

Astaxanthin interacting with metal clusters: free radical scavenger and photovoltaic materials

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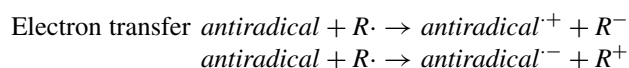
Abstract This investigation mainly intends to study the interaction of ASTA with metal clusters of up to ten atoms. Copper, silver, and gold atoms are used in this analysis. Lambda maximum values, electron donor acceptor capacity (to see the antiradical properties of these compounds), and the HOMO–LUMO gaps (to analyze the potential application of these molecules as materials for solar cells) are reported. None of these properties is linearly dependent on the number of metal atoms in the cluster. Contrarily, there is an even–odd oscillation. The bond of metal atoms and clusters to ASTA generates products (ASTA-M_x) that are redder in color, concurring with experimental results previously reported for shrimps. The production of redder compounds is confusing for consumers of red food products and could cause a health problem. ASTA-M_x molecules are better electron donors and better electron acceptors than ASTA, making them become better free radical scavengers. ASTA-Cu₄, ASTA-Cu₁₀, and ASTA-Au₇ have low values of the ionization energies and high values of the electron

affinity; i.e., there are good electron donors and good electron acceptors. They also have the lowest values (around 2.5 eV) of the HOMO–LUMO gap. These results could be useful for future applications.

Keywords Antioxidants · Solar devices · Red products · Oxidative stress

1 Introduction

Oxidative stress is produced by free radicals. It is associated with a large number of health disorders [1–9]. There are many substances, named antioxidants or antiradicals, which are very useful for preventing the oxidative stress, as they are able to scavenge free radicals [10–20]. One of these substances is astaxanthin (ASTA), a red carotenoid that is related to sexual selection in the animal kingdom [21–23]. There are many investigations concerning the ability of this molecule to reduce the oxidative stress [10–12, 15, 16, 19, 20]. One of the mechanisms for scavenging free radicals is the electron transfer that is represented as follows (*R*· is the free radical; antiradicals are able to either donate or accept electrons):



When the antiradicals gains or loses an electron, it becomes a radical cation or radical anion. These radicals are usually large molecules that are not as reactive as the free radicals that these molecules scavenge.

Another mechanism reported recently which prevents oxidative stress is related to the indirect action of carotenoids by chelating transition metal ions [24–29]. In this mechanism, ASTA does not scavenge free radicals but

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instead, inhibits its formation. There are experimental and theoretical reports about the reaction of ASTA with metal cations [28, 29] concluding that the presence of metal cations decreases the excitation energy and produces compounds that are redder in color.

The color of these compounds is very important, as it is indicative of health in animals. In particular, the concentration of ASTA [30] controls the intensity of the red pink coloration of shrimps. As ASTA is a beneficial substance because it is a free radical scavenger, more ASTA is related to good health. Human consumers of shrimps prefer more intense color as redder individuals also suggest better taste [31–35]. In fact, the food industry makes an important effort to increase the color of shrimps [33, 34] with natural products such as the Aztec marigold “cepsasu’chil” (*Tagetes erecta*) [34] because the profits from this product are related to the color; i.e., the redder the color, the higher the price [35]. However, the pink red color is not always linked to the concentration of ASTA. It was demonstrated in an experiment, that shrimps living in water with 1 ppm of copper become redder in 4 days [36]. This is a very interesting result, and there could be health implications. People may select redder shrimps because they appear more appetizing thus indicating more ASTA, whereas in fact it may be that they are redder because they have heavy metals such as copper and not because they have higher concentration of ASTA.

Concerning the modifications of spectra due to the presence of metals, it was previously reported that metallic nanoparticles interacting with biomolecules as peptides also significantly enhance photoabsorption and emission signals [37]. For example, the research concerning the interaction of silver cationic clusters with peptides concludes that the presence of clusters with three metal atoms is sufficient to enhance the signals of the spectra. This is very interesting and could be very important for nanobiotechnology.

In spite of the results previously indicating that ASTA chelates metal atoms, no studies exist that assess the bond between ASTA and metal clusters. Thus, the main aim of this investigation is to study the interaction of ASTA with metal clusters of up to ten atoms. This could be important since neutral metal clusters are very interesting stable systems. They show chemical and physical properties that are not linearly dependent to the number of metal atoms in the cluster. The interaction of neutral metal clusters with molecules as astaxanthin could give us an idea concerning the capacity of metal clusters to interact and modify the properties of this molecule.

Copper, silver, and gold clusters are used in this analysis. Lambda maximum values, electron donor acceptor capacity (to see the antiradical properties of these compounds), and the HOMO–LUMO gaps are reported. As subsequently apparent in this report, none of these

properties is linearly dependent to the number of metal atoms in the cluster.

The presence of metal clusters decreases the excitation energy and produces compounds that are redder in color. The reduction of the excitation energy is desirable for solar energy devices as the HOMO–LUMO gap allows us to decide about potential applications such as photovoltaic materials for the construction of solar cells. As explained, the production of redder compounds is confusing for consumers of red food products and could present a health problem; however, in the following I also discuss how this may be beneficial. It is important to note that previous reports exist concerning ASTA–metal ion complexes that are relevant for the food industry, but there is not experimental evidence for neutral metal clusters interacting with ASTA. However, the characterization of ASTA–metal complexes in living organisms is not easy, and it is not possible to assure that neutral metal clusters are not formed. In this context, this investigation is interesting from a fundamental standpoint, and it reveals a significant impact of neutral metal clusters on the physicochemical properties of ASTA that could be useful for future experiments.

2 Computational details

Calculations related to geometries optimization and anti-radical analysis of ASTA molecules interacting with metal clusters were undertaken using Gaussian 09 implementation [38]. Geometries were fully optimized with CAM-B3LYP functional [39] using LANL2DZ for metal atoms and D5DV basis sets for light atoms [40–42]. In order to verify optimized minima, harmonic analyses were performed and local minima were identified (zero imaginary frequencies). The UV–visible spectra were computed with time-dependent density functional theory (TDDFT) at the same level of theory.

CAM-B3LYP is a relatively new Coulomb-attenuated hybrid exchange–correlation functional that adequately predicts molecular charge-transfer spectra. Likewise, qualitatively good predictions for the spectra of porphyrin, some oligoporphyrins, and chlorophyll were reported, as well as an excellent agreement with complete-active-space plus second-order Møller–Plesset perturbation theory and symmetry-adapted cluster configuration interaction calculations [43]. The theoretical λ_{\max} of ASTA obtained in this investigation at CAM-B3LYP/D5DV level of theory is 460 nm, in good agreement with the experimental value (470 nm). Good performance of CAM-B3LYP for the first-row transition metal nuclei in several compounds was also reported [44].

In order to investigate the electron transfer mechanism, vertical ionization energy (IE) and vertical electron affinity

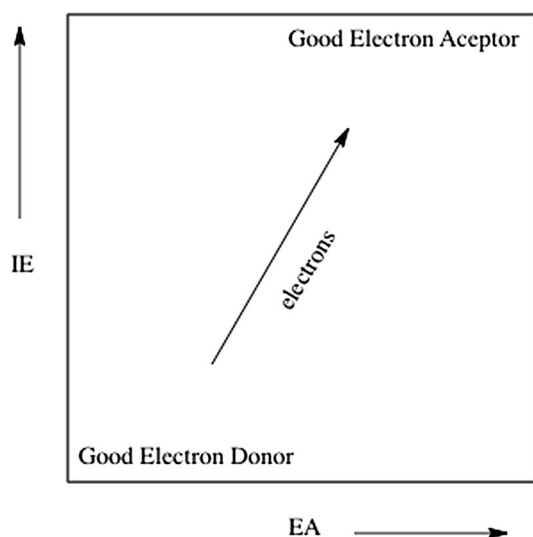


Fig. 1 Full electron donor–acceptor map (FEDAM)

(EA) were obtained from single-point calculations of cationic and anionic molecules, using the optimized structure of the neutrals. A useful tool reported previously [12, 15] for the purpose of analyzing the electron transfer mechanism is the full electron donor–acceptor map (FEDAM, Fig. 1). Molecules located down to the left are good electron donors and will therefore transfer electrons to the molecules situated up to the right (that are good electron acceptor). For the investigation of the electron transfer mechanism, the FEDAM was used.

