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Optical properties and charge distribution in rod-shape DNA-silver clusters emitters[†]

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While the atomic structure of DNA-Ag_n clusters remains unknown many efforts have been made to understand the photophysical properties of this type of systems. It is known that partial oxidation of the silver cluster is necessary for generation of fluorescent emitters. In this sense, the rod-shape model proposed by Gwinn and coworkers (Schultz, D., Gardner, K., Oemrawsingh, S. S., Markešević, N., Olsson, K., Debord, M., Bouwmeester, D. and Gwinn, E. 2013, *Adv. Mater.*, 25, 2797-2803), based on the idea that a neutral rod is generated with Ag⁺ acting as a “glue” in between the neutral rod and the DNA bases, is a good approximation in order to explain experimental results. With the aim to shed light towards the understanding of this systems, we explore the electronic dynamics and charge distribution in zigzag rod-shape DNA-Ag_n clusters, using Ag⁰/Ag⁺ stoichiometry found experimentally.

Introduction

In the past years, natural and artificial DNA molecules have been of great interest because of their applications in biological and material sciences. Metal-mediated base pairing has been widely studied due to its potential to extend the genetic code.¹ More recently, this property has been apply to develop DNA-protected silver emitters, called DNA-Ag_n hybrid clusters, that play an important role in biological and medical science,^{2–4} and are of great interest because of their photophysical properties.^{5,6} It's well known that this clusters present a common UV band due to the excitation of the DNA moiety,⁷ and a tunable band in the visible region that could correspond to the longitudinal plasmon excitation of the silver-core. The tunability of this band may be governed by the length of the neutral silver-core and the DNA bases sequence, but could also be modified by charge environment and cluster

shape.^{8–10} More interestingly, for emitting DNA-Ag_n clusters, the excitation on the UV band leads to the same fluorescence spectrum as in the case of the visible band excitation. This phenomena could be due to a charge transfer from the DNA-base to the silver-core when exciting the UV band. In this sense, recently, a charge transfer process from cytosine to Ag⁺ was observed experimentally upon UV excitation of the simplest cytosine-Ag⁺ complex in the gas phase, which could be the foundation for the electronic coupling process between the two moieties.¹¹ Berdakin *et al.* also investigated by electronic dynamics a Cyt-Ag_n complex that mimics DNA-Ag_n clusters and found that a charge transfer process from the DNA-base to the silver-core takes place regardless of backbone and structural disorder.¹²

Although many progresses have been made in order to understand the structural features that lead to the optical properties of these DNA-protected silver clusters^{12–18}, their atomic structures are still unknown. In this sense, Gwinn and coworkers have isolated and analyzed DNA-Ag_n clusters by HPLC coupled to ESI-MS and found that the silver-core is partially oxidized and that the ratio Ag⁰/Ag⁺ in those showing fluorescence is not random, but follows certain “magic numbers” of neutral Ag atoms.¹⁹ They also found that the visible band experiments show a red-shift as the number of neutral silver atoms increases, along with an enhancement of its intensity.⁸ This results led the authors to propose a rod-shape like DNA-Ag_n model with a zigzag neutral silver-core structure as a way to explain the inner charge of the metal-core, as well as the “magic numbers” of Ag⁰ and the tuning of the visible band. This model is based on the idea that a neutral rod is generated with Ag⁺ acting as “glue” in between the neutral rod

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and the DNA bases.²⁰

Even though for a rod shaped metal cluster the atomic charge tends to separate as further as possible to decrease charge repulsion, in this case, the strong Cytosine- Ag^+ interaction could have a major influence in the charge distribution of the DNA- Ag_n cluster. We think that the zigzag model proposed by Gwinn and coworkers is a suitable model in the way that satisfies the Ag^0/Ag^+ relation seen experimentally while keeping chemical sense and the rod-shape structure. In order to shed light toward the understanding of the photophysical properties of these systems we employ molecular dynamics simulations, density functional theory based tight-binding (DFTB+) and quantum dynamical calculations to explore the optical and dynamical properties of neutral and charged DNA- Ag_n clusters using the zigzag rod-shape model. Also, the structures used in this work were made with the Ag^0/Ag^+ stoichiometry found experimentally in order to get a better comparison with respect the experimental data.^{19,20} Although important results were obtained by analyzing the electronic dynamics of a simpler DNA- Ag_n cluster model,^{12,16} this work aims to obtain information about a more complex and realistic model towards the elucidation of the actual DNA- Ag_n structure, and its correlation with their optical properties. To the best of our knowledge, this is the first time a zigzag rod-shape DNA- Ag_n cluster model is analyzed with quantum mechanical methods.

