Electronic Supplementary Information (ESI) for:

A topological isomer of the Au₂₅(SR)₁₈⁻ nanocluster

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I. ReaxFF Parametrization

One issue that we discovered with existing ReaxFF parameters was that S-C bond dissociation occurred readily, which led to frequent S-C bond dissociation at room temperature. To address this, the S-C-H portion of previous Au-S-C-H parameter sets^{1,2} has been reoptimized and new parameters have been added (provided in the "ffield" document in the Electronic Supporting Information). A new training set ("trainset.in") has been developed; this consists of potential energy surfaces that describe S-H, S-C, and S-S bond dissociation; H-S-C, H-C-S, H-S-H, H-S-S, S-C-C, C-S-C, S-S-C, S-C-S, and S-S-S angle bending; and H-S-C-H, H-S-C-C, H-C-S-C, H-S-S-H, H-S-S-C, H-S-C-S, S-C-C-C, C-S-S-C, C-C-S-S, C-S-C-S, and S-S-S-S torsion angle twisting. Molecules included in the training set include hydrogen sulfide (H_2S) , methylthiol (HSCH₃), ethylthiol (HSC₂H₅), propylthiol (HSC₃H₇), phenylthiol (HSC₆H₅), disulfide (HSSH), dimethyldisulfide (H₃CSSCH₃), diethyldisulfide (C₂H₅SSC₂H₅), diphenyldisulfide methyl hydrogen disulfide $(C_6H_5SSC_6H_5),$ (HSSCH₃), 1,2-ethane-dithiol (HSCH₂CH₂SH), HSCH₂SCH₃, and sulfur (S_8). All potential energy surfaces in the training set were fit to density functional theory values calculated using the Perdew-Burke-Ernzerhof (PBE)³ exchange-correlation (xc) functional with a polarized triple-zeta (TZP) basis set utilizing the Amsterdam Density Functional (ADF)⁴ code. ReaxFF parameter reoptimization was performed using the ReaxFF package as distributed with the ADF code;⁵ these parameterizations were executed using a Monte Carlo algorithm.⁶

II. System Setup and MD Protocol

A) ReaxFF Simulations

ReaxFF-MD simulations were performed using the LAMMPS code.^{7,8} The model structure $Au_{25}(MET)_{18}$ (derived from the experimental crystal structure of $[Au_{25}(PET)_{18}]^-$ (refs. 9,10)) was inserted in a cubic box with periodic boundary conditions (PBC). The system was first minimized using the Polak-Ribiere version of the conjugate gradient (CG) algorithm¹¹ with a convergence criteria of $1.0e^{-5}$ (stopping tolerance for energy) followed by the Reax-MD simulations in the NVT ensemble starting from 200 K to 300

K for 80 ns and the time step was set to 0.5 fs. The temperature was controlled through the Nosé-Hoover thermostat. Data were collected every 20 ps.

B) DFT Calculations

Density functional theory was used to study dynamics, energetics and electronic, and optical properties of the $[Au_{25}(SR)_{18}]^{-}$ clusters with methyl (MET) and phenylethane (PET) thiols. For all DFT-calculations we used Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional³ and the real-space grid code GPAW¹² that includes scalar relativistic effects in the projector setups for gold. Molecular dynamics was done in three consecutive runs in three different temperatures 300 K, 450 K and 800 K using Langevin dynamics thermostat, 2 fs time step and 0.2Å grid-spacing. Dynamical behavior of [Au₂₅(MET)₁₈]⁻ cluster was studied starting from the known cluster geometry in previously reported crystal structures.^{9,13,14} For the MD-simulations, hydrogen atom masses were set equal to 2 a.u. From the ReaxFF and DFT MD-simulations the most interesting snapshot structures were selected for further investigation by structural relaxation using 0.2 Å grid spacing and 0.05 eV/Å relaxation criterion for the residual forces of atoms. These structures are labeled from 4 to 32. From the known crystal structures, we replaced the true PET-ligand with methyl groups maintaining the ligand direction and relaxed all the structures with PBE using total charge -1. The resulting conformation are represented in structures 1-3. The reference energy was finally selected to be the lowest calculated for 1-3. The rest of the structures, labeled as 4-32, were produced by ReaxFF and DFT calculations. The electronic shell structure was analyzed by projecting the Kohn Sham wavefunctions to the spherical harmonics centered at the center of mass of the cluster.¹⁵ Projection sphere included all the atoms of the cluster. Energy barriers for the structural transformations were calculated using constraint relaxation with 0.2 Å grid spacing. Transformation from the crystal structure cluster to the isomer structure geometry 4 was explored by decreasing the distance between the binding site Au-atoms of each protecting unit in 0.05 Å steps simultaneously over the whole metal core. The distance between the binding site Au-atoms of every protecting unit was kept fixed during the relaxation at each step while the rest of the structure was relaxed to 0.05 eV/Å force criterion.