For the HOMO–LUMO gap, HOMO is always the highest occupied molecular orbital and LUMO is always the lowest occupied molecular orbital (alpha or beta depending on the system). Several initial geometries were used in this investigation. Metal atoms and clusters bonded to the double bonds of ASTA, and also planar and three-dimensional metal clusters with different shapes, were used. This kind of geometric search was done by hand, following previous results for metal clusters and chemical intuition. Since several initial geometries were tested, I am confident that the geometries reported are near the global minimum or are similar to it. However, the possibility that the global minimum is missing is always there.

3 Results and discussion

3.1 Geometry optimization

The initial geometries used for the optimization are reported in Fig. 2. ASTA- M_x represents an ASTA molecule interacting with up to ten metal atoms ($M = \text{Cu}, \text{Ag}$ and Au ; $x = 1\text{--}10$). For each size of the system several initial

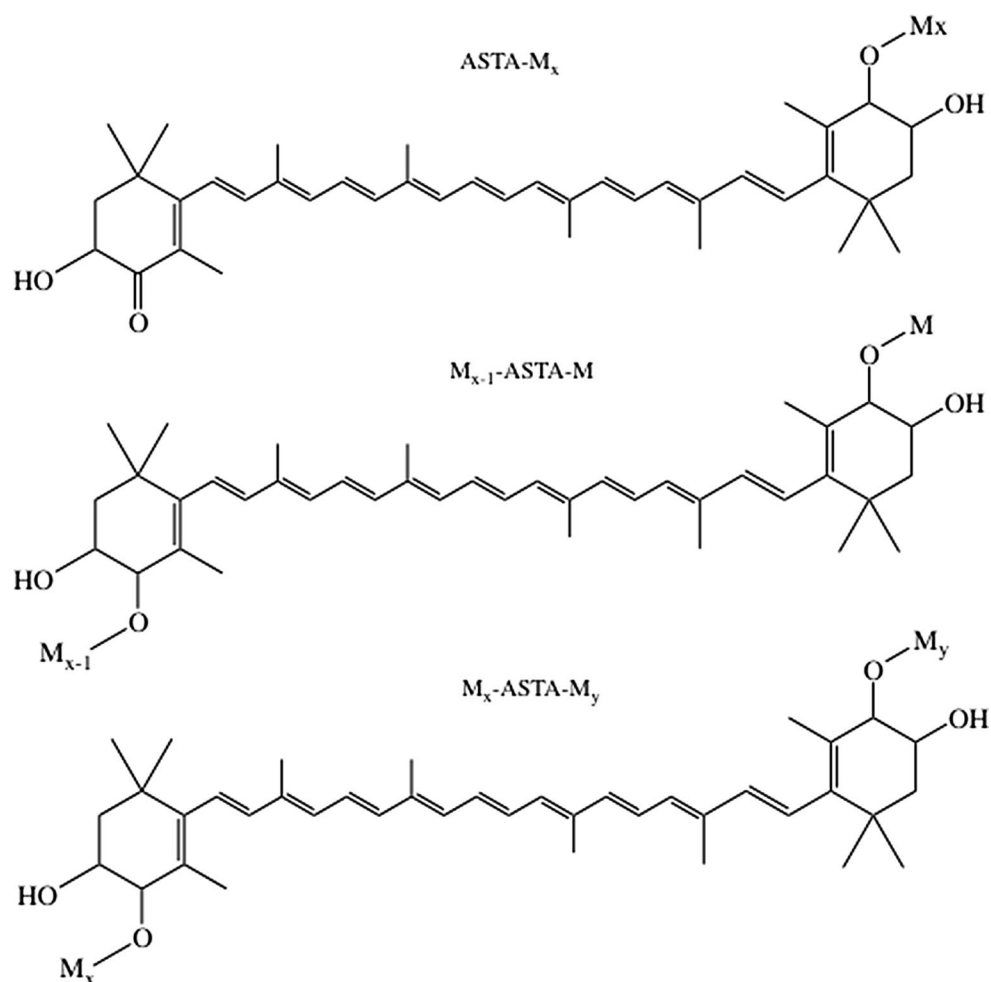
geometries were used. With two metal atoms, the system was optimized with a bimetallic cluster at one side of ASTA [ASTA- M_2] and also a molecule with two metal atoms bonded to two oxygen atoms at two sides of astaxanthin [M-ASTA-M]. With three metal atoms two initial geometries were optimized: ASTA- M_3 and M_2 -ASTA-M. Four metal atoms provide us with three possible combinations [ASTA- M_4 , M_3 -ASTA-M and M_2 -ASTA- M_2], whereas with five metal atoms we also have three possible initial geometries [ASTA- M_5 , M_4 -ASTA-M and M_3 -ASTA- M_2]. ASTA could be bonded to six metal atoms [ASTA- M_6 , M_5 -ASTA-M, M_4 -ASTA- M_2 and M_3 -ASTA- M_3]. Seven metal atoms also generated four possible structures: ASTA- M_7 , M_6 -ASTA-M, M_5 -ASTA- M_2 and M_4 -ASTA- M_3 . With eight and nine there are five combinations (ASTA- M_8 , M_7 -ASTA-M, M_6 -ASTA- M_2 , M_5 -ASTA- M_3 , M_4 -ASTA- M_4 ; ASTA- M_9 , M_8 -ASTA-M, M_7 -ASTA- M_2 , M_6 -ASTA- M_3 , M_5 -ASTA- M_4) and with ten metal atoms there are six: ASTA- M_{10} , M_9 -ASTA-M, M_8 -ASTA- M_2 , M_7 -ASTA- M_3 , M_6 -ASTA- M_4 and M_5 -ASTA- M_5 .

Figures 3, 4, and 5 present the optimized geometries of the most stable structures. All metal clusters present geometries that are similar to the isolated clusters reported before [45–47] Copper and silver clusters are planar for up to six atoms [45, 46] and gold clusters are all planar [47]. In all cases, molecules with an even number of metal atoms are singlets and molecules with an odd number of metal atoms are doublets.

The main difference between the three systems is that for silver and gold, the most stable structures present a cluster bonded to a single oxygen at one side of the ASTA molecule, while for copper this is not always the case. For ASTA bonded to copper clusters, there are two structures with similar stability for systems with an even number of metal atoms. When an odd number of copper atoms is found, the ground states are those with one copper cluster bonded at one side of the ASTA molecules (similar to silver and gold). In order to compare stability and reactivity, the ground states reported in Figs. 3, 4 and 5 will be used. The other optimized geometries are higher in energy by more than 7 kcal/mol (not included in these figures), and these will thus not be used in the analysis. Notice that for copper, more than one structure will be used in what follows, as there are two structures with similar stability. To compare with silver and gold, results with one copper cluster bonded at one side of the ASTA molecule have also been analyzed, even when this is not the most stable structure.

For systems with an even number of copper atoms, the energy difference between isomers containing two metal atoms is 1.4 kcal/mol and both are able to coexist under experimental conditions. The energy difference is 6.5 kcal/mol for ASTA- Cu_4 and Cu_3 -ASTA-Cu, the former being more stable than the second. The most stable structures

Fig. 2 Schematic representation of the initial structures used for the optimization



for systems with 6, 8 and 10 metal atoms have a pentamer (Cu_5) bonded at one side of the ASTA molecule. For ASTA bonded to six copper atoms, the most stable structure is Cu_5 -ASTA-Cu followed by Cu_3 -ASTA- Cu_3 . These two isomers have the same stability (energy difference of 0.2 kcal/mol), and therefore both are able to exist under experimental conditions). ASTA- Cu_6 is less stable than Cu_5 -ASTA-Cu by 17.1 kcal/mol, which is included in Fig. 3 in order to compare with analogue structures of silver and gold. With eight metal atoms, the ground state is Cu_5 -ASTA- Cu_3 , which is more stable than ASTA- Cu_8 by 2.4 kcal/mol. Under experimental conditions both can be present. For the system with ten metal atoms, Cu_5 -ASTA- Cu_5 is more stable than ASTA- Cu_{10} by 7.0 kcal/mol.