Computational section

The DNA- Ag_n clusters in this work were generated by the Nucleic Acid Builder (NAB) script²¹ together with the Visual Molecular Dynamics (VMD) visualization program.²² Molecular dynamics were carried out using the large-scale atomic-molecular massively parallel simulator (LAMMPS).²³ Simulations of solvated and charge-neutralized DNA- Ag_n clusters were performed in an NVT assembly, using a 60-Å-side cubic box with explicit water. The parameters used to describe the DNA- Ag_n clusters interactions were described in a previous work.¹² First, an energy minimization was performed, followed by a 10 ns run at a temperature of 300 K. After stabilization of thermodynamics properties an ensemble of evenly-spaced 10 structures was selected from each simulation. Besides including the effect of thermal noise and structural disorder in the DNA backbone and silver cluster, this strategy allows to account for the fluctuations of structural parameters such as Ag-Ag and Ag-N bond distances and Ag-Ag-Ag and N-Ag-N angles in the photophysical properties studied within this report. All the results were calculated as the ensemble average of this manifolds of obtained structures.

The methodology to study the electronic properties has been described previously.^{24–26} Within a TD-DFTB model, the methodology is based on the time propagation of the one electron density matrix under the influence of external time-varying electric fields. The electronic dynamics is fully described taking into account to all orders the influence of the external field. The electronic structure is obtained from a density functional theory based tight-binding (DFTB) Hamiltonian.²⁷ The electronic structure of the DNA- Ag_n clusters in its ground state was modeled with the DFTB+ code, using the mio 1.1 DFTB parameter set.^{28,29} The

electronic parameters between Ag and all other elements were obtained by DFT calculations as was explained elsewhere.¹² To obtain the optical absorption spectra an initial perturbation is applied with a Dirac delta pulse shape to the initial ground-state density matrix.²⁵ Then, by time integration of the density matrix equation of motion we can calculate the evolution of the density matrix. The absorption spectrum within the linear response regime is obtained by deconvolution of the dipole moment signal from the excitation, after a Fourier transform. To get information about the nature of the electronic transitions, a sinusoidal time-dependent electric field perturbation is tuned with respect the absorption maximum of the band to analyzed. Also, the polarization direction of the field applied should match the transition dipole moment vector direction at the chosen energy. Under this conditions, the population of each state, as well as each atom charge, can be extracted from the density matrix and followed in time. The details of the procedure employed have been described elsewhere.^{24,26,30}

Results and discussion

For the purpose described above, two model structures with different neutral silver-core length were analyzed. The structures consist in two oligonucleotides strands of 3 and 4 cytosine length in transoid orientation. The Ag^+ cations acts as a binding bridge to the neutral silver core composed of 4 or 6 Ag atoms (hereafter N4_cluster and N6_cluster) shown in figure 1.

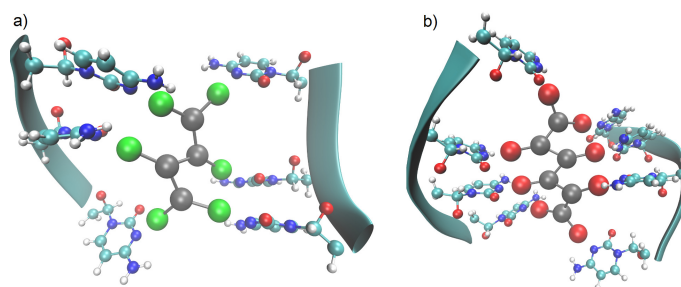


Fig. 1 N4_cluster and N6_cluster structures obtain at 5 ns of the molecular dynamics simulation. Green and red silver atoms represent the silver cations in each structure, while the neutral silver-core is shown in grey in each case. The backbone is shown as cartoon for simplification.

