SUPPORTING INFORMATION

On the structure of the Thiolated Au_{15} Cluster

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1. Computational Details.

The proposed candidates were full relaxed by using SIESTA[1] program and including PBE[2] as XC-functional. After that, the structure of the lowest energy isomers were yield in the Amsterdam Density Functional (ADF)[3] program and a new optimization stage was performed. ADF calculations included the PBE functional and the polarized triple (TZP) Slater type basis set with a [$1s^2$-$4f^{14}$] frozen core for Au, a [$1s^2$-$2p^6$] frozen core for S, and a [$1s^2$] frozen core for C atom. A convergence criterion of 10^{-4} Hartree and a gradient convergence criterion of 10^{-3} Hartree/Å were used. Moreover, it was considered a scalar relativistic effects through the Zeroth Order Regular Approximation (ZORA)[4]. For the calculation of the optical and chiroptical spectra a Time-dependent DFT approach was utilized, through the calculation of its excitation energies, and oscillator and rotatory strengths.[5] To calculate the optical absorption and circular dichroism spectra (1.5 - 4.5 eV), the lowest 200 excited (singlet) states were considered, using the same XC functional and basis set as for the structural calculations.

1. Soler, J. M.; Artacho, E.; Gale, J. D.; García, A.; Junquera, J.; Ordejón, P.; Sánchez-Portal, D. *J. Phys.: Condens. Matter* **2002**, 14, 2745-2779.

2. Perdew, P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865.

3. te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* 2001, **22**, 931-967.

4. van Lenthe, E.; Baerens, E. J.; Snijders, J. G. J. Chem. Phys. 1993, 99, 4597-4610.

5. Autschbach, J.; Ziegler, T.; Gisbergen, S. J. A.; Baerends, E. J. J. Chem. Phys. 2002, 116, 6930-6940.

2. How to choose the length of the oligomer motifs?

An easy way to make an initial guess for candidates for the $Au_{15}(SR)_{13}$ cluster is following the next assumptions:

1.- The small core reported is the Au_4 unit.

2.- The number of oligomer motifs must be half of the number of available gold atoms of the core to attach them. We have four atoms in the core, then we need 2 motifs. This assumption is based in the principle number three of Tsukuda et al.

3.- The sum of the Au adatoms is equal to 15-4.

Using the divide and protect concept.

core + No. atoms in oligomers equals 15 Au atoms. 13 S atoms are included in RS ligands.

Au_4 + $i[Au_mS_n] + j[Au_pS_q] = 15Au, 13S$

$4 + i*m + j*p = 15$ (1) <-----core Au atoms

$i*n + j*q = 13$ (2) <----- S atoms

then: $i*m + j*p = 11$ (3) <---Au adatoms

Considering oligomers following the formula $-SR-(Au-SR)_m$ or $Au_m S_{m+1}$, then

$n = m+1$, and $q = p+1$

Substituting in (1): $i*(m+1) + j*(p+1) = 13$

$(i*m + j*p) + i + j = 13$

$i + j = 2$ or $i = j = 1$

and substituting in (3)

$m + p = 11$

The problem reduces to find a combination of two numbers (i.e. two oligomers) which sum is 11.

PART II

Table S1. Various isomers of the $Au_{15}(SR)_{13}$ cluster. Estimation of their relative energy, and HOMO-LUMO gap value by SIESTA calculations.

Core	Type of staple motifs	E relative (eV)	HL gap (eV)
Au_4	Tetramer, heptamer	0.0	1.83
Au_4	Pentamer, hexamer	1.4	2.0
Au_5	1 dimer, 2 Tetramers	1.12	0.9
Au_6*	3 dimer, 3 monomers	1.97	0.71

* The structure based on the $[Au_{12}(SR)_9]^+$ cluster has monomer motifs linked between dimer motifs in an interstaple mode.

From Table S1 is noticeable that isomers with the Au_4 core show HL gaps values around 2.0 eV, which is comparable with the 1.75 eV experimental value of the $Au_{15}(SR)_{13}$ cluster.