Results are different when there are an odd number of copper atoms. In this case, there is a clear preference for systems with one copper cluster located to one side of the ASTA molecule. With three copper atoms, the molecule with ASTA- Cu_3 is more stable than the other by more than 30 kcal/mol, showing an apparent preference for the formation of the trimer. This is also the situation for molecules with five copper atoms (ASTA- Cu_5 is more stable

than Cu_4 -ASTA-Cu by 28.5 kcal/mol); with seven copper atoms ASTA- Cu_7 is more stable by 17.2 kcal/mol than Cu_4 -ASTA- Cu_3 , which is the second most stable structure); and with nine copper atoms (ASTA- Cu_9 that is more stable than Cu_8 -ASTA-Cu by 29.2 kcal/mol).

For systems with silver and gold (Figs. 4, 5), the ground states are those structures with one metal cluster bonded to an oxygen atom located at one side of the ASTA molecule. These structures are more stable than the others with the same stoichiometry by more than 10 kcal/mol. There are only two systems with two geometries with similar stability: ASTA- Ag_{10} and Ag_5 -ASTA- Ag_5 ; ASTA- Au_4 and Au_2 -ASTA- Au_2 . Likewise in these two cases, the ground state is also found with the metal cluster at one side of ASTA; however, they can coexist in an experiment with the isomers of similar stability. In spite of the differences between copper, silver and gold, generally they behave in such a way that metal atoms become bonded to the oxygen atoms of ASTA. In any case, the results concerning λ_{max} and HOMO-LUMO gap for the structures with similar stability are alike. For this reason, in what follows, only the results for the ground state molecules will be included.

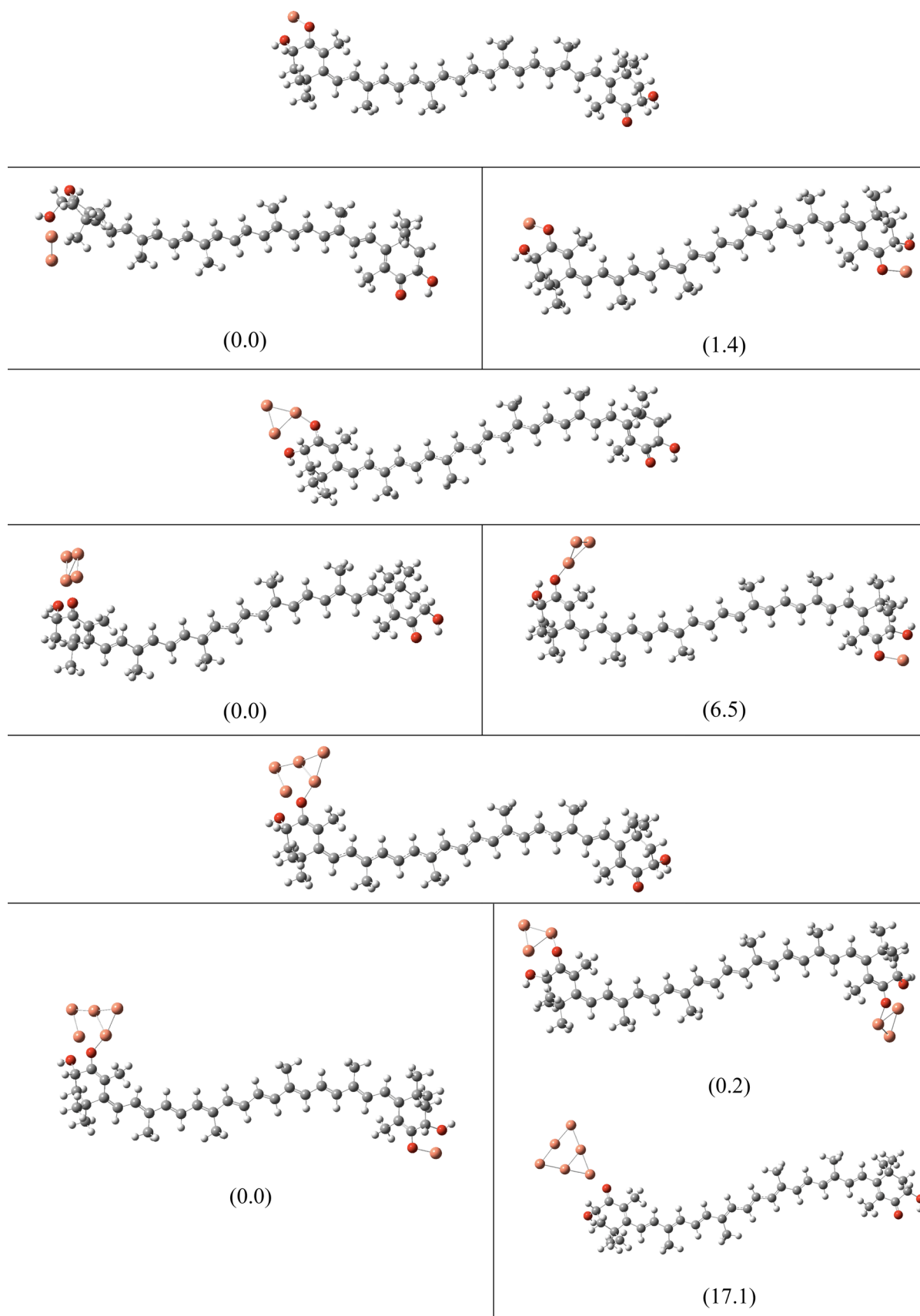


Fig. 3 Optimized geometries of the most stable structures for molecules with *copper*. Energy differences in *brackets* are reported in kcal/mol

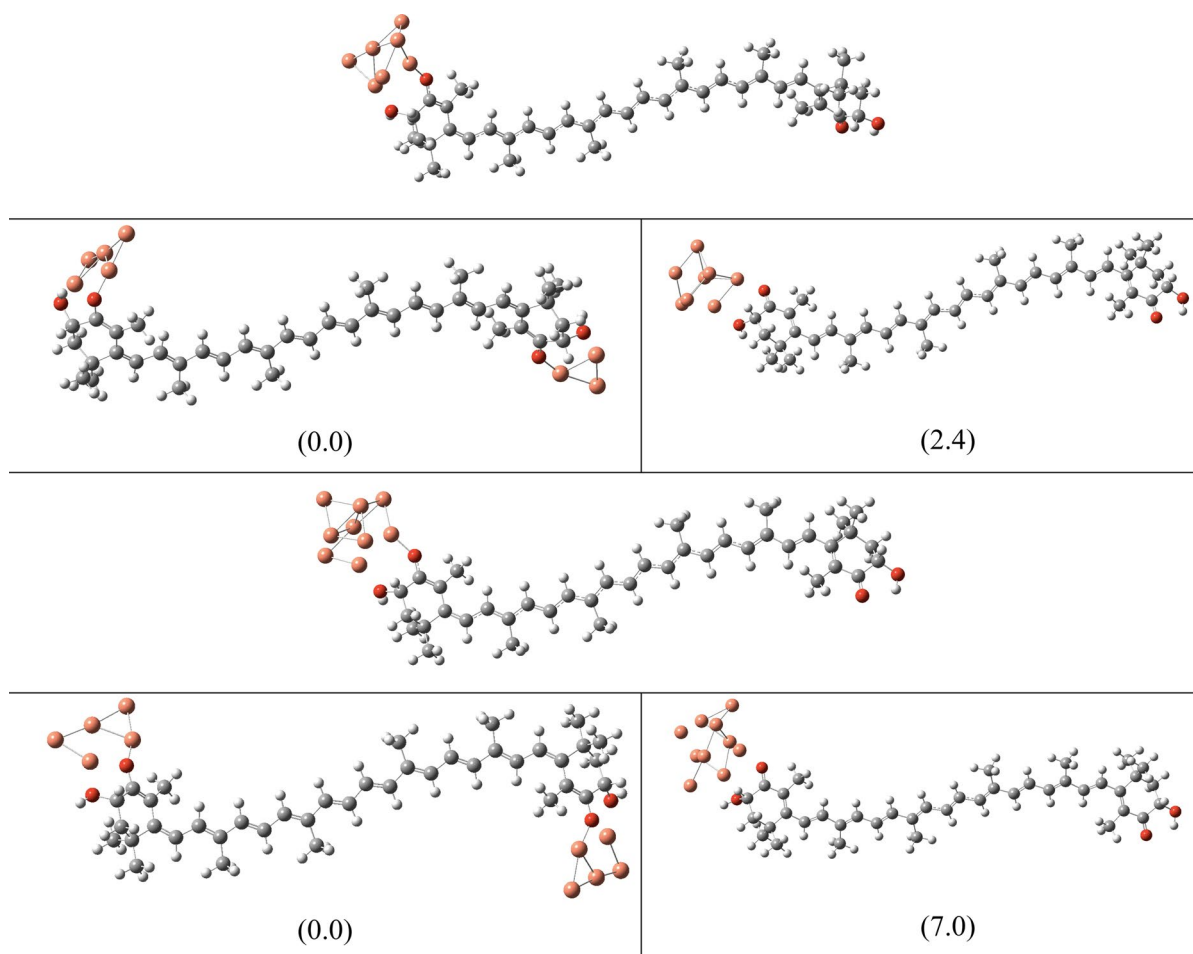
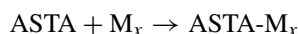