The choice of the system employed arises from the fact that 4 and 6 are “magic numbers” of neutral silver-core atoms for green and red emitting DNA- Ag_n clusters found by Gwinn and coworkers²⁰. Also, Ag^0/Ag^+ stoichiometry of 4/6 and 6/8 was used in both N4_cluster and N6_cluster structures respectively, as was observed experimentally, to allow a more reliable comparison between the computational results and the experimental data. These structures were already analyzed by molecular dynamics by Copp et. al. to obtain information about the connection between the total cluster charge and the structure shape.¹⁹

In a first step, each structure was explore by a 10 ns NVT molecular dynamics simulation of the system embedded in water, as explicit solvent, and chlorides as counter-ions to neutralize the charge. This was made to ensure an statistical distribution of configurations and to take into account structural disorder of the sys-

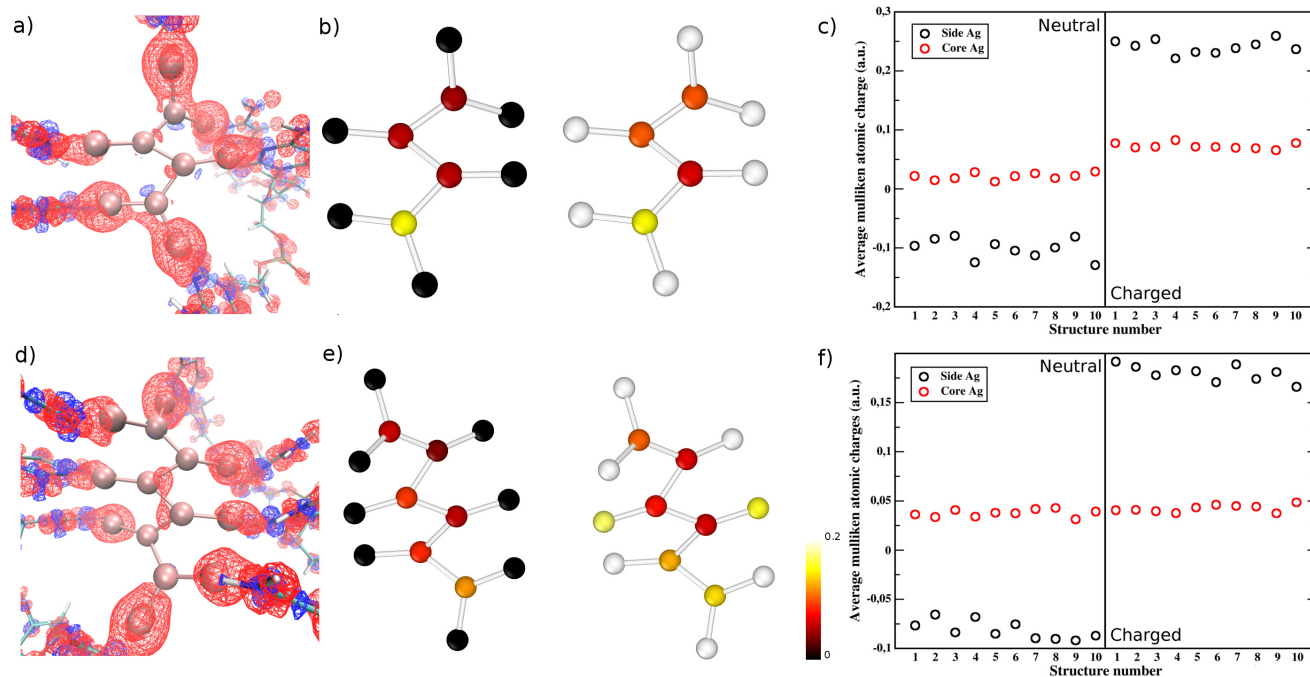


Fig. 2 (a and d) Charge density difference between charged and neutral N4_cluster (a) and N6_cluster (d) respectively. Red and blue grids correspond to positive and negative charge differences respectively. A ± 0.0025 isovalue of the surface was used in all cases. (b and e) Mulliken atomic charges of the silver cluster of a neutral (left) and charged (right) N4_cluster (b) and N6_cluster (e) structures shown in Figure 1. DNA and backbone are not shown in this Figure for simplification. The color coding scale represent the atomic charge. (c and f) shows the average atomic charge for side-Ag and core-Ag of the manifold of structures for N4_cluster (c) and N6_cluster (f), when the system is neutral (left panel) and charged (right panel).

