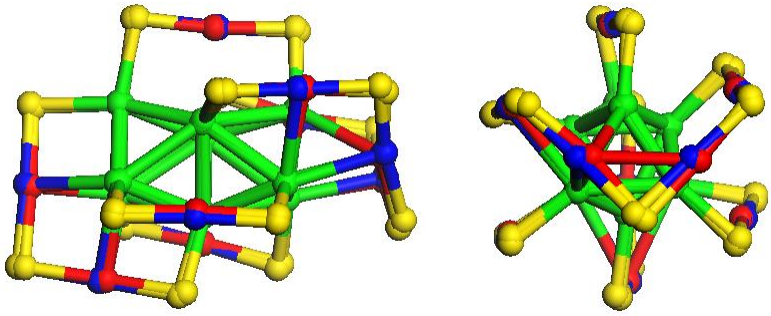


Figure S2. Comparison of cores (green balls) and Au-S framework of thiolated Au_{18} cluster protected by -SPh ligands. Structure with Au atoms in blue corresponds with the un-corrected (DFT) compound. It is easy to note that the distortion occurs in the tetramer staple. The orientation is same that the one displayed on Figure S2.

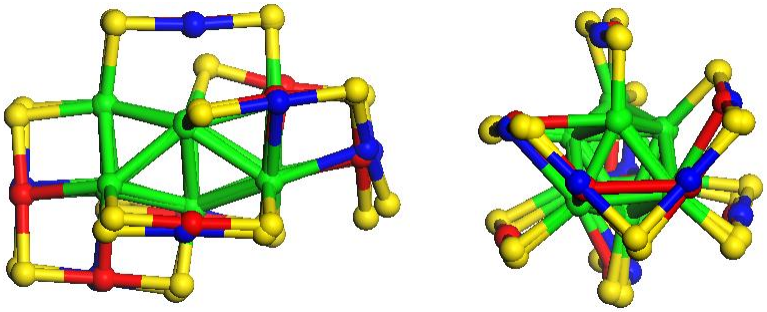


Figure S3. Comparison of cores (green balls) and Au-S framework of thiolated Au_{18} cluster protected by $–SPhNO_2$ ligands. Color corresponds with Figure S2. The distortion occurs in the tetramer motif mainly.

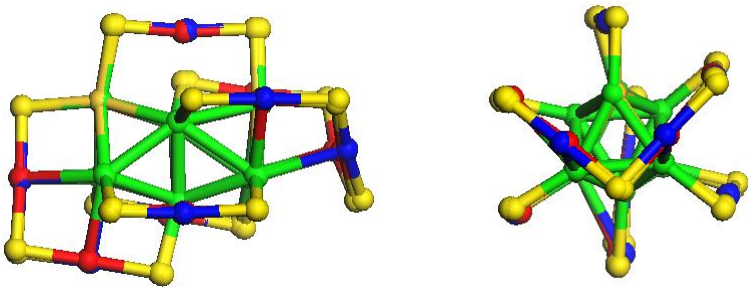


Figure S4. Comparison of cores and Au-S framework of thiolated Au_{18} cluster protected by cyclohexyl ligands. Both structures are not indistinguishable despite the bulky ligands, the different orientation of the ligands and the consideration of the long range interactions. Color of Au ad atoms are in agreement with previous figures.

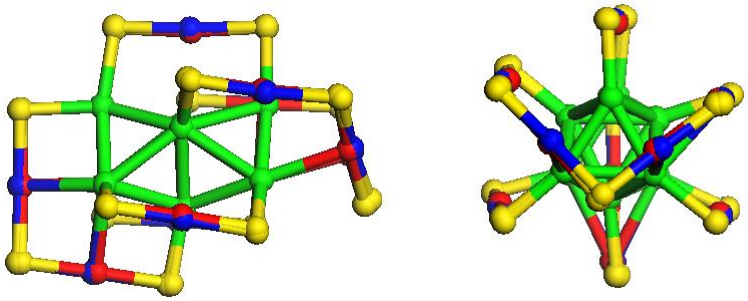


Figure S5. Comparison of cores and Au-S framework of thiolated Au_{18} cluster protected $–SCH_3$ ligands. Both structures are not indistinguishable. Color of Au ad atoms are in agreement with previous figures.