To study the optical properties, we built first a PET-version of the special isomer structure 4 that was then relaxed with 0.05 eV/Å force criterion. Optical absorption spectrum of the isomer 4 using PET-ligand and the PBE -relaxed $[Au_{25}(PET)_{18}]^-$ crystal structure were calculated using 0.25 Å grid spacing and linear response time-dependent density functional theory (Ir-TDDFT) with PBE-functional as a xc-kernel.¹⁶ The optical spectra were plotted from the single transition eigenvalues and their oscillator strengths by using Gaussians with 0.1 eV sigma parameter. The combined optical spectra we constructed from the single transition eigenvalues of both selected structures and weighted the oscillator strengths with ratios 1:1 and 2:1 for the known crystal structure and isomer 4, respectively.

III. Structural Analysis

A) Radius of gyration

Radius of gyration (R_g) is a measure of the overall size of a body and is widely used as an indicator of the structure compactness.¹⁷ R_g is defined as the root mean-square distance of each atom in the body from their common center of mass:

$$Rg = \sqrt{\frac{1}{M} \sum_{i=1}^{n} m_i (r_i - r_{cm})^2}$$

where M is the total mass of the body, m_i is the mass of the *i*th atom, r_i and r_{cm} are the coordinates of the *i*th atom and the center of mass position of the body, respectively.

Conformational changes of $Au_{25}(MET)_{18}$ cluster were monitored through R_g fluctuations over simulation time. Radius of gyration were computed for Reax-MD and DFT-MD trajectories by using the *measure rgyr command* in VMD¹⁸ with *weight* option. The masses were defined as 196.9665, 12.0107, 1.00794 and 32.0649 (amu) for Au, C, H and S, respectively.

B) Many-Body Tensor Representation

Many-body Tensor Representation (MBTR) is a global descriptor developed for representing nanoscale atomistic systems for machine learning methods. MBTR is based on Bag of Bonds description that characterizes the nanoscale system based on the pairwise distances of atoms.¹⁹ Based on the similar type of idea, MBTR creates a global representation of the system as a set of broadened functions using the atomic distances for different element pairs found from the system. This creates N_{elements} x N_{elements} x n_d sized tensor that is used to describe the system. Variable n_d is a sweeping parameter of the representation as is described in more detail in ref. 20.

The structural differences between **1-32** were analyzed through MBTR, which is implemented in the DScribe package.²¹. For classification, we calculated the Euclidean distances between the MBTR tensors of all the structures using cluster **2** as a reference. MBTR-distances were calculated using all the atoms and using only Au- and S-atoms.

C) Estimation of the Collision Cross-Section

Cross sections of the clusters were calculated as space angle averaged values using a simple approach of stochastic mapping of collisions of a spherical probe of size 1.4 Å (mimicking the buffer gas ions) to the cluster structure.^{22,23} The atoms of the cluster itself

were described as a hard spheres with sizes resembling the van der Waals radii of the atoms, Au: 1.66Å, S: 1.8 Å, C: 1.7Å and H: 1.2 Å. For one individual space angle orientation, the area was calculated up to 0.03 Å² standard deviation (STD) error accuracy. Space angle average was calculated over 1,500 random space angle projections that gave final modeled cross sections with 0.30-0.45 Å² STD error. From the four selected clusters, three were calculated directly in their experimental crystal structure geometries^{9,13,14} and the isomer **4** in the PBE-relaxed geometry. In cross-section modeling, we used true PET-ligand in all structures. We checked, by relaxing the experimental structure shown in Fig. 4a of the main text, that PBE introduces approximately 20-30 Å² inaccuracy into the cross section for the studied systems because of slight overestimation of Au-Au bond lengths. This inaccuracy is of the same size as the inaccuracy due to the ligand layer conformation as is observed by modeling the known experimental structures.