PART III

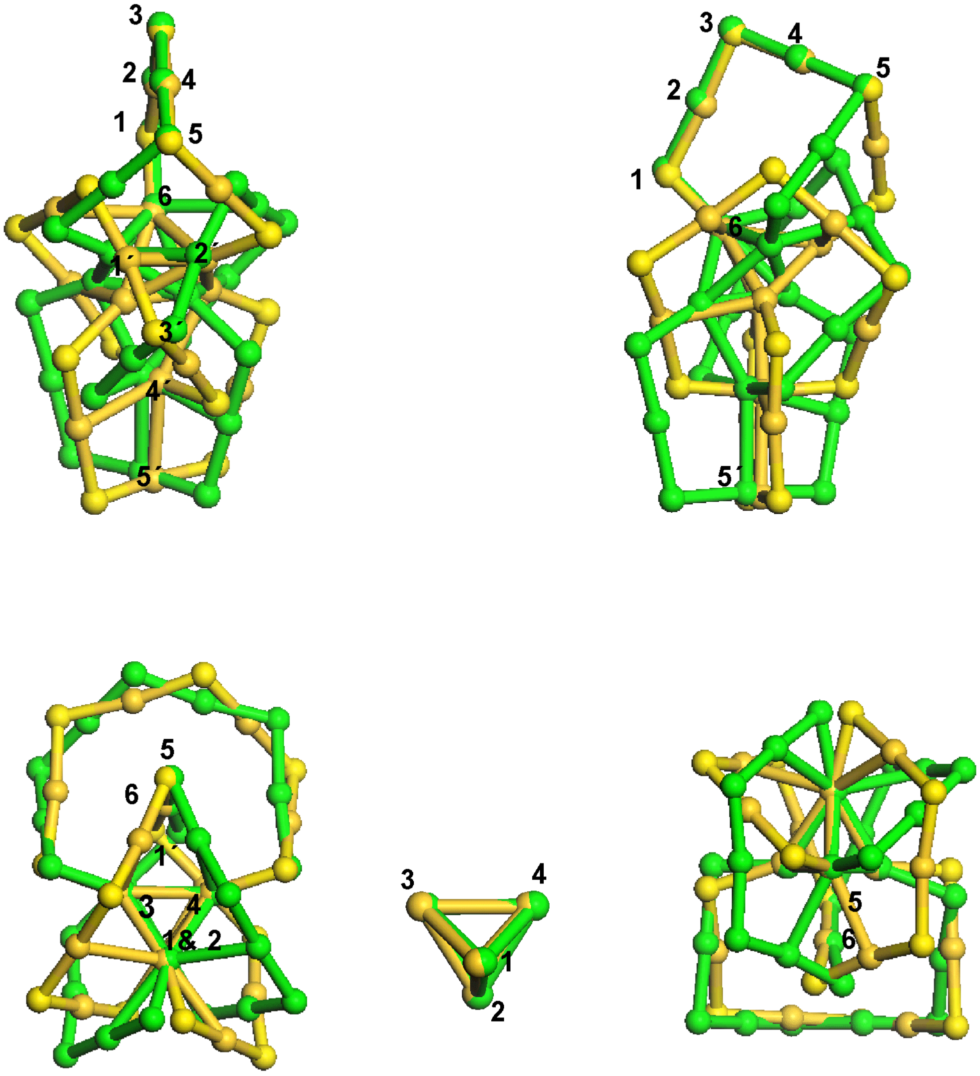


Figure S1. Superimposition of both enantiomers of DJ1 (upper) and AT1 (lower) clusters. It was found a plane where a major number of atoms superimposes. DJ1 shows six coincidences and another five pair of atoms with no perfect overlapping. AT1 enantiomers show less coincidences, four pair of gold atoms of the Au4 core and two extra pair of atoms overlapping. The pair labeled as 1´shows a poor overlap.

Figure S1 shows clearly that AT1 isomer features less coincidences than the DJ1 isomer.