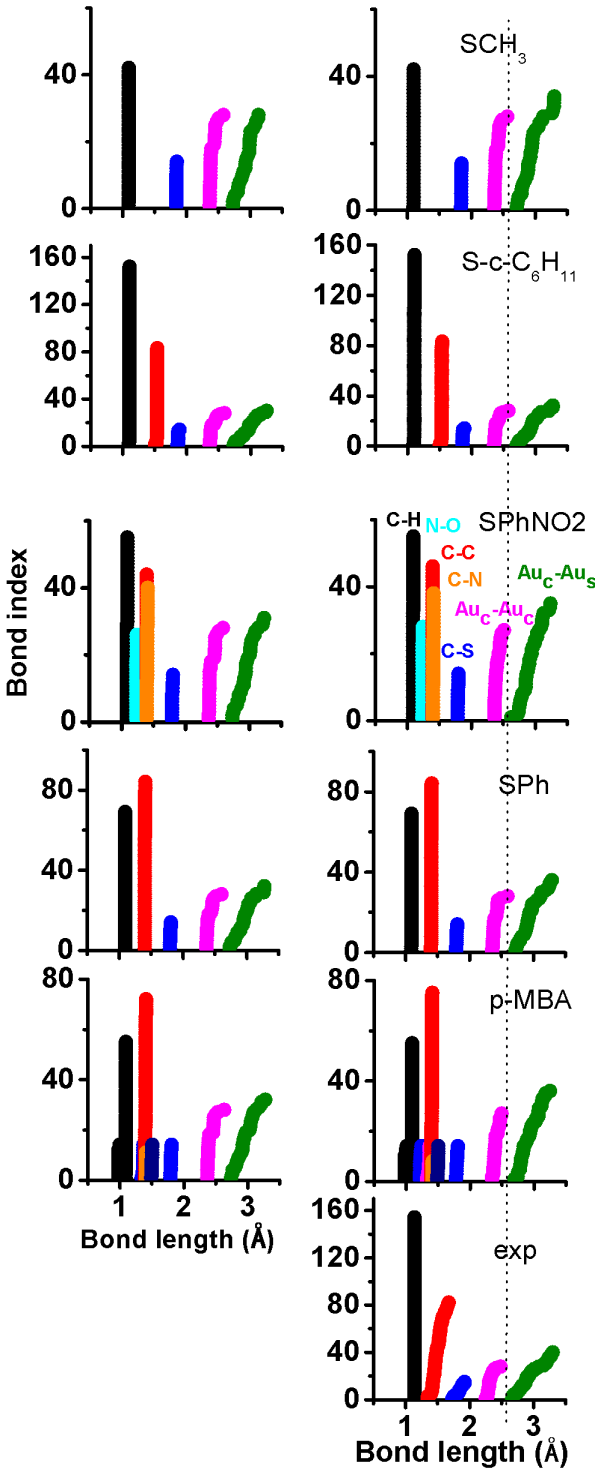
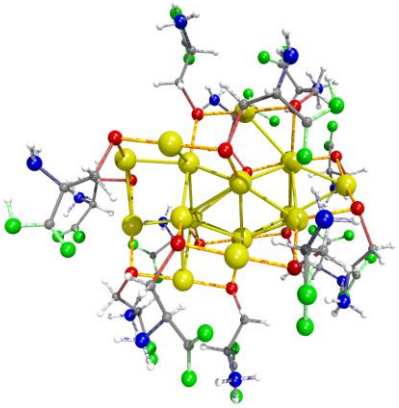
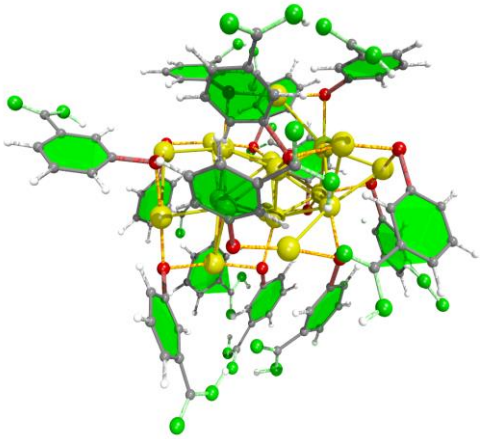


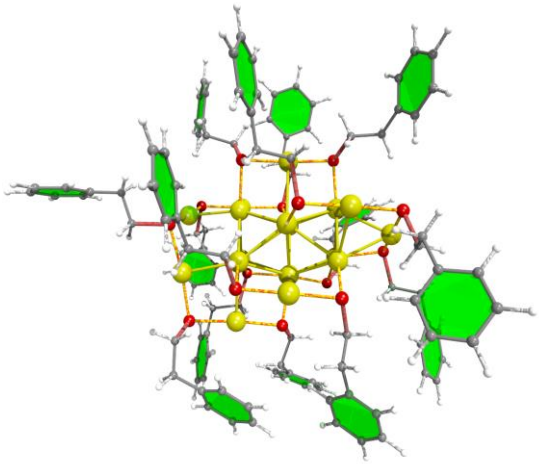
Figure S6. Bond lengths of all studied structures. Left panel corresponds with uncorrected structures (DFT calculations) and right panel are structures calculated by a DFT-D approach. It is notable that all structures feature more ordered bonds than the experimental one (right panel and bottom graph). a) Compounds including p-MBA or $PhNO_2$ show their major differences in the Au-Au and Au-S bonds. b) The structure protected with bulky S-c-C_6H_{11} ligand shows almost the same Au-S and Au-Au bonding of the SCH_3 ligand which means that both the core is intact and Au-S framework is similar independently of the correction (DFT-D).