Fig. 3 continued

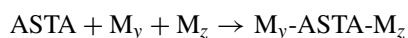
3.2 Binding energies and molecular orbital pictures

In order to better understand the interaction of ASTA with metal atoms or clusters, in Fig. 6 the binding energies (ΔE_f) are reported for the optimized structures of Figs. 3, 4 and 5. Binding energies are defined according to the following equations:



$$\Delta E_f = E(\text{ASTA-M}_x) - [E(\text{ASTA}) + E(\text{M}_x)]$$

M_x corresponds to the cluster that is present in ASTA-M_x . For $\text{M}_y\text{-ASTA-M}_z$, the binding energies correspond to



$$\Delta E_f = E(\text{M}_y\text{-ASTA-M}_z) - [E(\text{ASTA}) + E(\text{M}_y) + E(\text{M}_z)]$$

Based on previous definitions, negative values mean that products are more stable than reactants, and therefore, the reaction is thermodynamically possible. In Fig. 6, binding energies are reported. The systems with more negative binding energies are with copper. Among those containing

copper and comparing between isomers (systems with the same number of copper atoms), those binding energies for systems containing pentamers are more negative related to the other isomers. The exception is $\text{Cu}_3\text{-ASTA-Cu}_3$. Systems with one to five copper atoms present an odd–even oscillation in terms of the binding energies, with the higher binding energies for molecules with odd numbers of copper atoms. From systems with five to ten copper atoms, this phenomenon is reversed; those with an even number of metal atoms present higher binding energies than those with odd number of metal atoms. These later systems present Cu_5 in their structures. Apparently, the binding of Cu_5 and the interaction of this pentamer with ASTA stabilize the systems.

In the case of silver, the binding energy also manifests an odd–even oscillation (the exception is $\text{Ag}_5\text{-ASTA-Ag}_5$). Systems with an odd number of metal atoms (doublets) are more stable than those with an even number of metal atoms (singlets). The molecules with higher binding energies are $\text{Ag}_5\text{-ASTA-Ag}_5$, ASTA-Ag_5 and ASTA-Ag_9 . Apparently, ASTA-Ag has the silver atom weakly bonded to ASTA.

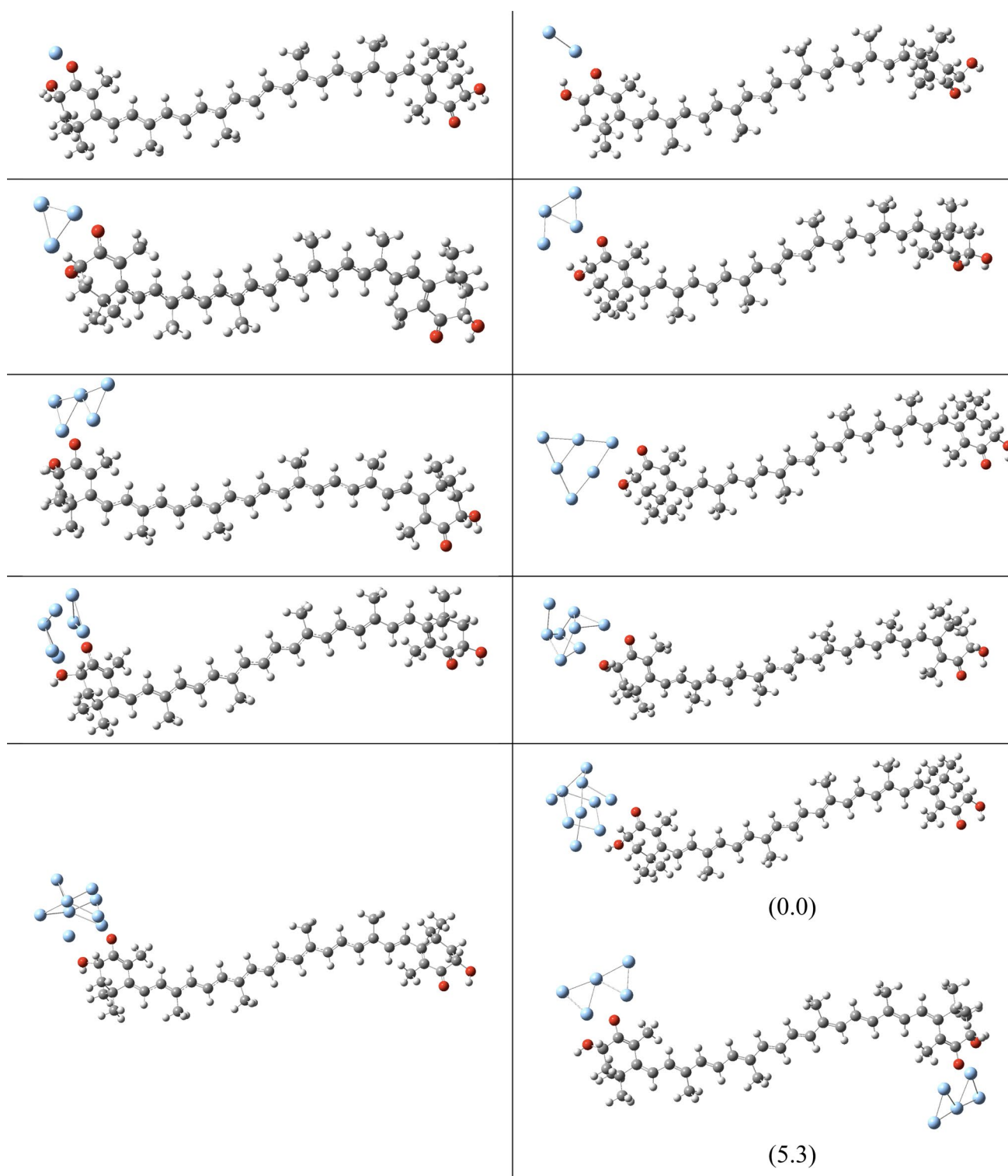


Fig. 4 Optimized geometries of the most stable structures for molecules with silver. Energy differences in *brackets* are reported in kcal/mol

For gold, $\text{Au}_2\text{-ASTA-Au}_2$ is not the most stable structure with four gold atoms; however, it shows the highest binding energy. ASTA-Au_3 is the ground state with the highest binding energy followed by ASTA-Au_4 . There

are two systems of gold with equal binding energy: ASTA-Au_8 and ASTA-Au_{10} . As with silver, ASTA-Au contains one gold atom weakly bonded to ASTA. Binding energies of molecules with gold atoms do not show

