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DNA-Protected Silver Emitters: Charge Dependent Switching of Fluorescence [†]

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The relationship between the state of charge and spectroscopy of DNA-protected silver emitters is not yet well understood. This remains one of the major issue to unveil in order fully disentangle the spectroscopic features of this novel systems. It is a well known fact that fluorescence response arises upon chemical reduction of silver cations attached to DNA, leading to neutral (or partially oxidized) "bright" clusters. It is important to note that the absence of fluorescence from completely ionic complexes is universal in the sense that it does not depend on any experimental variable. This suggests that its origin may be founded on the nature of the interaction between DNA bases and silver cations. Nevertheless, to the best of our knowledge, no explanation exists for this charge dependent switching between dark completely ionic complexes and bright (neutral or partially oxidized) clusters. In this brief report we address this experimental fact on the basis of the electronic structure of the complex as a function of its charge and quantum dynamical simulations of the processes following photoexcitation. These data provides a dynamical picture of the correlation between charge and fluorescence.

In the past years, natural and artificial DNA molecules have been of great interest because of their potential applications in biological and material science.[1–4] In this context, the development of DNA-protected silver emitters (just clusters from now

on) have attracted the attention of scientist from a wide range of disciplines due to their potential applications,[5–7] and the fact that they constitute a new generation of small and biocompatible fluorophores.[8,9] A distinctive feature of the optical properties of these clusters is that they present two intense absorption bands. One of these bands, in the visible range, is tunable by changing the DNA base sequence, the number of Ag atoms and/or the state of charge of the cluster. The other band, in the UV spectral region, is common to all of them regardless of the position of the visible band.[8,10–13] It has been established that the UV excitation band is located in the spectral region where the isolated bases and DNA strands absorb (260 - 270 nm).[10] Interestingly, the excitation of the common UV band leads to the same fluorescence spectrum as the excitation of the tunable visible band.[10]

Although big progress has been achieved in the lasts years regarding the comprehension of the nature of DNA-protected silver emitters, the relationship between the state of charge and the spectroscopy of this fluorophores is yet not well understood. This remains one of the major issues to unveil in order fully disentangle the spectroscopic features of these novel systems. Intriguingly, it has been know from the firsts reports on this materials that silver ions have to be chemically reduced in order to obtain fluorescent clusters.[12] More recently, new experiments have established that complete chemical reduction is not necessary for the development of fluorescence, but at the same time have confirmed that no fluorescence can be obtained from completely ionic DNA-silver complexes $(DNA-Ag_n)^{n+}$.[14,15] It is important to note that the absence of fluorescence from $(DNA-Ag_n)^{n+}$ complexes is universal in the sense that it does not depend any experimental variable. This suggests that its origin may be founded on the nature of the interaction between DNA bases and silver cations. Nevertheless, to the best of our knowledge no explanation exists for this charge dependent switching between dark completely ionic complexes and bright (neutral or partially oxidized) clusters. In this brief report we address this experimental fact, trying to understand the absence of fluorescence from $(DNA-Ag_n)^{n+}$ complexes from the electronic structure of the system and quantum dynamical simu-

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[†] Electronic Supplementary Information (ESI) available: Density of states of $((C_2Ag)_6)$ as function of the total charge of the system. Total density charge difference with respect the neutral cluster as function of charge. Absorption spectra of $((C_2Ag)_6)$ as function of total charge, and comparison of the results for the cisoid/transoid $((C_2Ag)_6)$ structure. See DOI: 10.1039/b000000x/

lations.