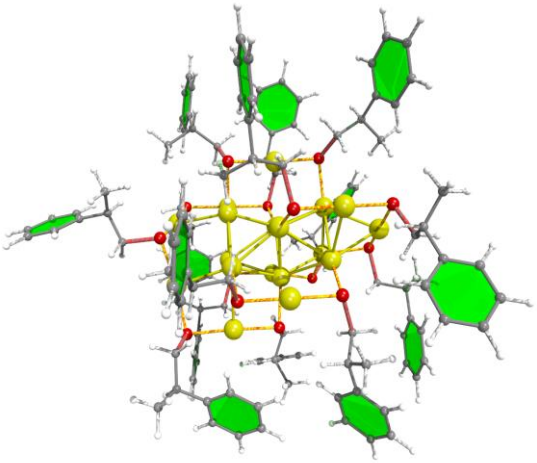
L-cysteine



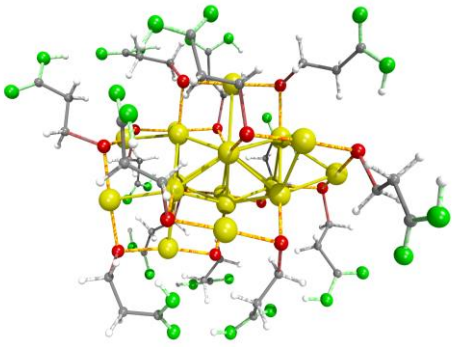
m-MBA



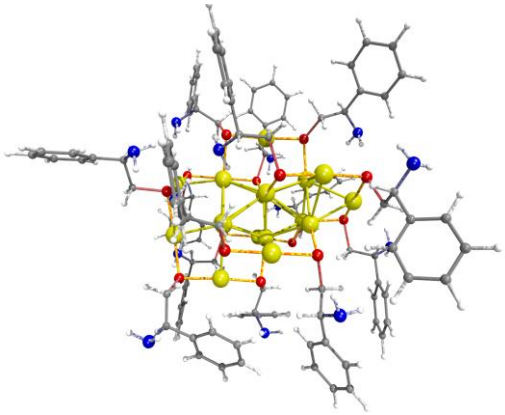
2-PET



2-PET-Met



MPA



2-PET-NH_2

Figure S7. Relaxed structures by means of DFT calculations. Chiral ligands were considered. 2-PET and MPA are achiral ligands.

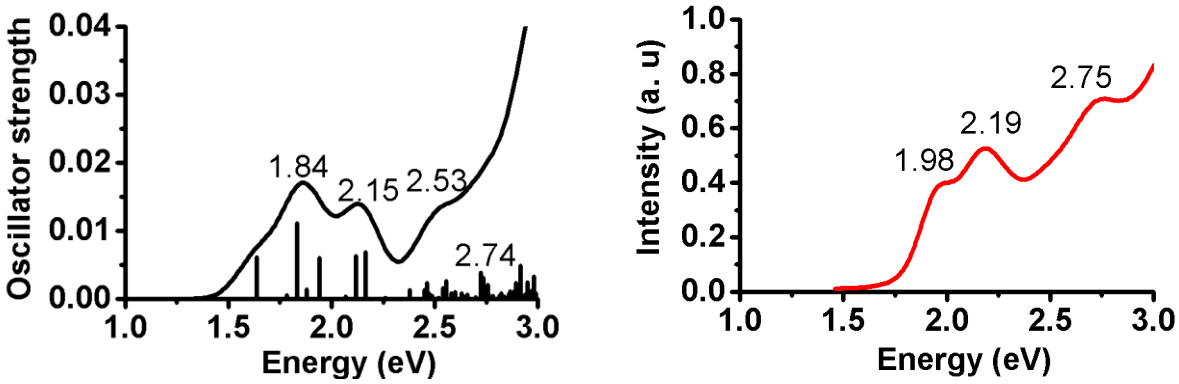


Figure S8. Calculated absorption spectrum of the Au_{18} cluster protected by S-c-C_6H_{11} ligand (left panel) based on DFT-D approach. The used Gaussian broadening is of 0.22 eV. The experimental spectrum is shown at right panel. It is important to note that the same ligand is found in both spectra. Interestingly the relative intensity of first two peaks is better reproduced by considering the ligand used during experiments. See reference 16 for a comparison with the structure protected by SCH_3 ligands.