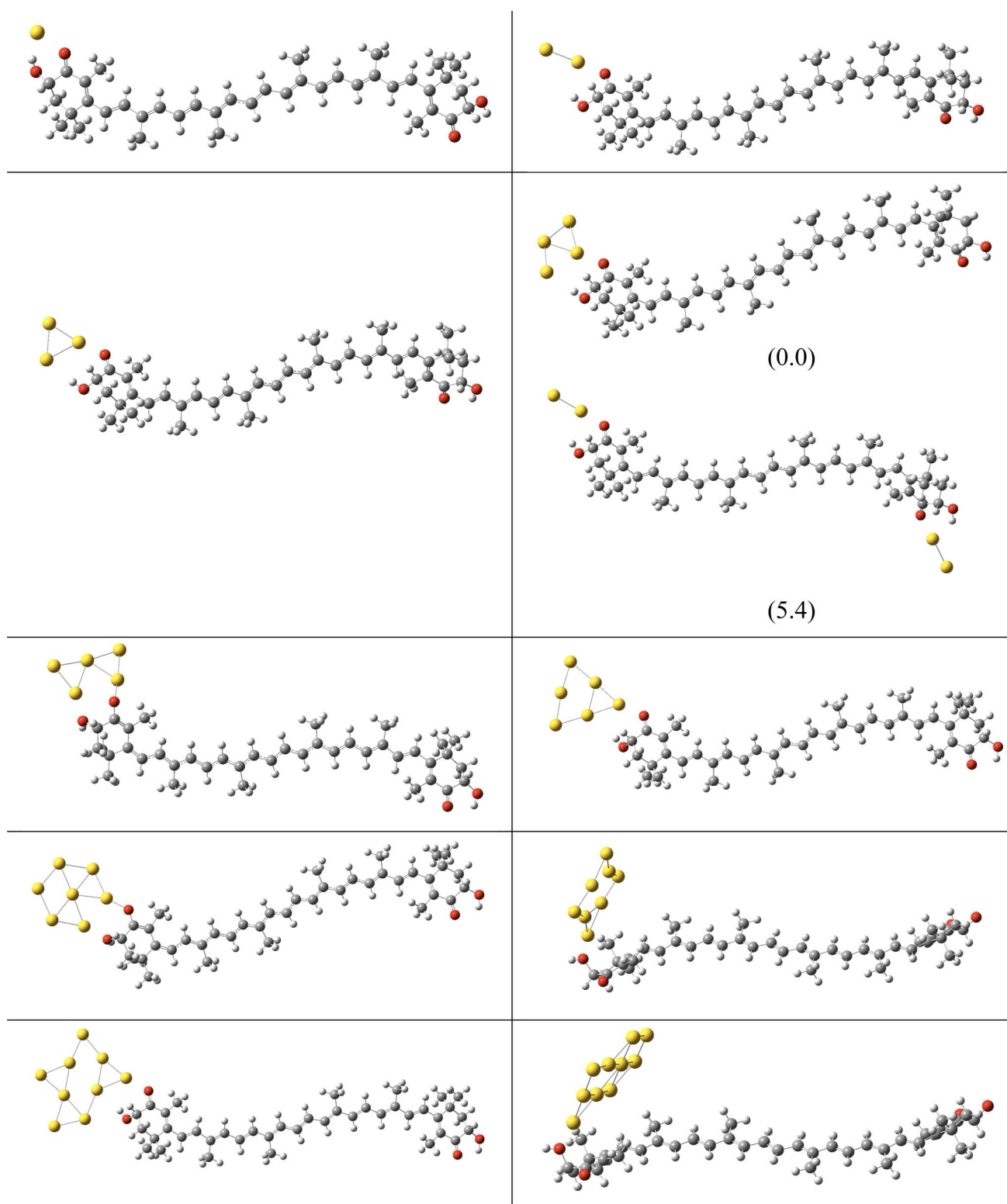


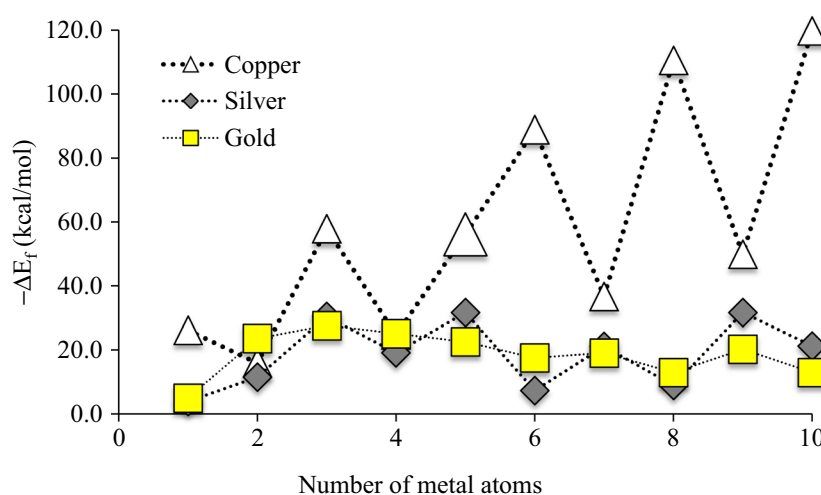
Fig. 5 Optimized geometries of the most stable structures for molecules with *gold*. Energy differences in brackets are reported in kcal/mol

an odd–even oscillation. With these results, it is possible to deduce that metal atoms and clusters are linked to ASTA.

In order to find some explanation relating to the differences in the binding energies, the molecular orbitals of systems with one and with ten metal atoms are analyzed.

Fig. 6 Binding energies (ΔE_f in kcal/mol) for the most stable structures of each molecule. The values for the less stable structures are in *italics*. A graph with $-\Delta E_f$ for the ground states is also included. The *dashed lines* are add observation

x	Copper	ΔE_f	Silver	ΔE_f	Gold	ΔE_f
1	ASTA-Cu	-26.1	ASTA-Ag	-3.9	ASTA-Au	-4.9
2	ASTA-Cu ₂	-15.9	ASTA-Ag ₂	-11.5	ASTA-Au ₂	-23.6
3	ASTA-Cu ₃	-57.8	ASTA-Ag ₃	-30.4	ASTA-Au ₃	-27.6
4	ASTA-Cu ₄	-24.7	ASTA-Ag ₄	-19.1	ASTA-Au ₄	-25.1
	<i>Cu₃-ASTA-Cu</i>	<i>-69.2</i>			<i>Au₂-ASTA-Au₂</i>	<i>-43.5</i>
5	ASTA-Cu ₅	-56.1	ASTA-Ag ₅	-31.7	ASTA-Au ₅	-22.5
6	Cu ₅ -ASTA-Cu	-88.9	ASTA-Ag ₆	-7.3	ASTA-Au ₆	-17.5
	<i>Cu₃-ASTA-Cu₃</i>	<i>-114.5</i>				
	<i>ASTA-Cu₆</i>	<i>-13.8</i>				
7	ASTA-Cu ₇	-36.6	ASTA-Ag ₇	-21.1	ASTA-Au ₇	-19.1
8	Cu ₅ -ASTA-Cu ₃	-110.5	ASTA-Ag ₈	-8.9	ASTA-Au ₈	-13.0
	<i>ASTA-Cu₈</i>	<i>-18.9</i>				
9	ASTA-Cu ₉	-49.9	ASTA-Ag ₉	-31.7	ASTA-Au ₉	-20.2
10	Cu ₅ -ASTA-Cu ₅	-119.7	ASTA-Ag ₁₀	-21.2	ASTA-Au ₁₀	-13.0
	<i>ASTA-Cu₁₀</i>	<i>-27.0</i>	<i>Ag₅-ASTA-Ag₅</i>	<i>-71.1</i>		



In Fig. 7, the frontier molecular orbitals of ASTA-M are reported. The lowest unoccupied molecular orbital (LUMO) is mainly a non-bonding s orbital of Cu, while in the case of Ag and Au there is a π contribution from ASTA and a bonding sigma orbital between oxygen and the metal atom. The highest occupied molecular orbital (HOMO) is similar for Cu and Ag. They are mainly located in ASTA, with a contribution from the p orbitals of oxygen atoms. For Au this contribution is not present. HOMO-1 is also different for Au as it is a non-bonding s orbital of Au, while for Cu and Ag this orbital is a π orbital of ASTA. HOMO-4 orbitals also show some differences. While for Au, this orbital is a p orbital of ASTA, and there is no contribution made by Au, and in the case of Cu and Ag, it is a π bonding orbital of the metal and the oxygen atom of ASTA. In spite of these differences, no factor in these molecular orbitals explains the higher binding energy of ASTA-Cu compared to ASTA-Ag and ASTA-Au. The only possible explanation is that Ag and Au are more stable isolated atoms than Cu.