PART IV

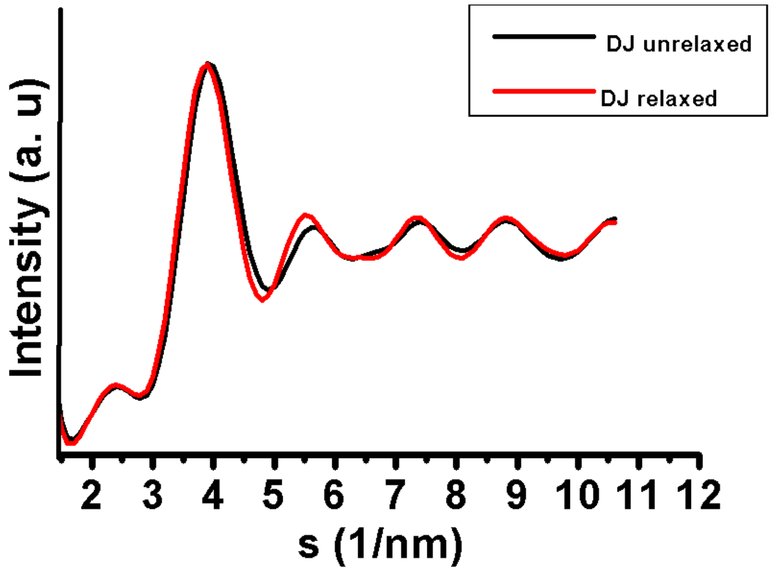


Figure S2. Comparison of calculated XRD patterns for the unrelaxed $Au_{15}(SR)_{13}$ model reported by De-en Jiang et al (Ref. 13) with the relaxed structure (DJ1 isomer). In the manuscript is given a comparison between the relaxed model and the experimental XRD pattern.

The simulated XRD patterns were obtained by using the Debye formula and parameters given by Iwasa et. al.

Ref. Iwasa, T.; Nobusada, K.; *J. Phys. Chem. C*. **2007**, *111*, 45.

PART V

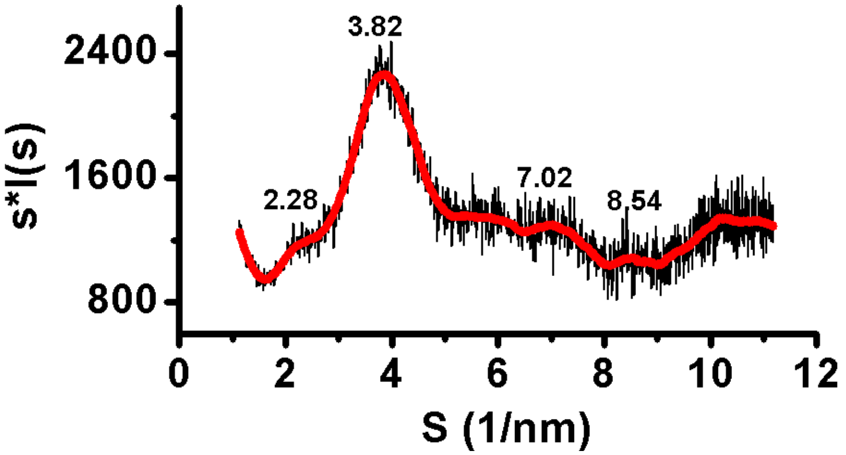


Figure S3. Experimental XRD pattern (black curve) and its smoothed curve (red curve) used in Figure 5 of the manuscript.