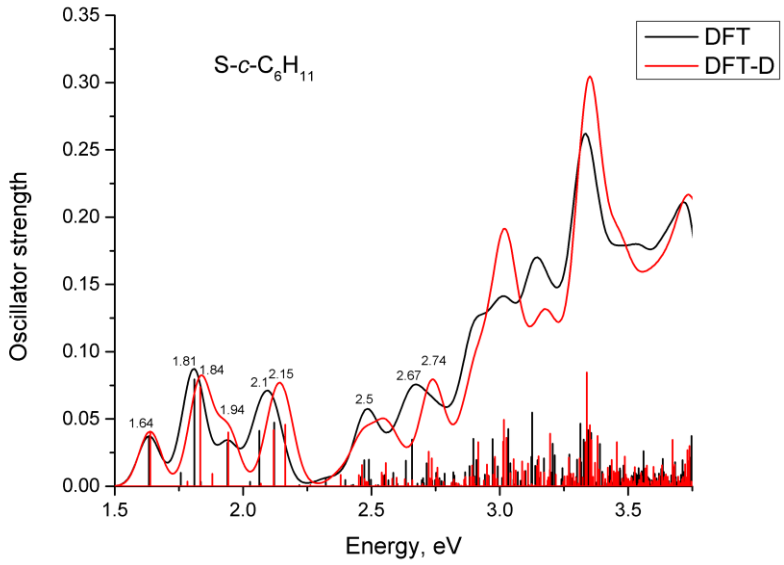


Figure S9. Comparison of calculated absorption spectra of the Au_{18} cluster protected by S-c-C_6H_{11} ligand based on DFT (black curve) and DFT-D approach. The used gaussian broadening is od 0.22 eV. It is evident that DFT-D approach enhances the agreement between calculations and experiment.

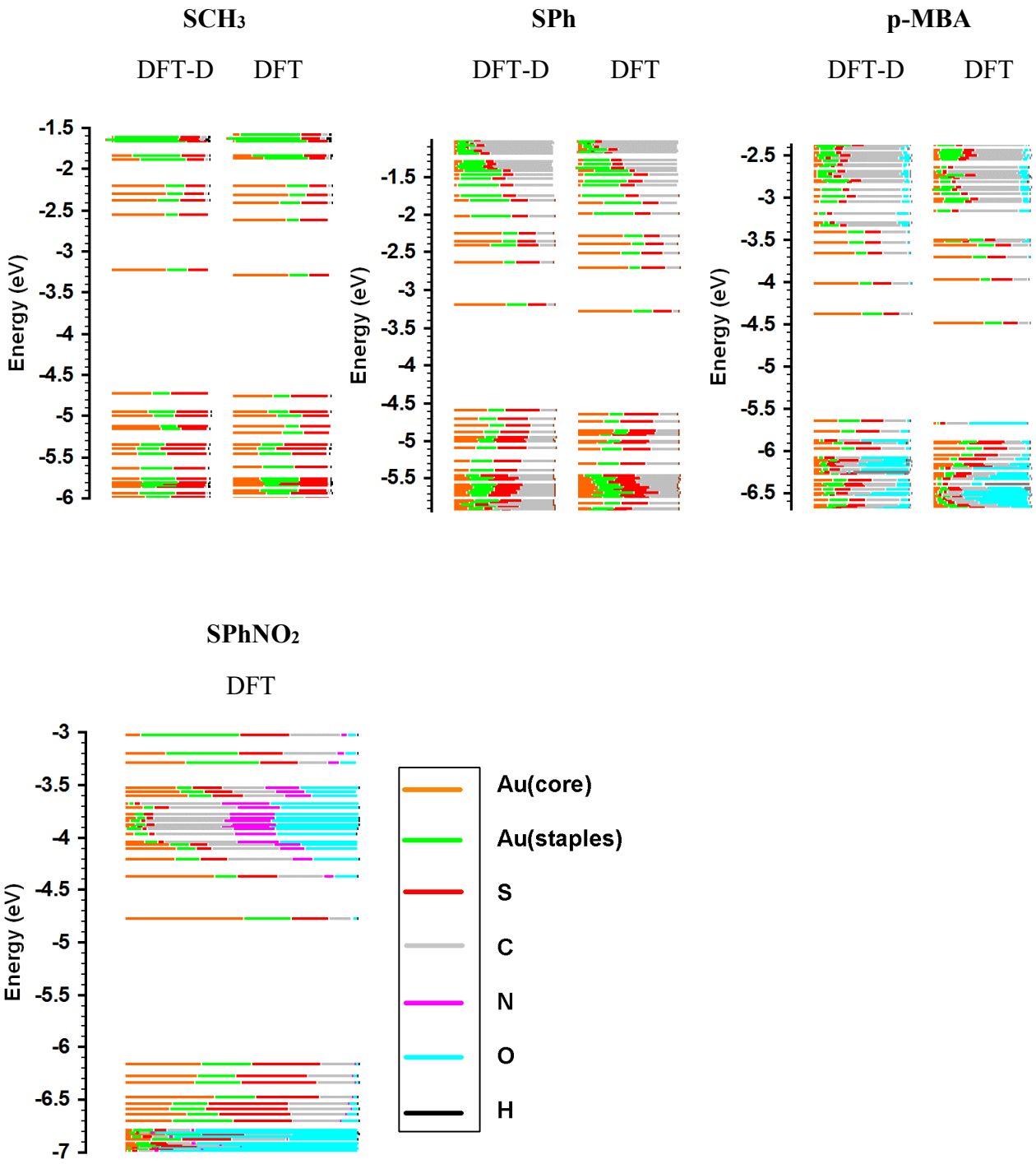
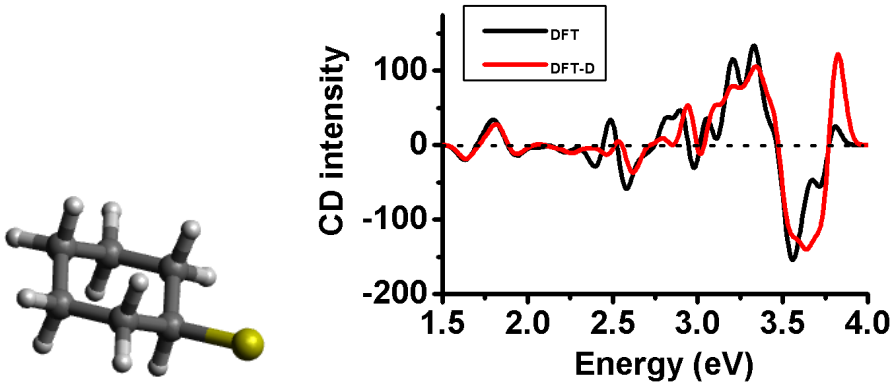