Fig. S1 (a) Isomer energy and (b) MBTR distance as a measure of "similarity index" with respect to the reference structure **2** considering all the atoms (blue line) and only Au- and S-atoms (orange line). The grey "band" in (a) shows all the isomers that are within 0.3 eV from **2**. The arrows point to isomers **4** and **25** that are further discussed in the main text.



Fig. S2 Snapshots of low-energy isomers within 1 eV with respect to the reference structure **2**. Au₁₃ core is depicted as spheres and the six RS-Au-SR-Au-SR units with balls and sticks (Au: golden yellow; S: yellow; C: gray; H: white).



Fig. S3 Arrangement of one PET-Au-PET unit at the surface of $[Au_{25}(PET)_{18}]^{-}$ (a) in the DFT-optimized crystal structure and (b) in isomer 4. The average Au-S-Au angles are: (a) $\theta_1 = 86.9^{\circ}$, $\theta_2 = 101.1^{\circ}$; (b) $\theta_1 = 101.2^{\circ}$, $\theta_2 = 82.6^{\circ}$.



Fig. S4 Center-of-mass-projected angular momentum components of the electronic density of states of $[Au_{25}(PET)_{18}]^{-}$ for (a) the known crystal structure and (b) isomer **4** with PET-ligand. HOMO-LUMO energy gap is centered around zero. While both clusters show the expected superatomic P⁶ – D¹⁰ character of HOMO and LUMO manifolds, the gap size and splitting of states around the HOMO-LUMO gap differ significantly. This is reflected in the calculated UV-vis absorption spectrum shown in Fig. 3 of the main text.

Table S1. PBE-energies for the relaxed structures of $Au_{25}(SCH_3)_{18}$ cluster isomers. Clusters 1-3 are based on crystal structures with charge states +1, 0 and -1, respectively. Cluster 4 is the isomer structure relaxed based on the DFT MD-simulation, while 5-32 are relaxed isomer structures based on ReaxFF MD-simulation.

Structure Index	Energy (eV)
1	+0.067
2	+0.000
3	+0.229
4	+0.096
5	+0.257
6	-0.129
7	-0.201
8	-0.048
9	+0.835
10	+0.783
11	+2.331
12	+2.407
13	+0.027
14	-0.009
15	+0.512
16	+0.060
17	+2.027
18	+2.127
19	-0.058
20	+0.082
21	+0.077
22	-0.065
23	+2.112
24	+2.214
25	+0.242
26	+0.414
27	+0.501
28	+0.454
29	+0.763
30	+0.763
31	+0.841
32	+2.978

D) DFT-optimized coordinates of isomer 4 (with MET ligand and PBE functional). Unit: Å

Au	12.800885	14.130242	13.789515
Au	10.998670	11.958240	14.099419
Au	12.484541	13.145691	16.402981
Au	11.648640	16.677788	13.391130
Au	8.179364	10.099550	12.504722
Au	18.068768	15.938343	16.473928
Au	15.169645	14.047860	15.314387
Au	8.848394	16.102867	18.114038
Au	13.035945	16.002457	15.899452
Au	10.334132	14.627357	15.110235
Au	11.585517	17.306732	18.925285
Au	12.470981	10.344371	18.624409
Au	13.825896	8.697109	16.503275
S	9.917357	9.826740	14.020318
S	13.495506	17.588768	17.634228
S	12.528525	8.008098	18.332363
S	6.470268	10.508763	10.953839
S	12.576638	12.645082	18.735651
S	9.608605	17.002966	20.142464
S	8.220094	15.068357	16.130632
S	17.074881	13.854162	16.736088
S	10.371017	18.702497	13.335157
С	8.832302	18.664324	20.286625
Η	7.779340	18.521303	20.558205
Η	9.348735	19.212296	21.084011
С	14.870825	16.859613	18.625664
Η	14.533187	16.636755	19.641680
Η	15.230868	15.944347	18.146357
С	11.431628	19.953703	14.161682
Η	11.561428	19.631050	15.200573