Figure 8 presents the frontier molecular orbitals of the systems with ten metal atoms. These are closed-shell configurations. Two systems are included for copper: the ground state (Cu₅-ASTA-Cu₅) and ASTA-Cu₁₀, which can be compared to the ground state molecules with silver and gold. In general, there are no bonding orbitals between metal atoms and ASTA in any system. LUMO are π bonding orbitals of ASTA when the metal atom is Cu or Ag, while for Au it is a bonding orbital of Au₁₀. In the case of the HOMO, it is the reverse situation; for ASTA-Cu₁₀ and ASTA-Ag₁₀ it is a bonding orbital of the cluster, and for ASTA-Au₁₀ it is a π bonding orbital of ASTA. Comparing Cu₅-ASTA-Cu₅ with ASTA-Cu₁₀, it is possible to see that HOMOs and HOMOs-1 are different. They are located in ASTA for Cu₅-ASTA-Cu₅ and they are bonding orbitals of Cu₁₀ in ASTA-Cu₁₀. In summary, it is not possible to explain the differences in the binding energies from the molecular orbital picture. The only possible explanation is that the presence of Cu₅ stabilizes Cu₅-ASTA-Cu₅. The

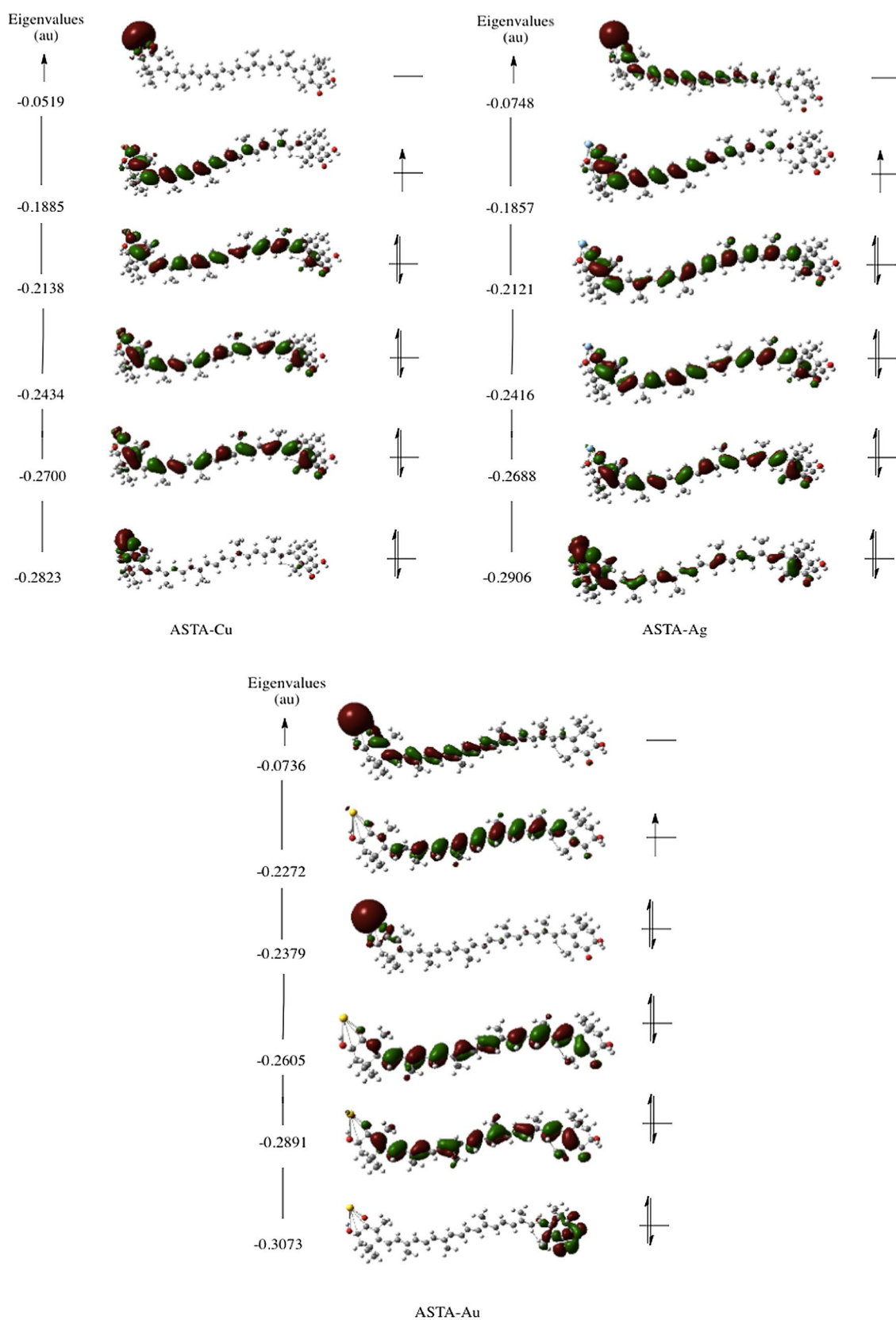


Fig. 7 Frontier molecular orbital pictures of ASTA-M (M = Cu, Ag and Au) for the most stable optimized structures