Figure S10. Contribution to the energy levels from atoms constituting thiolated Au_{18} clusters protected with achiral ligands. In three upper figures is depicted the energy levels of relaxed structures with and without consideration of the correction of long range forces. It is important to note that p-MBA structure has contribution from the Oxygen atoms (cyan color) in such manner that oxygen atoms are modulating its electronic structure. The lower figure depicts the energy levels of the Au_{18} cluster protected by $SPhNO_2$ ligands. Again, it is obtained a significant contribution from the oxygen atoms.



S-c-C_6H_{11} ligand

Figure S11. Comparison of CD spectra of Au_{18} cluster protected by S-c-C_6H_{11} ligands. Red curve corresponds with DFT-D calculation. Minor differences are found in a range from 2.25 to 2.8 eV approx. between both spectra.

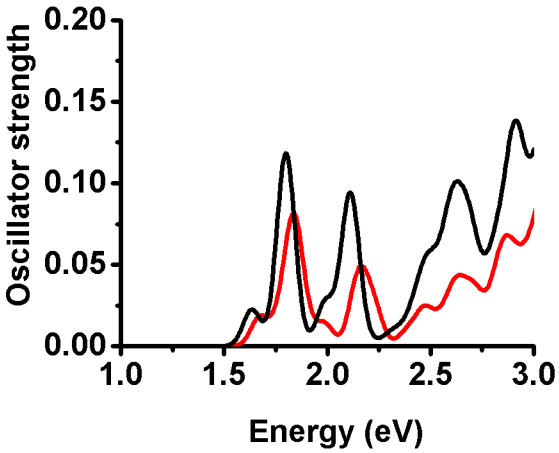
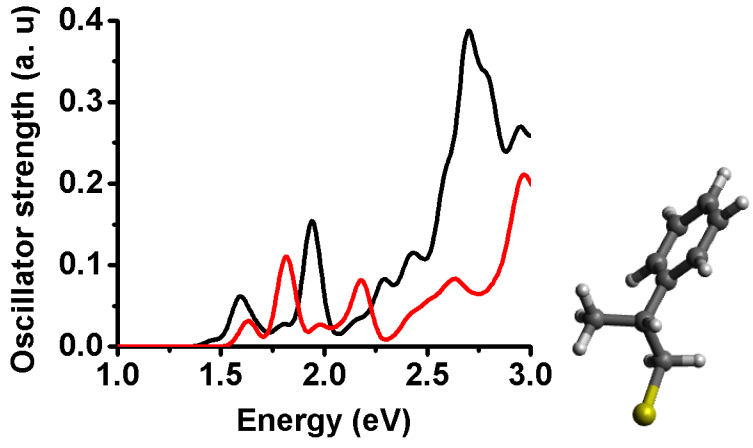


Figure S12. Comparison of UV spectra of Au_{18} cluster protected by 2-PET (S-CH_2-CH_2-Ph and black curve), and SCH_3 ligands (red profile). Both structures were obtained by DFT calculations. In this case both ligands are achiral but is evident that the ligand including phenyl rings feature a slight more intense profile.



S-CH_2-$CH(CH_3)$-Ph ligand

Figure S13. Comparison of optical absorption spectra of Au_{18} cluster protected by S-Ph (Black line) and S-CH_2-$CH(CH_3)$-Ph. Is evident that *the achiral ligand (S-Ph) features a slightly stronger signal than the chiral one* (Red line). Both calculations do not include van der Waals interactions. However, Fig. 8 in manuscript shows that S-Ph ligand holds a similar profile for DFT and DFT-D calculations.