tem. Then, an ensemble of 10 evenly-spaced structures were selected after stabilization of the thermodynamics properties. Once the structures were obtained, the electronic properties of neutral and charged DNA $_{Ag_n}$ clusters (+6 and +8 for N4_cluster and N6_cluster, respectively) were calculated with DFTB+ package.²⁸ All the analysis in this work was made with the ensemble average of the manifold of structures selected (for details see the Computational Methods section). Figure 1 shows two structures obtained for N4_cluster and N6_cluster respectively, at 5 ns of the molecular dynamics simulation.

It can be assumed, based on electrostatic assumptions, that for a rod-shape metallic system charge will tend to go to the ends of the rod to minimize charge repulsion. In the case of the structures analyzed in this work, charge may also go to the silver atoms on the side of the metal cluster, where the cytosine is attached (hereafter "side-Ag") since the length and the width of the silver cluster are comparable. Nevertheless, it is known that Cytosine and Ag^+ have a very strong interaction,^{31,32} and this could generate a charge localization that favours the charge distribution proposed by Gwinn and coworkers for the DNA $_{Ag_n}$ clusters.

To enlighten this matter we compare the charge distribution obtained for the silver cluster in neutral and charged DNA $_{Ag_n}$ clusters. Figure 2 a) and d) shows the charge density difference between charged and neutral cluster for N4_cluster and N6_cluster respectively. In both DNA $_{Ag_n}$ clusters, when the system is charged, a positive charge accumulation appears on the side-Ag. Meanwhile, for the silver atoms in the core, the ones that cytosine is not attached to (now on "core-Ag"), the charge remain

practically unaltered, in comparison with the neutral DNA $_{Ag_n}$ cluster. In accordance with the charge density difference, figure 2 b) and e) shows that when the system is charged, in both N4_cluster and N6_cluster cases, Mulliken atomic charge tends to go to the side-Ag, while the charge of the core-Ag remains nearly unchanged and close to zero.

To ensure that this behavior is independent of the structural disorder we compared the Mulliken atomic charge average for the side-Ag and the core-Ag, for neutral and charged clusters of the complete manifold of structures used in this work. In figure 2 c) and f), each pair of red and black circles correspond to the atomic charge average of side-Ag and core-Ag, respectively, of each structure. The left panel shows the results for the neutral structures while the right panel shows the results for the charged structures. Once again, for the manifold of structures obtained, in both N4_cluster and N6_cluster cases charging the system affects mainly the side-Ag, while the core-Ag remains practically unaltered.

In order to get information about the optical properties of these systems the absorption spectra of the manifold of structures for both clusters, neutral and charged, were calculated. See Computational Methods section for more information. Then, an average spectrum was calculated to take into account the structural disorder of the system. Figure 3 shows the absorption spectrum average obtained for N4_cluster (a) and N6_cluster (b) clusters. In black the average for the clusters with neutral charge is represented and in red for the charged ones. Figure S1 shows the manifold of spectrums obtained for both cluster, neutral and charged.

For both clusters, neutral and charged, a band in the UV range appears at ≈ 4.9 eV. This band has been reported before both experimentally⁷ and theoretically in a chain-like DNA_Ag_n cluster¹² and corresponds to the excitation of the DNA bases.