Η	12.408949	20.036079	13.675416
С	10.975156	13.186980	19.442106
Η	10.937374	12.870193	20.490223
Η	10.946826	14.283059	19.384335
С	9.139109	9.568052	15.660928
Η	9.955854	9.503099	16.390898
Η	8.470206	10.390785	15.927226
С	13.710944	7.342632	19.578087
Η	14.309909	6.558137	19.100334
Η	14.365111	8.128083	19.967176
С	7.494232	16.404139	15.100220
Η	6.563423	16.738480	15.571667
Η	8.183999	17.245028	14.979002
С	6.934288	9.583277	9.435822
Η	7.998690	9.689536	9.209171
Η	6.698339	8.525955	9.603073
С	18.178268	12.673771	15.860423
Η	18.391125	13.000656	14.837933
Η	19.109472	12.580254	16.432159
Au	14.574007	16.295340	13.382580
Au	13.037515	15.119515	11.167385
Au	13.917404	11.562851	14.304703
Au	17.412800	18.268682	14.497836
Au	7.474708	12.625254	10.809590
Au	10.428960	14.234417	12.209173
Au	16.645489	11.980716	9.469144
Au	12.634921	12.253105	11.681232
Au	15.188137	13.457665	12.468633
Au	13.923803	10.782730	8.668498
Au	11.877282	17.685160	8.758933
Au	10.429867	19.253469	11.082371

S	15.712503	18.358540	12.930870
S	12.090810	10.574065	10.065043
S	10.656656	19.689919	8.794900
S	19.033482	18.057814	16.172968
S	12.973303	15.641313	8.831674
S	15.865055	11.161324	7.412442
S	17.297714	12.806229	11.538826
S	8.440725	14.723209	10.971850
S	15.053263	9.486398	14.699064
С	16.674496	9.527071	7.177229
Н	17.722544	9.704580	6.905510
Н	16.160786	9.011817	6.356320
С	10.728712	11.349597	9.107190
Н	10.443005	10.668278	8.296339
Н	11.039479	12.314552	8.694475
С	14.555616	8.415493	13.288745
Н	14.992013	8.845973	12.379341
Η	13.467821	8.370021	13.189598
С	14.689007	15.888988	8.237694
Н	15.207243	16.672230	8.798485
Η	14.654199	16.152205	7.174266
С	16.558090	18.178837	11.311935
Η	15.776132	18.112814	10.546169
Н	17.182085	17.281448	11.284484
С	9.031853	19.304796	8.024131
Н	8.330952	20.102821	8.295834
Н	8.643171	18.340731	8.363329
С	18.206444	14.366706	11.208662
Н	18.378061	14.857458	12.175014
Η	17.634113	15.033511	10.558671
С	18.397326	19.126173	17.530405

Η	18.672535	20.159845	17.292233
Н	18.877651	18.818104	18.465628
С	9.021332	15.126877	9.278980
Н	8.147836	15.260524	8.628018
Н	9.670715	14.342202	8.879017
Н	8.899286	19.224710	19.348799
Н	15.679569	17.599436	18.657055
Н	10.914752	20.920094	14.133760
Н	10.127521	12.770036	18.890133
Н	8.586374	8.621502	15.638001
Н	13.124044	6.909603	20.398781
Н	7.278522	15.968065	14.117232
Н	6.333087	9.967229	8.603833
Н	17.658762	11.709187	15.828056
Н	16.623779	8.921935	8.087858
Н	9.881415	11.501192	9.791572
Н	14.962544	7.412033	13.456403
Н	15.214312	14.933276	8.363593
Н	17.174158	19.069410	11.137258
Н	9.171480	19.286804	6.936853
Н	19.166561	14.120020	10.740328
Η	17.310780	19.048429	17.622965
Н	9.592425	16.064087	9.342120

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