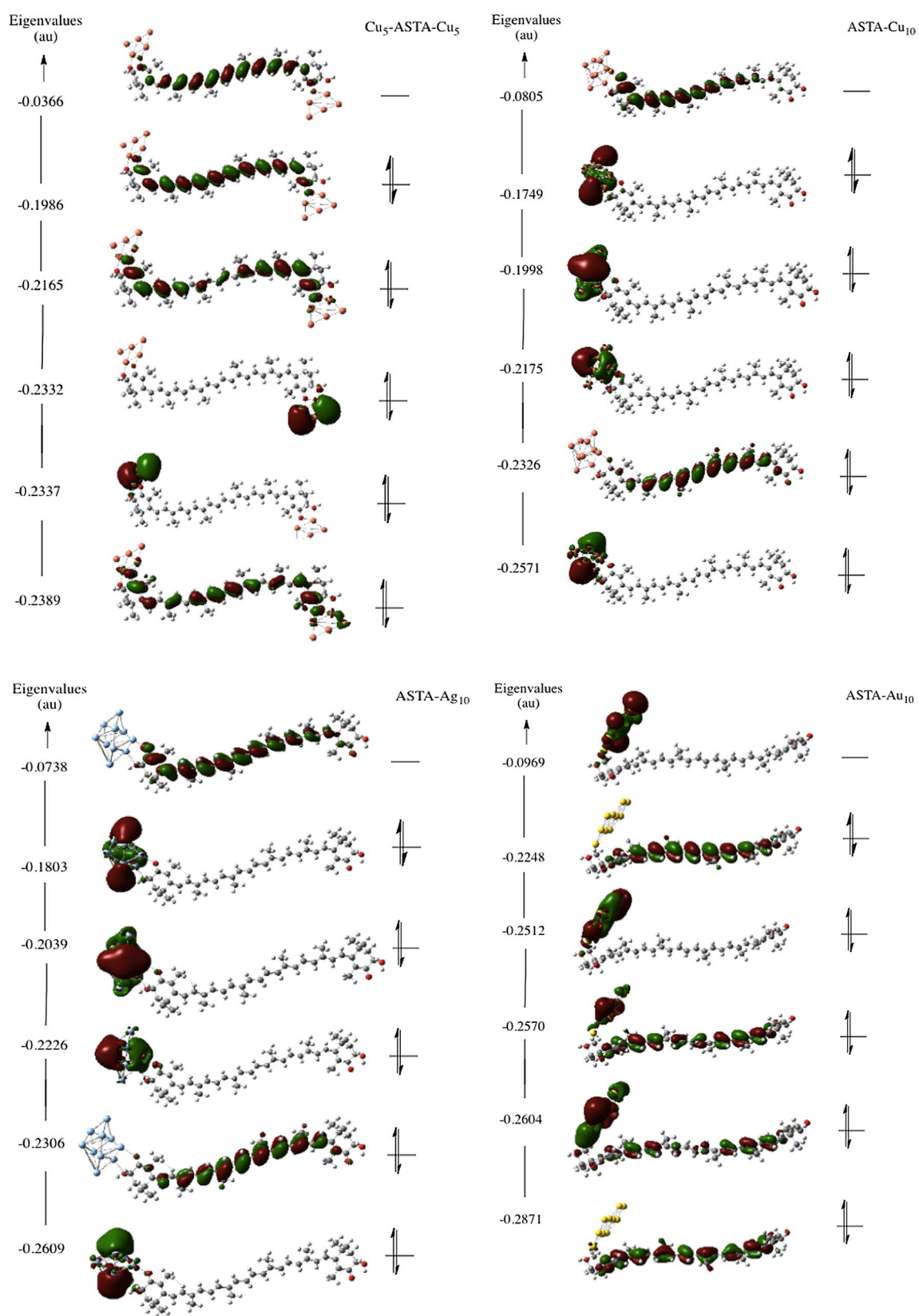
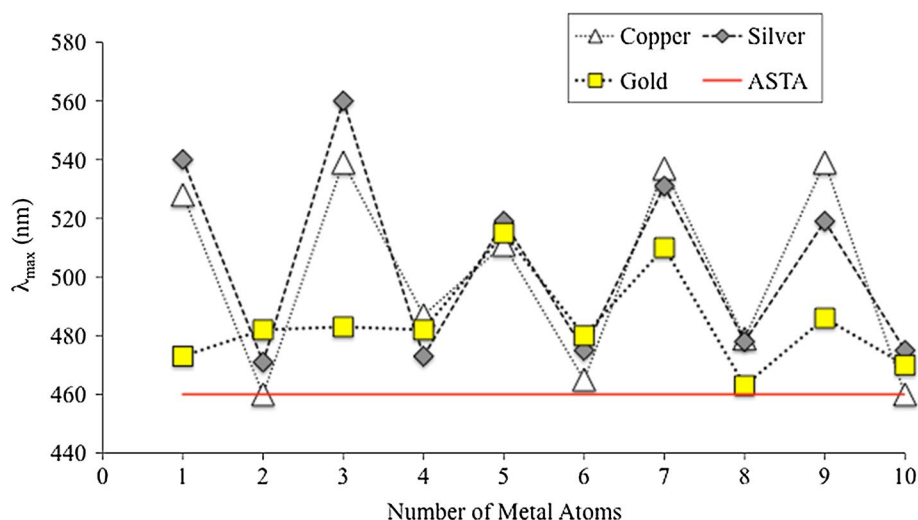


Fig. 8 Frontier molecular orbital pictures of ASTA-M_x (M = Cu, Ag and Au; x = 10) for the most stable optimized structures

Fig. 9 Values of λ_{\max} (in nm) dashed lines are to help aid observation of oscillations



molecules with M_{10} present similar values in terms of binding energies.

3.3 Lambda maxima (λ_{\max})

As explained in the introduction, the color of these compounds is very important. They are indicative of health in animals as usually a red pink color is directly related to the amount of astaxanthin. It was previously reported that one metal atom bonded to ASTA increases the values of λ_{\max} so that the color becomes redder. In order to assess the influence of the amount of metal atoms on the color of $ASTA-M_x$, Fig. 9 presents a graph with the values of λ_{\max} for the most stable structures. All metal systems with an odd number of metal atoms are redder in color than ASTA, but there is no a linear dependence regarding color and the “concentration” of the metal atoms, i.e., more metal atoms do not mean larger λ_{\max} values. In general, systems with odd numbers of metal atoms have larger λ_{\max} than those with an even number of metal atoms. Exceptions are for systems with 1–4 gold atoms that present similar values of λ_{\max} . ASTA is a closed-shell molecule, as are systems with an even number of metal atoms. This could explain why λ_{\max} values for systems with an even number of metal atoms are closer to the value of ASTA than molecules with an odd number of metal atoms that have open-shell configuration systems. For ASTA, λ_{\max} is equal to 460 nm. With an even number of metal atoms, λ_{\max} is in the range of 460–487 nm, while with an odd number of metal atoms, values are between 511 and 560 nm. Apparently, what is important for increasing the value of λ_{\max} is the number of electrons that allow the open-shell configuration, but there is also influence from the metal. In some of the systems ($ASTA-Cu_9$), the presence of copper clusters increases the λ_{\max} more than the existence of silver clusters, but there are

others where the presence of silver clusters has more influence on λ_{\max} than the presence of copper clusters ($ASTA-Ag$ and $ASTA-Ag_3$). The influence of gold clusters is generally less than the effect of copper and silver. Modifications of the color of these compounds in the presence of metals may cause confusion, as humans select seafood, fruits and vegetables because they are redder which normally indicates they have more astaxanthin. However, they may in fact be redder because they have more metals, which are not good for health, unless metals remain linked to ASTA.

3.4 FEDAM (antiradical capacity)

As explained previously in this report, carotenoids as ASTA prevent the formation of free radicals by chelating metal atoms. In this mechanism, ASTA does not scavenge free radicals but instead, inhibits their formation. However, the compounds formed with ASTA and metals could scavenge free radicals by the electron transfer mechanism. In order to analyze this mechanism, Fig. 10 presents the *FEDAM* for all the systems being studied. The best electron-acceptor molecule is $ASTA-Au_9$ followed by $ASTA-Au_7$ and $ASTA-Au_{10}$. The best electron donors are compounds with Cu_5 ($Cu_5-ASTA-Cu_5$, $Cu_5-ASTA-Cu$ and $Cu_5-ASTA-Cu_3$). In general and with respect to ASTA, the presence of copper and silver decreases the values for IE and the presence of gold increases the values of EA. There are also some molecules with copper and silver that have higher values for the EA than ASTA and therefore are better electron acceptors. Likewise, there are compounds with gold that have lower values of IE than ASTA, which are thus better electron donors. In order to scavenge free radicals, antiradicals can either donate or accept electrons. From the *FEDAM*, it is possible to conclude that the presence of metal atoms and clusters increases the antiradical capacity of ASTA, with

Fig. 10 Full electron donor–acceptor map (FEDAM) of compounds being studied. Values for the most stable optimized structures are reported