Another broad band appears at 1.7 eV that corresponds to the plasmon-like longitudinal excitation of the metal cluster as was also reported before.^{8,20,33,34} In accordance with the charge distribution proposed for this type of systems, the features of this visible band remains practically unchanged when the system is charged. Also, a small red shift of this band is observed when increasing the neutral core-Ag length, as was also reported before experimentally by Gwinn and coworkers.⁸ It is worth noting that multiple partially resolved peaks are observed for this band as well. Several works in the literature suggests that optical properties of this kind of systems may be sensitive to cluster shape and internal coordinates.^{8,10} In this sense, the presence these peaks, that are not observed in experimental results, most probably arises due to the limited number of structures considered for the average spectrum. Also, even though the energy obtained for this band is lower than the one observed experimentally, it is known that DFT methods underestimate the energy of plasmon-like excitations in this type of systems. It is important to note that despite these small spectral differences, the description of the optical and dynamical properties of the system is not affected, as was pointed out in previous works.^{12,16}

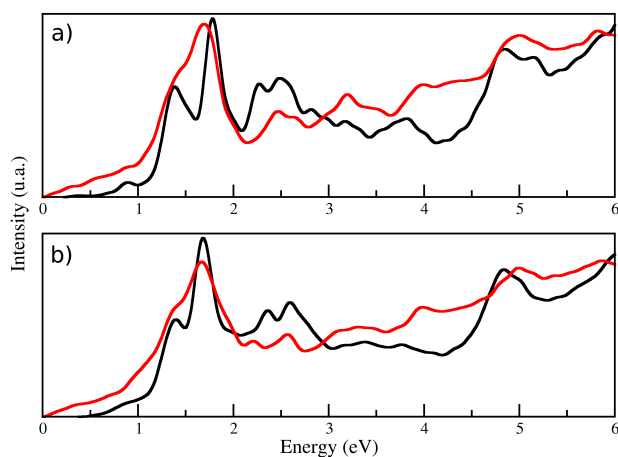


Fig. 3 Average of absorption spectra of N4_cluster (a) and N6_cluster (b) emitters. Black lines represent the neutral clusters. Red lines represent the charged clusters.

Furthermore, for neutral clusters, a third band appears at ≈ 2.5 eV that strongly decreases when the system is charged. Interestingly, this band has not been reported experimentally for this type of systems. Theoretical studies of neutral silver nanowires show that transversal plasmon-like excitations lie at higher energy than the longitudinal excitations and have a small blue shift when the wire length increases.^{33,34} To obtain more insight on the origin of this band we followed the molecular orbital populations of the neutral clusters during light irradiation at 2.59 eV and 2.54 eV for N4_cluster and N6_cluster, respectively. Figure S2 and S3 shows that this band correspond to a transverse excitation within the metal cluster, involving orbitals with no contribution from the

DNA moiety. Moreover, when the system is charged, the intensity of this band strongly decrease, while the longitudinal plasmon-like band remains nearly unchanged. This could be explained based on the new charge distribution. Because the charge goes to the side-Ag atoms, transversal excitations within the metal cluster are affected, leading to a decrease of the intensity of the band.

Similar results were obtained by Berdakin et al. for a chain-like silver DNA_Ag_n cluster model. They studied the dependence of the optical properties with the charge and observed that the longitudinal plasmon-like excitation of the silver chain vanish when the total charge of the system reaches the number of silver atoms.¹⁶ This results suggest that the band observed at ≈ 2.5 eV for neutral clusters may correspond to a transverse plasmon-like excitation of the metal cluster, and the fact that this band was not observed experimentally for charged DNA_Ag_n cluster supports the charge distribution proposed by Gwinn and coworkers.²⁰ Other small bands are observed at higher energies than

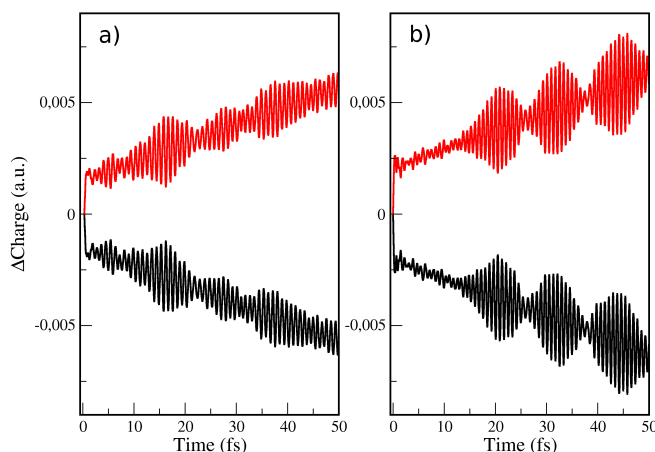


Fig. 4 Average time-dependent Mulliken atomic charges with respect to the ground state charge (Δ Charge). Panels a and b show the results obtained for charged N4_cluster and N6_cluster, respectively. DNA and Ag Δ Charge are shown in red and black lines, respectively.