PART VI

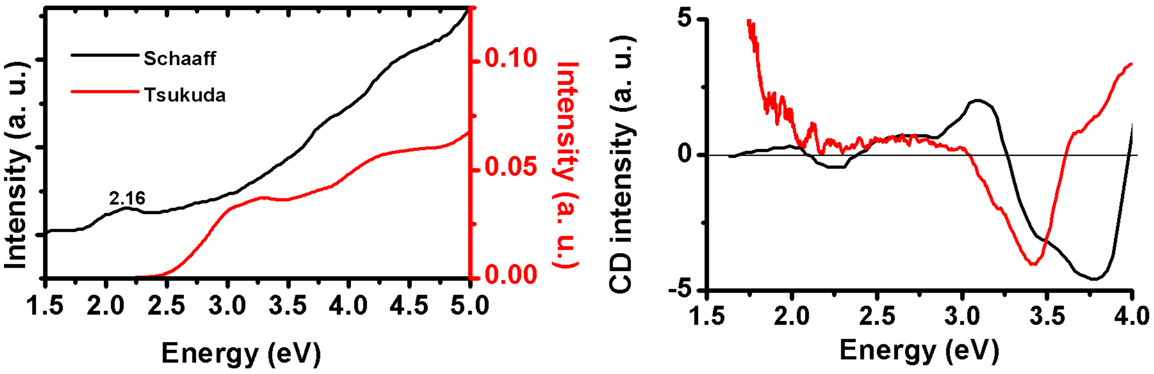


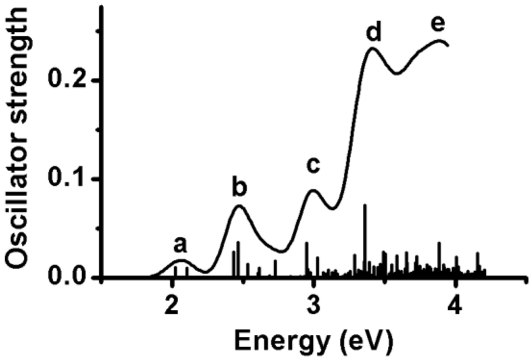
Figure S4. Comparison of experimental UV-vis and CD curves of the Au$_{15}$(SG)$_{13}$ of Ref. 3b and 4e in the manuscript. The curve of the UV-vis given by Schaaff et al. shows a peak located at 2.16 eV. The calculated optical spectra are in agreement with this first peak.

Regarding experimental CD spectra is evident that spectrum reported in Ref. 3b shows more features. It share similar features with Tsukuda data (Ref. 4e) in the region comprised between 1.5 to 3.5 eV where the 3.48 eV negative peak is located. However in the range 1.5-2.5 eV it shows a better agreement with the calculated peaks.

PART VII

Tables S2. Excitation energy, oscillator strength, electronic transitions and their weights for peaks of studied isomers.

DJ1 isomer



Peak	**E_{peak}, eV**	**f**	**Transition from occupied -> unoccupied orbital**	**Weigth, %**
a	2.052	0.0101	HOMO--- -> LUMO	98.70
	2.103	0.0097	HOMO -> LUMO+1	98.40
	2.433	0.026	HOMO-1 -> LUMO	84.54
			HOMO -> LUMO+2	3.94
b	2.4648	0.0354	HOMO -> LUMO+2	87.48
			HOMO-1 -> LUMO+1	5.86
c	2.9492	0.0349	HOMO-4 -> LUMO	54.59
			HOMO -> LUMO+5	7.94
			HOMO-5 -> LUMO	7.02
	3.0246	0.0205	HOMO-2 -> LUMO+2	36.71
			HOMO-3 -> LUMO+1	18.32
			HOMO-6 -> LUMO	12.55
d	3.3603	0.0732	HOMO-4 -> LUMO+2	27.50
			HOMO-3 -> LUMO+2	13.66
			HOMO -> LUMO+11	11.37
e	3.8842	0.0352	HOMO-14 -> LUMO+2	14.09
			HOMO-2 -> LUMO+10	7.35

Peak	E_{peak}, eV	f	Transition from occupied -> unoccupied orbital	Weigth, %
	2.1012	0.00545	HOMO--- -> LUMO	92.98
	2.2427	0.01380	HOMO-1--- -> LUMO	88.37
a	2.3670	0.0332	HOMO-2 -> LUMO	83.09
b	2.6411	0.0227	HOMO -> LUMO+1	65.79
			HOMO-4 -> LUMO	12.58
c	2.8337	0.0331	HOMO-6 -> LUMO	51.28
			HOMO-2 -> LUMO+1	28.74
d	3.1	0.0409	HOMO-1 -> LUMO+3	28.11
			HOMO-2 -> LUMO+2	23.36
			HOMO-10 -> LUMO	14.39
e	3.4988	0.0239	HOMO-1 -> LUMO+8	29.05
			HOMO-3 -> LUMO+5	13.58
			HOMO-5 -> LUMO+2	12.15