

Electronic Supplementary Information

How to Control Optical Activity in Organic-Silver Hybrid Nanoparticles

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Atomic models

Atomic data of the lowest-energy configurations obtained performing unconstrained relaxations within density functional theory (DFT) can be found at:

<http://www.fisica.unam.mx/cecilia/Structures/Ag55SCH3n>

and <http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn>

- Achiral $\text{Ag}_{55}-(\text{SCH}_3)$

<http://www.fisica.unam.mx/cecilia/Structures/Ag55SCH3n/Ag551SCH3.dat>

- Achiral $\text{Ag}_{55}-(\text{SCH}_3)_2$

<http://www.fisica.unam.mx/cecilia/Structures/Ag55SCH3n/Ag552SCH3.dat>

- Chiral $\text{M}-\text{Ag}_{55}-(\text{SCH}_3)_3$

<http://www.fisica.unam.mx/cecilia/Structures/Ag55SCH3n/MAg553SCH3.dat>

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- Chiral P–Ag₅₅–(SCH₃)₃
<http://www.fisica.unam.mx/cecilia/Structures/Ag55SCH3n/PAg553SCH3.dat>
- Chiral Ag₅₅–(L-Cys)₁
<http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn/Ag55Lcys1.dat>
- Chiral Ag₅₅–(L-Cys)₂
<http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn/Ag55Lcys2.dat>
- Chiral Ag₅₅–(L-Cys)₄
<http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn/Ag55Lcys4.dat>
- Chiral Ag₅₅–(L-Cys)₆
<http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn/Ag55Lcys6.dat>
- Diastereomer M–Ag₅₅–(L-Cys)₃
<http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn/MAg55Lcys3.dat>
- Diastereomer P–Ag₅₅–(L-Cys)₃
<http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn/PAg55Lcys3.dat>
- Diastereomer M–Ag₅₅–(L-Cys)₅
<http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn/MAg55Lcys5.dat>
- Diastereomer P–Ag₅₅–(L-Cys)₅
<http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn/PAg55Lcys5.dat>
- Diastereomer M–Ag₅₅–(L-Cys)₇
<http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn/MAg55Lcys7.dat>
- Diastereomer P–Ag₅₅–(L-Cys)₇
<http://www.fisica.unam.mx/cecilia/Structures/Ag55Lcysn/PAg55Lcys7.dat>

Circular Dichroism (CD) precision

CD calculation of the icosahedral Ag_{55} shows that this achiral structure has a null CD within a numerical error smaller than 10^{-3} [liters/(mol cm)], as shown in the Figure ESI-1. Notice that chiral cases show CD values about 10^5 larger.

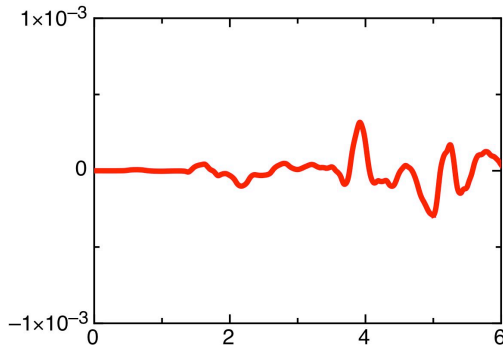


Figure ESI-1: CD calculation of the icosahedral Ag_{55} with null optical activity.

Optical absorption spectra

Within the DFT scheme, the imaginary part of the dielectric function was calculated. Figure ESI-2 shows the imaginary part of the dielectric function or optical absorption of bare Ag_{55} and $\text{Ag}_{55}-(\text{SCH}_3)$ NPs. The optical absorption of bare Ag_{55} exhibits well-defined peaks associated with transitions between molecular-like electronic states which are highly degenerated because of its five-fold symmetry. The optical response is dictated by the electronic density of states (DOS) of each system discussed in Fig. 9 in the article. For instance, electron transitions from occupied states at about -0.6 eV to empty states around $+0.9$ eV are responsible for the absorption band located at 1.5 eV. The optical band with two shoulders centered around 2.0 eV comes from transitions between occupied and empty states at -0.9 and $+0.9$ eV, and between -0.6 and $+1.6$ eV.