the longitudinal plasmon-like excitation of the silver cluster that could be due to an overestimation of d-electron transition within the silver cluster. These types of transitions were observed previously in literature for raw silver nanowire systems.^{9,10,34} Although the calculated spectrum does not accurately reproduce the experimental spectrum, it is clear that the major spectral features of this type of system, i.e. the longitudinal silver plasmon excitation and the DNA bases excitation, as well as the intrinsic photophysics, are nevertheless observed.

Photodynamical properties of the charged systems were investigated as well. As was pointed out before, fluorescence emission of DNA_Ag_n clusters upon UV excitation of the DNA bases, could undergo by a charge transfer process from the DNA to the silver cluster, where the emitter center may be located. This charge transfer was seen theoretically by Berdakin et al. in a poly-cytosine silver-chain like DNA_Ag_n cluster model¹² and experimentally observed for cytosine-Ag⁺¹¹ and (cytosine)₂ Ag⁺ complexes in gas phase.³⁵

To enlighten this matter, we explored the charge dynamics dur-

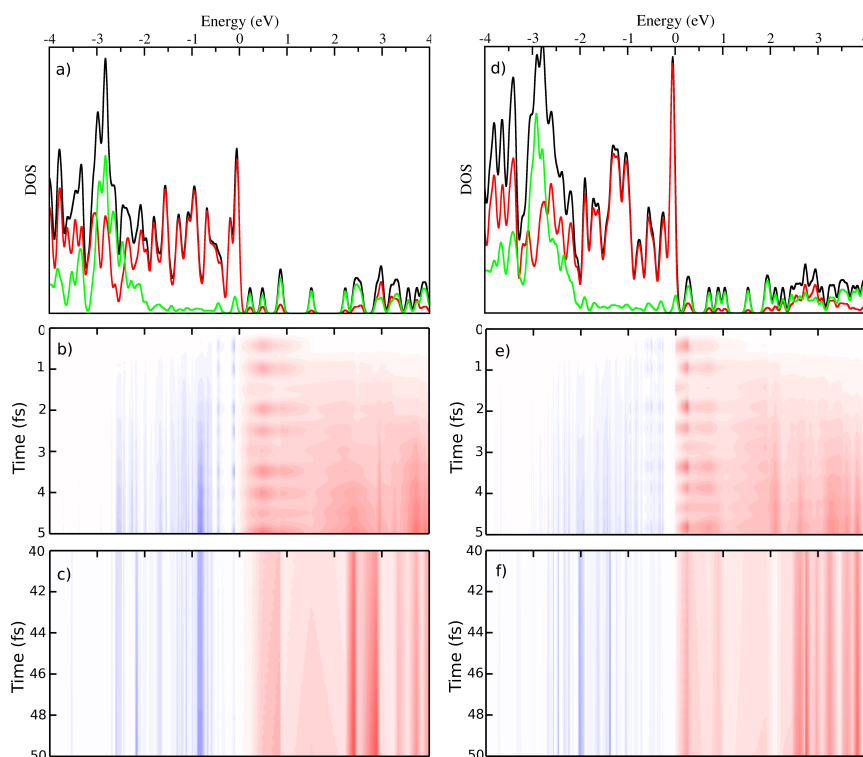


Fig. 5 Evolution of the molecular orbital population of charged DNA_nAg_n clusters during light irradiation at the UV band, as a function of time and the energy of each eigenstate (“DynPop”). (b and e) shows the DynPop obtained from 0 to 5 fs and (c and f) from 40 to 50 fs. The color map represents the increase (red) or decrease (blue) of each state population as a function of time, compared with the corresponding population of the unperturbed ground state. (a and d) Black lines shows the total DOS in order to aid interpretation of the result. Red and green lines represent the PDOS for DNA and Ag atoms, respectively