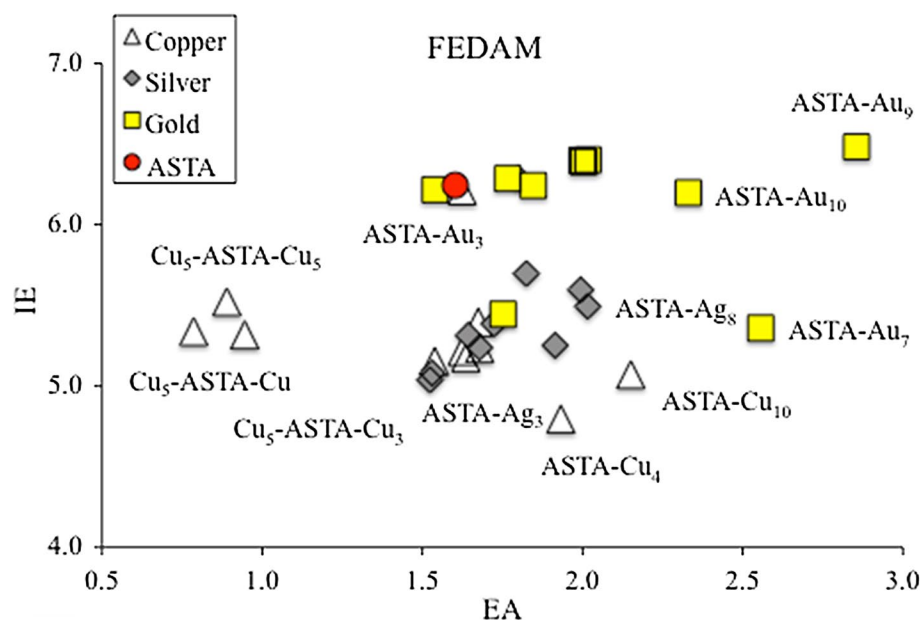
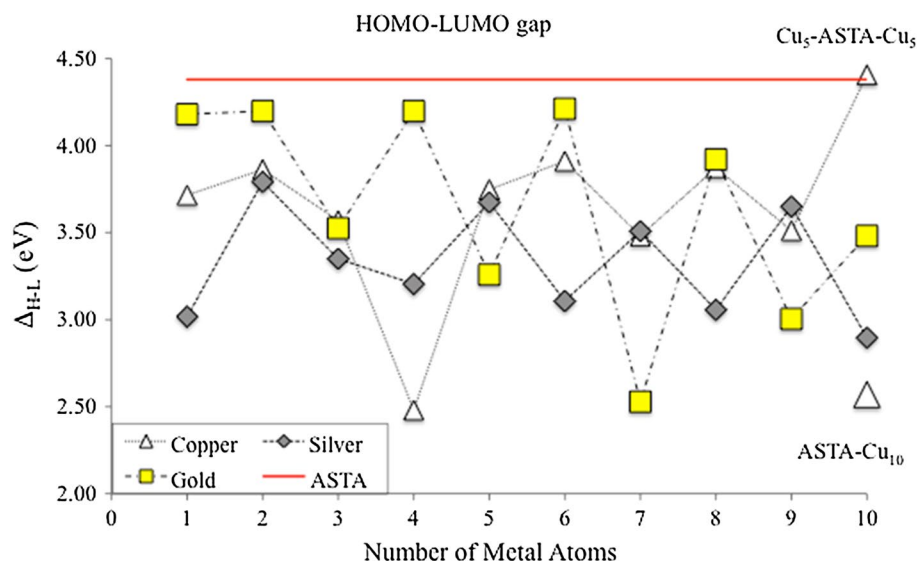


Fig. 11 HOMO–LUMO gap values for the most stable optimized structures



ASTA-Au_7 being the best antiradical. This could represent good news in relation to health. ASTA with metals form better free radicals scavengers than isolated ASTA, which is a very well-known antiradical molecule. As long as metals are bonded to ASTA, they are not bioavailable and are thus prevented from damaging the organism and furthermore are able to help prevent oxidative stress. Should this be the case, the formation of ASTA-M_x compounds could be beneficial to health. ASTA prevents the formation of free radicals by chelating metal atoms and clusters and also scavenging free radicals because the compounds formed with ASTA and metals are better electron donor-acceptors compounds. This finding deserves further investigations.

3.5 HOMO–LUMO gap

Figure 11 reports the values of the HOMO–LUMO gaps for the systems being studied, considering the most stable geometries in each case. ASTA-Cu_{10} is included for comparison. In all cases, the presence of metals reduces the HOMO–LUMO gap of ASTA, with the exception of $\text{Cu}_5\text{-ASTA-Cu}_5$ for which the values are similar. For systems with copper the HOMO–LUMO gap does not follow any systematic oscillation related to the number of copper atoms. However, in the case of silver and gold (starting with three metal atoms) there is an odd–even oscillation of the HOMO–LUMO gap. For molecules with silver, lowest

values of the HOMO–LUMO gap correspond to those with an even number of silver atoms and highest values correspond to systems with an odd number of silver atoms. For molecules with gold atoms, it is just the opposite. The highest values are for molecules with an even number of gold atoms.

ASTA- M_x molecules with an even number of metal atoms are closed-shell systems, whereas molecules with an odd number of metal atoms are open-shell systems. Apparently this has no effect on the HOMO–LUMO gap. As seen in Fig. 8, the HOMO orbital with gold systems is mainly a π bonding orbital of ASTA with no participation of the metal atomic orbitals, while with silver the HOMO is a bonding orbital of the metal cluster. This could explain the differences in the HOMO–LUMO gap. When there are ten copper atoms bound to ASTA, the results in Fig. 11 are presented for two possible structures: ASTA-Cu₁₀ and Cu₅-ASTA-Cu₅. There is a difference of almost 2 eV in the HOMO–LUMO gap of these two systems, being ASTA-Cu₁₀ the molecule with the lowest value. Comparing the molecular orbitals in Fig. 8, it is evident that HOMO and LUMO orbitals of these systems with copper are quite different. Frontier molecular orbitals of the pentamers bounded to ASTA are π bonding orbitals of ASTA. This explains why the values are similar to the values for ASTA. In ASTA-Cu₁₀ the LUMO is similar but the HOMO is a bonding orbital of the copper cluster and this reduces the gap. In summary and as expected, the presence of metal atoms modified the molecular orbitals which reduced the HOMO–LUMO gap in most cases.

The HOMO–LUMO gap represents an important criterion when defining which materials are apt for the construction of solar cells. The maximum in the solar energy radiation spectrum corresponds to 2 eV approximately and therefore, in order to have photovoltaic materials, the HOMO–LUMO gap of the electron donor has to be around this value. ASTA-Cu₄, ASTA-Cu₁₀, and ASTA-Au₇ are all systems with low values of the ionization energies and high values of the electron affinity; i.e., there are good electron donors and good electron acceptors. They also have the lowest values for the HOMO–LUMO gap, and these are around 2.5 eV (close to 2 eV). Based on these results, there is a remote possibility that these systems could be good candidates to build solar cells.

4 Conclusions

The interaction of ASTA with metal clusters of up to ten atoms (Cu, Ag and Au) produce stable structures with negative binding energies. Comparing these metal products, copper atoms are more strongly bonded to ASTA than silver and gold. For ASTA-Cu_x there are isomers with similar

stability when the systems have an even number of metal atoms. When there is an odd number of metal atoms, there is a ground state with a copper cluster bound to one side of the ASTA molecule. The ground states of ASTA-Ag_x and ASTA-Au_x have the metals forming a cluster at one side of the ASTA molecule.

As expected, all properties are modified by the presence of metals but none of these properties has a linear dependence on the number of metal atoms bonded to ASTA. In fact, there is an even–odd oscillation. ASTA bonded to an even number of metal atoms presents λ_{\max} in the range of 460–487 nm, whereas with an odd number of metal atoms, these values are between 511 and 560 nm. What is important for increasing the value of λ_{\max} is the number of electrons that allow the open-shell configuration, and there is also an influence of the metal that is involved. Compounds with copper and silver are redder than molecules with gold. The production of redder compounds is confusing for consumers of red food products and could be a problem for health,

In order to scavenge free radicals, antiradicals can either donate or accept electrons. From the FEDAM, it is possible to conclude that compounds formed with ASTA and metals are better electron donor-acceptors molecules. The presence of metal atom and clusters increases the antiradical capacity of ASTA, with the best antiradical being ASTA-Au₇. This could be good news in relation to health. As long as metals are bonded to ASTA, they are not bio-available and are therefore unable to damage the organism, but instead they may in fact help to prevent oxidative stress.

A reduction in excitation energy is desirable for solar energy devices as the HOMO–LUMO gap is a good criterion that allows us to decide about molecules that have potential applications as photovoltaic materials for the construction of solar cells. This value needs to be around 2 eV as the maximum in the solar radiation energy spectrum corresponds to this value. ASTA-Cu₄, ASTA-Cu₁₀ and ASTA-Au₇ have low values of the ionization energies and high values for the electron affinity; i.e., there are both good electron donors and good electron acceptors. They have also the lowest values (around 2.5 eV) of the HOMO–LUMO gap (close to 2 eV).

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