Given the size and complexity of the system a time-dependent self-consistent density functional tight-binding (TD-SCC-DFTB) approach was chosen as the tool to provide a dynamical picture of the excitation, and the processes that take place upon UV light absorption. TD-SCC-DFTB provides an adequate balance between computational cost and precision, allowing us to obtain qualitative information that would be impossible or at least very expensive to obtain using more traditional time-dependent density functional theory based methods. Our approach has been used in the past to obtain the absorption spectra and study the photodynamics of a wide range of systems such as chlorophylls,[16,17] semiconductor nanoparticles,[18] metallic nanoparticles[19] and graphene nanoflakes.[20] The method was also employed to explore the photodynamics of charge transfer in donor-acceptor molecular complexes,[21] and in dye semiconductor nanoparticles.[22–24,24] Moreover the method has been recently proven to be a powerful tool to study the spectroscopic features of DNA based systems, as the effect of intercalation compounds on the absorption spectra of DNA[25] and the photoinduced dynamics in DNA-protected silver emitters.[26] All of these problems are, at present, out of reach of ab-initio treatments.

The methodology employed to study electronic properties applied in this work has been widely described[16,17,23] and is based on the time propagation of the one electron density matrix under the influence of external time-varying electric fields within a time dependent density functional tight binding model. The electronic dynamics is fully described taking into account the influence of the external field to all orders. Dynamical observables that are shown in this work stem from the dynamics of the whole single particle density matrix evolving in the external field, allowing for arbitrary mixing of excited states. This methodology allows to obtain optical information of the system both within and outside the linear response regime. The electronic structure is obtained from a density functional theory based tight-binding (DFTB) Hamiltonian.[27] The DFTB+ code,[28] which implements self-consistent DFTB, was used to model the electronic structure of the cluster system in its ground state, using the mio 1.1 DFTB parameter set.[28,29] As described in a previous report[26] the standard mio 1.1 parameter set was extended to include Ag by running the required DFT calculations for the generation of the matrix elements with all the rest of the mio set atoms setting all parameters (compression radii, basis set, etc.) as used in the generation of the mio set. The new electronic parameters between Ag and all other elements in the mio set are therefore fully consistent. These parameters are available from the authors upon request. Parameters for Ag were obtained from PBE calculations, with the zeroth order regular approximation employed, and DFTB compression radii of $r_{dens} = 14$ Å for the density and $r_{wf} = 3.75$ Å for the wavefunction. Optical absorption spectra are obtained by introducing an initial perturbation in the shape of a Dirac delta pulse to the initial ground-state density matrix.[16] After pulse application, the evolution of the density matrix can be calculated by time integration of its equation of motion. Within the linear response regime the absorption spectrum can be obtained from deconvolution of the dipole moment signal from the excitation waveform after a

Fourier transform. In order to gain insight into the nature of the electronic transitions that are observed in the spectrum, a perturbation consisting in a sinusoidal time-dependent electric field is tuned with the absorption maximum of the band of interest with the polarization direction of the field chosen to match the transition dipole moment vector direction at that energy (obtained from diagonalization of the energy dependent polarizability tensor). Under this irradiation conditions, the population of each state (i.e. the ones that are populated and the ones that are being depopulated due to irradiation) can be straightforwardly obtained from the density matrix as a function of time, as well as the charge of each atom in the system. The details of the procedure employed have been described elsewhere.[17,22,23]
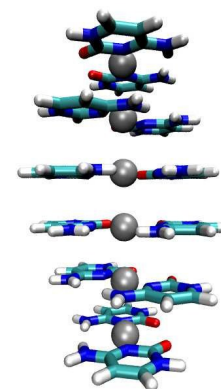
Fig. 1 Reductionist approach of the $(dpC_6)_2Ag_6$ cluster. The geometry was obtained by the replication of the (C_2Ag) pairing, holding up the structural parameters of a B-DNA double helix. The replication index is 6, giving rise to the $((C_2Ag)_6)$ structure

For the described purpose, and taking into account recent results that characterize the structure of DNA-protected silver emitters, before and after chemical reduction, as rods generated between and along the DNA strands,[14,30–32] a reductionist approach of complexes composed by a double strand of 6 deoxypolycytosine bases and a six silver atoms rod was employed $((dpC_6)_2Ag_6)$. This model structure was obtained by the replication of the cisoid Cytosine-Ag-Cytosine (C_2Ag) pairing (the effect of the cisoid/transoid isomerism is addressed at the end of this report) following as a template the structural parameters of DNA, namely base to base distance and base pair rotation. Figure 1 presents the $((C_2Ag)_6)$ structure obtained after six replications of the C-Ag$^+$-C pairing.