ing light irradiation by calculating the time-dependent Mulliken atomic charge changes with respect to the ground state charge (ΔCharge) in both DNA and Ag moieties. Each structure for both DNA_nAg_n clusters was irradiated at the maximum of the UV band and the moiety charges upon time were followed. For more information see Computational Methods section. The average moiety charges for both N4_{cluster} and N6_{cluster} clusters are shown in Figure 4a and 4b, respectively. Red lines represent the DNA moiety and black lines silver moiety. As can be clearly observed, upon UV light irradiation, a net negative charge is transferred from the DNA moiety to the Ag moiety for both N4_{cluster} and N6_{cluster} clusters. Nevertheless, in both cases, two processes can be distinguished. First, an ultrafast charge separation occurring within the first femtoseconds of the dynamics. Given the rate of this process, it could correspond to a charge transfer excitation in which the system is excited from a state of the DNA to a state of the Ag moiety. This behavior was observed experimentally for cytosine-Ag⁺ complex in gas phase, in which upon UV irradiation a charge from cytosine was transferred to the Ag, resulting in fragmentation to cytosine⁺ and Ag⁰.¹¹ The second process involves a slower charge transfer process which is observed until the end of the dynamics. “Slower” here is taken in comparison to the first process; the charge transfer is, indeed, ultrafast but comes out as a result of the evolution of the excited wave packet. This kind of charge transfer was already observed by Berdakin et al. for the chain-like silver DNA_nAg_n clusters^{12,16} and corresponds to a charge transfer

in which the excited state has contribution of both Ag and DNA moieties. In this scheme, the charge transfer from DNA moiety to silver moiety occurs as the population of the excited state increases over time.

To understand more about this phenomena, we analyzed the evolution of the molecular orbital population throughout the dynamics, for both charged DNA_nAg_n clusters, at short and long times. These results are shown in Figure 5 plotted next to the density of states (DOS) of the system and the projected density of states (pDOS) for DNA and silver. In both N6_{cluster} and N4_{cluster}, the orbital population varies over time. For the first process, at short times (Figure 5 b) and e), respectively), the states involved in the charge transfer are close to the Fermi energy. Fig. S4 and S6 shows that the populated states in this process have major contribution from the Ag moiety. For the second process instead, the states involved are far away from the Fermi energy, and the DNA moiety contribution in the populated states becomes appreciable. (Fig. S5 and S7)

On the other hand, the populated states at short times have major contribution from the Ag moiety, while at long times the DNA contribution in the populated states becomes appreciable. This can also be observed in the orbitals involved in the charge transfer process at short and long times in Fig. S4, S5, S6 and S7 for both DNA_nAg_n clusters.

Conclusions

Within the present report we analyze the optical and dynamical properties of a zigzag rod-shape model of poly-cytosine DNA_n clusters obtained by molecular dynamics simulation.

The charge distribution comparison between neutral and charged DNA_n clusters suggests that a neutral silver rod is indeed generated when the cluster is charged. The Ag cations act as “glue” in between the neutral rod and the DNA bases that could be favored by the strong Cytosine-Ag⁺ interaction.

Absorption spectra calculated in this work shows all the features observed experimentally for this type of systems. When systems go from neutral to charged, characteristic bands remains nearly unchanged, namely the longitudinal plasmon-like excitation in the visible region and the DNA bases excitation in the UV region. A third band appears when the systems are neutral, that may correspond to a transverse plasmon-like excitation, that decrease in intensity when the DNA_n clusters is charged. The fact that this band was not reported experimentally supports the charge distribution proposed for this type of systems.

Also, the electronic dynamics analysis shows a charge transfer from DNA moiety to silver moiety when the UV band is irradiated, as was seen previously for a chain-like DNA_n cluster model. Nevertheless, two processes occur upon UV light irradiation. First, a charge transfer excitation in which the system is excited from a state of the DNA to a state of the Ag moiety, followed by a slower charge transfer process in which the excited state has both contribution from DNA and Ag moiety. To the best of our knowledge this is the first time that optical and dynamical properties of the zigzag rod-shape model in DNA_n clusters are analyzed. Furthermore, the results obtained suggests that this model might be a good model to interpret the experimental data.

Conflicts of interest

There are no conflicts of interest to declare.

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