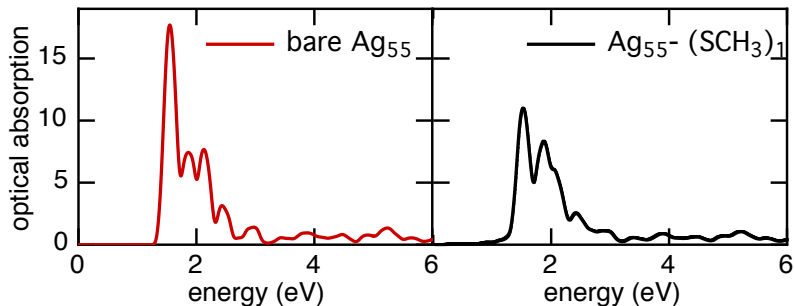


Figure ESI-2: Calculated optical absorption of bare Ag_{55} and $\text{Ag}_{55}-(\text{SCH}_3)_1$.

The right-hand side of Figure ESI-2 displays the imaginary part of the NPs' dielectric function after adsorption of SCH_3 , such that the NP electronic degeneracy is partly broken, spreading occupied and empty electronic states at higher and lower energies around the Fermi level. This originates that the optical absorption peak at 1.5 eV diminishes its intensity about 40%. Sulfur electron states are extended over a wide energy range below the Fermi level, which means that they are occupied. It is observed that the main differences in the absorption spectra can be followed by looking the contribution from the S atom.

In Figure ESI-3 the optical absorption and CD spectra of the achiral arrangements cases of $\text{Ag}_{55}-(\text{L-Cys})_n$ with $n = 1, 2, 4,$ and 6 ligands are shown. As the number of adsorbed ligands increases the intensity of the optical absorption systematically diminishes, but CD intensity increases. As it is discussed in the main manuscript, when L-Cys ligands are adsorbed the DOS degeneracy of Ag_{55} is partly broken, spreading the electronic states in energies between -3 eV to $+3$ eV. Simultaneously, the electronic states belonging to S atoms of the ligands, also extend over the same energy region, but particularly with larger density between -1 eV to -2 eV. DOS distributions of Ag_{55} change as the number of adsorbed ligands increases, being more evenly distributed in the energy window $[-3, +3]$ eV. Notice that the number of electronic states is conserved, therefore the optical intensity around this energy window diminishes. On the other hand, the electronic states associated with the molecules do not suffer large variations, except for the states of the S atom that extend over a large energy window as well. These states are not directly related with the CD of L-Cys ligands. The

electronic states associated with the ligands are quite proportional to the number of ligands, as discussed in the main manuscript. Therefore, the intensity around of L-Cys ligand is proportional to the number of ligands as well.