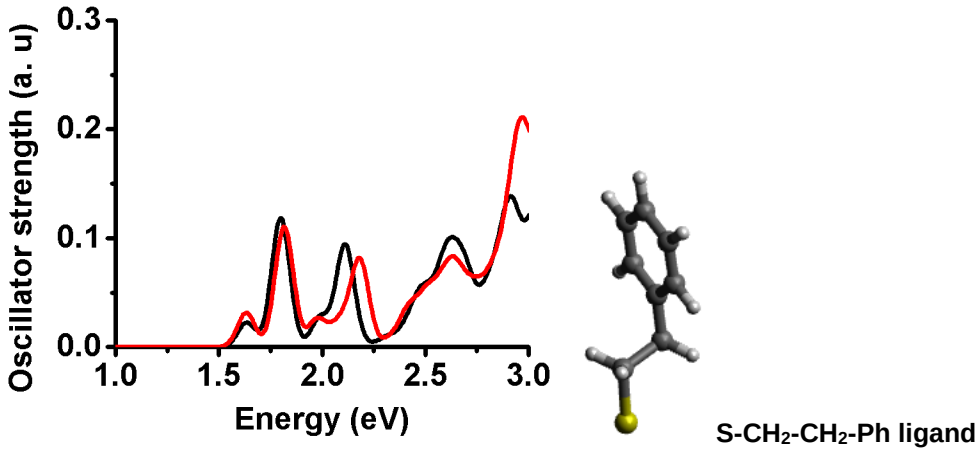


Figure S14. Comparison of optical absorption spectra of Au_{18} cluster protected by achiral S-CH_2-CH_2-Ph (Black line) and chiral S-CH_2-CH(CH_3)-Ph ligands. Profiles are similar and *chiral ligand* (red curve) *does not feature a strong profile*.

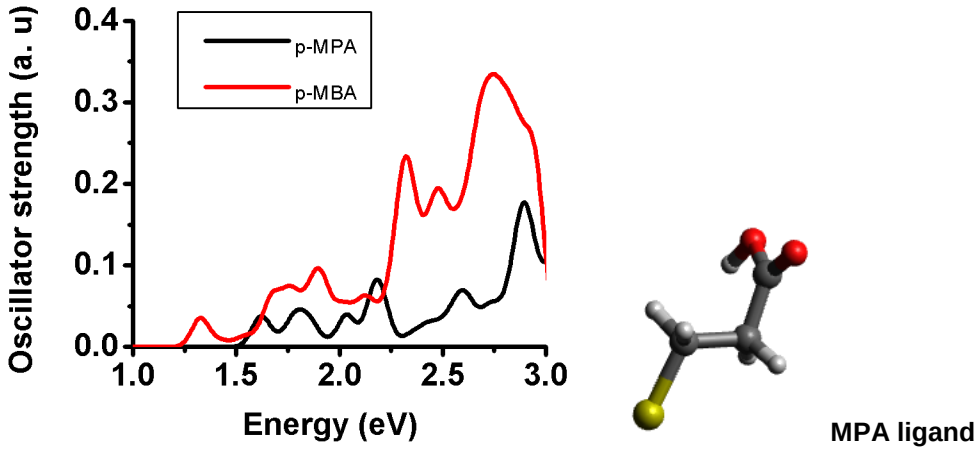


Figure S15. Comparison of optical absorption spectra of Au_{18} cluster protected by p-MBA (red curve) and mercaptopropionic acid (MPA) ligands. The distinct profiles must be ascribed to the presence of the phenyl ring in p-MBA.

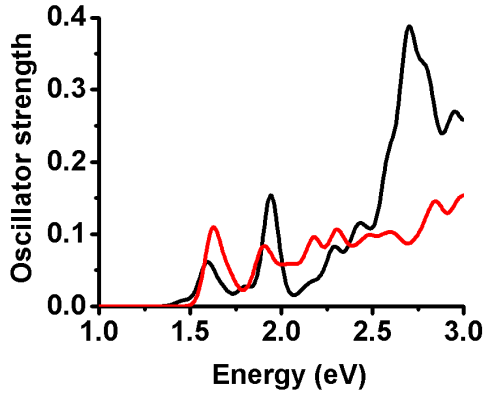


Figure S16. Optical absorption spectra of Au_{18} cluster protected by L-cysteine (red curve) and SPh ligands. The more intense profile of SPh can be ascribed to the presence of phenyl rings. L-cysteine was calculated by considering water as solvent. Noteworthy is the enhanced HOMO-LUMO peak in L-cysteine which might result in the observed fluorescence of the Au_{18} cluster protected by glutathione (Ref 4).