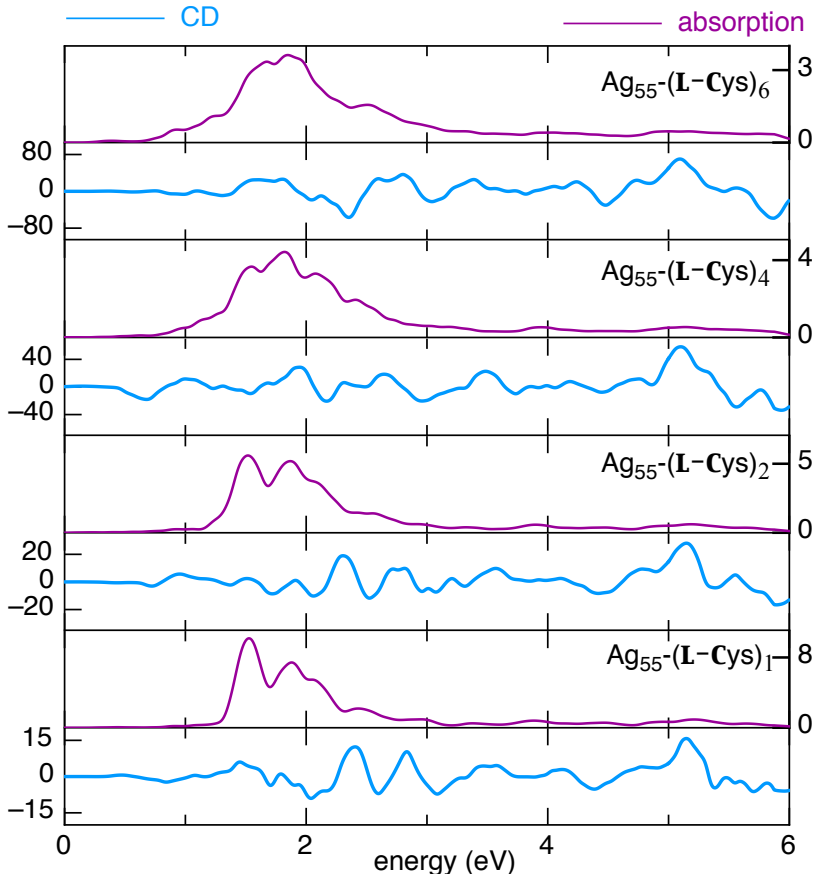


Figure ESI-3: Calculated optical absorption and CD spectra of achiral ligand arrangements of $\text{Ag}_{55}-(\text{L-Cys})_n$ with $n = 1, 2, 4,$ and 6 .

In Figure ESI-4 the optical absorption and CD spectra of the chiral cases of $\text{Ag}_{55}-(\text{L-Cys})_n$ with $n = 3, 5$ and 7 ligands is shown. Again, the optical response is dictated by the electronic density of states (DOS) of each system shown in Fig. 9 and discussed in the main text. In all the cases, the intensity of the optical absorption systematically diminishes, but CD intensity increases as the number of adsorbed ligands also does. The optical absorption spectra of M- and P- chiral arrangements for a given number of ligands are indistinguishable among them, because optical absorption is proportional to product of the electric dipole moment operators, $\langle 0 | \hat{\mu} \cdot \hat{\mu} | n \rangle$, and thus proportional to the electronic transitions and to

DOS.

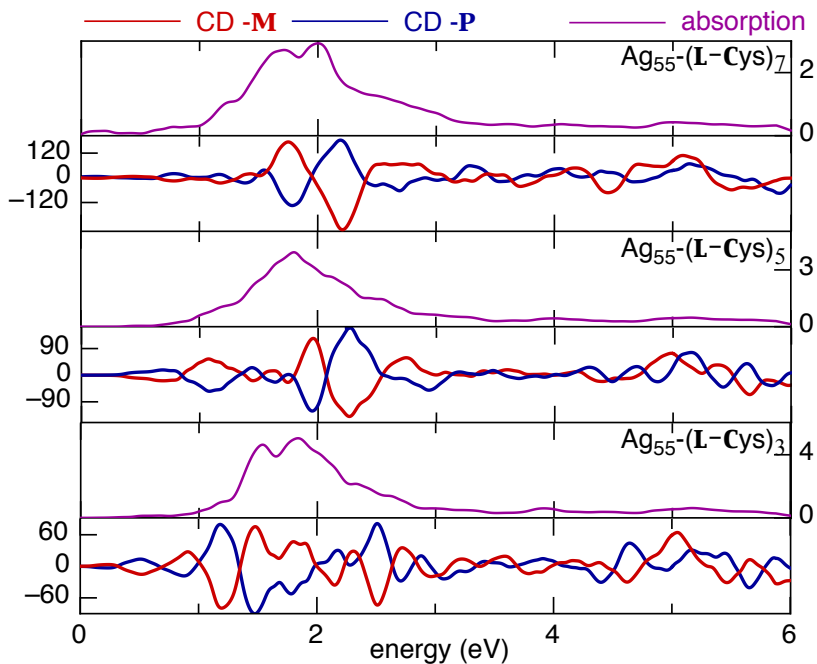


Figure ESI-4: Calculated optical absorption and CD spectra of chiral ligand arrangements of $\text{Ag}_{55}-(\text{L-Cys})_n$ with $n = 3, 5$ and 7 .

On the other hand, CD calculations are directly related to the alignment of the electric and magnetic dipole moments, $\langle 0|\hat{\mu} \cdot \hat{m}|n\rangle$, where \hat{m} is given by the orbital angular momentum of the electrons in the absence of an external magnetic field. Although CD is also proportional to the electronic transitions, its intensity is ruled by how much the electric and magnetic dipole moment are aligned. Therefore, there is not a direct relation between optical absorption and CD spectra, except that where there is optical absorption it could be also CD since $\langle 0|\hat{\mu}|n\rangle \neq 0$. However, if $\hat{\mu}$ and \hat{m} are orthogonal between them, thus $\text{CD}=0$. On the contrary, CD is maximum if they are parallel.