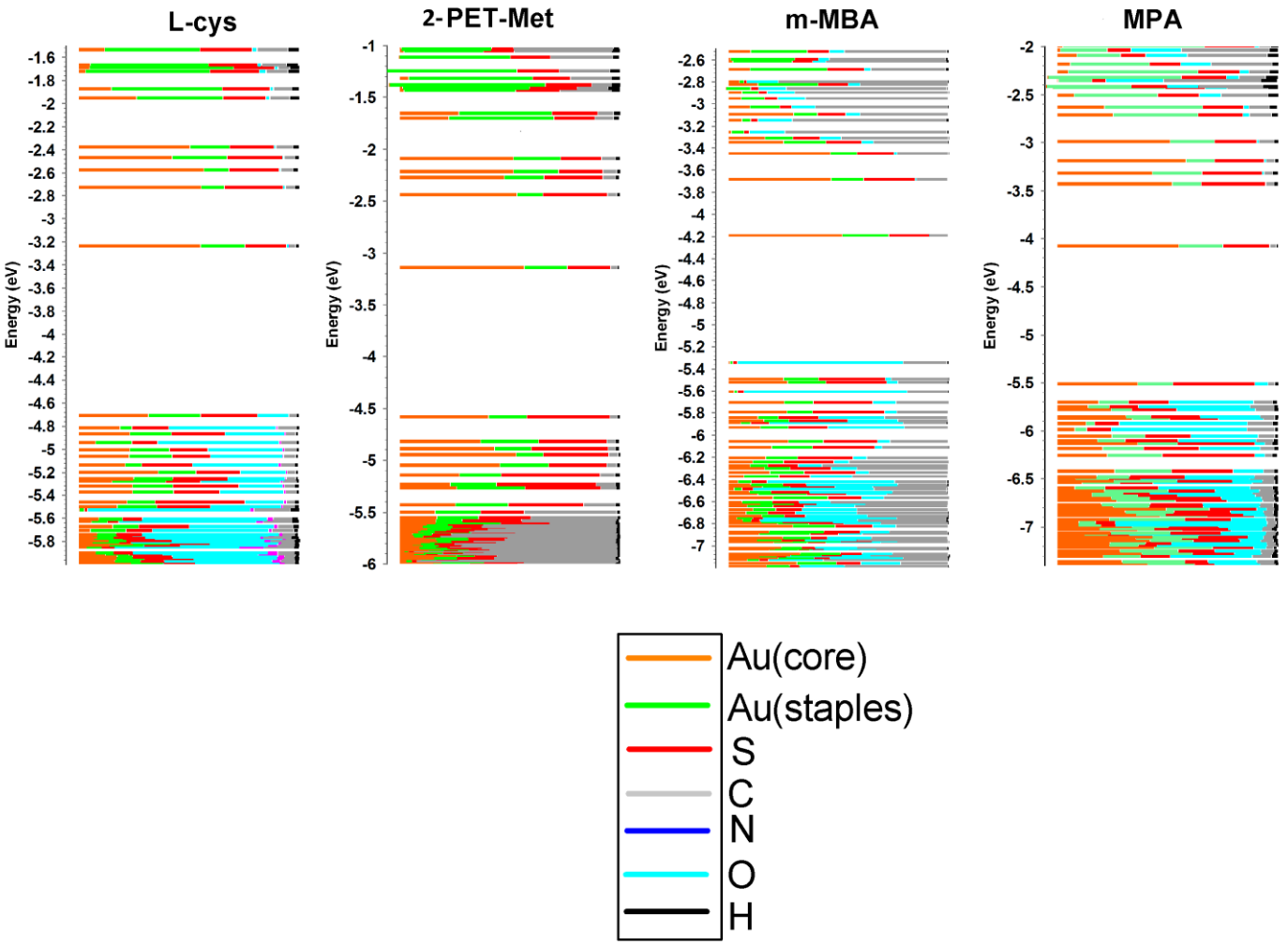


Figure S17. Contribution to the energy levels from atoms constituting thiolated Au_{18} clusters protected with chiral and achiral ligands (m-MBA) shown in Figure 9. Oxygen atoms contribute to the frontier orbitals of m-MB, MPA and L-cysteine. This contribution is indicated as cyan lines. Noteworthy is that for L-cysteine, the contribution of oxygen atoms up to the HOMO level is larger than for the cluster protected by m-MBA ligand.

Section 2

Cartesian coordinates of relaxed Au_{18} cluster by means of DFT-D calculations and protected by p-MBA ligand.

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Au	0.080020	-0.700653	1.768084
Au	-2.389579	0.884136	0.593372
Au	0.480115	1.570992	0.247726
Au	0.977367	-1.010295	-0.933620
Au	-3.323028	-1.572421	2.576851
Au	-1.803075	-1.659079	-0.343477
Au	-1.365316	0.624016	-1.919047
Au	-0.854019	1.916740	3.462255
Au	0.696532	-3.924849	0.504526
Au	-1.999636	3.523556	-1.324784
Au	2.952435	-1.522635	1.121346
Au	3.261437	0.769027	-0.404758
Au	1.585054	1.672531	-3.185840
Au	4.393270	-1.697200	-1.664730
Au	2.431542	0.976644	2.270229
Au	-4.758927	-1.366145	-0.459801
Au	-4.259682	1.092964	-2.730575
Au	5.619156	-0.002104	1.223050
S	2.331699	-1.984041	-2.800196
S	-1.202815	-1.676560	3.640066
S	-1.352154	-4.030464	-0.686483
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S	0.102178	3.923687	-0.315752
S	2.752273	-3.875970	1.711088
S	-0.523241	1.185472	-4.184765
S	3.728648	2.222777	-2.343669

S	1.381107	2.359220	4.066340
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C	3.519750	3.869655	-1.511580
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H	6.558271	0.790020	-1.903773
C	7.701558	-0.674509	-3.036414
C	3.960248	-4.757203	0.611471
H	3.798149	-4.436129	-0.428923
H	3.741143	-5.833630	0.682461
C	5.400269	-4.473192	1.050995
C	5.301767	2.887883	3.044547
H	6.399016	2.939254	3.123169
H	4.864331	3.349972	3.944443
C	4.867132	3.632042	1.778888
C	2.020868	-3.813834	-2.843501
H	1.933242	-4.196147	-1.814665
H	2.896980	-4.281459	-3.318335
C	0.741452	-4.086611	-3.626620
C	-0.254212	-0.417297	-5.072763
H	0.332527	-1.060924	-4.399706
H	0.373188	-0.181428	-5.949967
C	-1.589146	-1.080360	-5.463385

C	-6.059648	-1.905221	-3.362269
H	-6.064766	-1.902120	-4.462498
H	-6.848040	-1.230286	-3.001892
C	-6.218114	-3.318714	-2.802404
C	-3.338190	3.869051	-4.334273
H	-4.229154	3.880128	-4.981786
C	-2.640279	5.236058	-4.407310
C	-3.693220	3.546092	2.738740
H	-2.825960	4.211625	2.838946
H	-4.305484	3.658735	3.648787
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C	-3.835303	-5.198245	-0.388188
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H	1.408655	2.262733	6.439571
H	2.867978	1.535781	5.763739

C	1.150436	0.170108	5.995953
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H	5.559883	-4.836331	2.081728
H	5.583466	-3.384530	1.061291
H	3.849424	4.047036	1.877830
H	4.839362	2.924995	0.926696
H	6.838392	-1.197030	-3.494144
H	8.478860	-1.441864	-2.864901
H	-3.675907	-6.034395	-1.091977
H	-4.080624	-4.321168	-1.011189
H	0.093674	0.146246	5.676647
H	1.129983	0.045452	7.094854
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H	-5.463125	0.144594	4.087869
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H	-2.626098	5.548798	-5.470116
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H	-5.401910	-3.969655	-3.168821
H	-2.057562	-0.545649	-6.309900
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H	1.854428	4.518496	-2.770728
H	3.376669	5.362593	-3.111718
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O	7.062112	4.652167	1.775231
O	5.490305	5.701015	0.584976
H	4.510602	5.718271	0.397454
C	8.204451	0.377293	-4.029049
O	8.106534	1.576599	-3.860035
O	8.766194	-0.117691	-5.170803
H	8.780283	-1.094426	-5.133956
C	-5.109976	-5.495011	0.405155
O	-6.215409	-5.429320	-0.131957
O	-5.031139	-5.817910	1.704491
H	-4.109591	-5.917708	2.061818
C	1.779549	-1.128073	5.481737
O	1.246449	-2.207066	5.697508
O	2.969558	-1.094365	4.834256
H	3.270605	-0.177535	4.640711
C	-5.153067	5.258876	1.662521
O	-4.606255	6.301676	1.302462
O	-6.340906	5.293950	2.283921
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O	-2.672171	-6.345253	3.166517

O	-0.774033	-6.464608	4.315180
H	-0.210410	-5.886559	4.868194
C	-1.253246	6.706990	2.497427
O	-0.333949	6.771096	3.298802
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H	-3.136554	7.009518	2.088270
C	-1.192057	5.348290	-3.930063
O	-0.314321	4.378000	-4.276512
H	-0.741754	3.572724	-4.650731
O	-0.770784	6.339593	-3.341533
C	-7.550622	-3.975682	-3.166495
O	-8.278574	-3.568214	-4.056915
O	-7.854936	-5.068609	-2.433639
H	-7.193964	-5.208522	-1.706778
C	-1.386087	-2.547556	-5.816473
O	-1.942866	-3.469232	-5.233924
O	-0.487023	-2.832455	-6.796962
H	-0.124521	-2.003636	-7.169304
C	2.365654	6.062903	-1.339214
O	2.945467	6.253951	-0.265768
O	1.360477	6.873020	-1.688356
H	0.809350	6.537241	-2.448427
C	0.256075	-5.532835	-3.466709
O	-0.850892	-5.851735	-4.174377
H	-1.192727	-5.066290	-4.673928
O	0.807048	-6.348513	-2.745273