The election of size and binding motif of the model system, together with its limitations, are addressed on the following points: 1) Recently, in an outstanding publication, Copp et al.[15] found that DNA-protected silver emitters present magic numbers of neutral Ag atoms, which are related in turn to magic colors on the fluorescent emission of these fluorophores. The magic numbers of neutral atoms found in the aforementioned publication are 4 and 6. These structures fluoresce around 540 nm and 630 nm respectively. Interestingly, the structure of the emitters is also accompanied by a non magical number of Ag$^+$ ions. 2) Schultz et al.[14] and Copp et al.[15] studied the fluorescence response of

purified DNA-protected silver emitters with different number of silver atoms and charges. The results published in these works confirm the fact that completely ionic systems do not fluoresce, and the complex containing six Ag^+ is the biggest completely ionic system studied. In our opinion, these two considerations justify the choice of 6 Ag/Ag+ atoms in the structure in order to assess the effect of total charge on the fluorescence response of DNA-protected silver emitters. 3) Regarding the number of cytosine molecules employed, it is well known that silver ions bind to adenine (A), cytosine (C) and guanine (G).[14,33] Recently Swasey et al.[34] studied the specific interaction of Ag^+ with different size A, C, G and thymine (T) strands. In the case of C_6 strands, they found that both single strand (with 3 Ag^+ ions) and double strand (with 6 Ag^+ ions) complexes were obtained. Therefore, choosing 12 cytosine molecules for the model is a reasonable assumption. Furthermore the binding motif of the $[C_2Ag]^+$ dimer has been studied in the aforementioned publication,[34] in other liquid phase experiments,[35–37] and by mean of mass spectrometry coupled to infrared spectroscopy experiments in gas phase.[38] All this reports agree on the fact that Ag^+ binds together two cytosine molecules, resulting in the C-Ag^+-C pairing where the cation is placed between the N3s of both bases. In this context, the cisoid/transoid base pair motif employed here are plausible model structures based on the experimental and theoretical information available. 4) It is important to highlight that, despite the experimental and theoretical information described in the above paragraph, there is not yet any definitive structural characterization of DNA-silver fluorophores. Therefore, the authors cannot rule out the existence of structures with different coordination number, which would lead of course to different amount of cytosine molecules involved in the model structure. However, the absence of experimental structural information in this regard constitutes a major drawback towards the extension of the model to include more binding motifs. 5) Readers have to be aware that electron removal might induce rearrangements in the binding motif between DNA and Ag/Ag^+ and in the overall structure of the complexes, spanning from different coordination of the cations to different metal-metal arrangements. Thus, the lack of detailed charge dependent structural characterization of this systems is a major drawback in order to account for structural rearrangements in our model, so we make no conjectures here about the effect that it might have in the photophysical properties of these systems.

On our previous publication on DNA-protected silver emitters[26] this model structure and a more complete one, containing the sugar-phosphate backbone and thermal noise, were successfully employed to calculate the absorption spectra and the photodynamics triggered after light absorption. In the aforementioned report, we describe a photoinduced charge transfer process from the DNA bases to the silver wire, that may constitute the underlying mechanism to explain the common fluorescence obtained when the UV and the visible bands are irradiated. Moreover, in that report we pointed out that neither the presence of the backbone nor the structural disorder of the system quantitatively modifies the main photodynamical features observed.

As a first step, the effect of charge on the electronic structure

of the model system was explored. For this purpose the density of states (DOS) was computed varying the total charge of the system from zero to six (only even charges were studied in order to maintain singlet multiplicity given that, in its present form, the code employed for the quantum dynamical simulations does not include spin polarization). The results obtained for all states of charge considered are presented in Figure S1 and, for clarity, Figure 2a and 2b show in black lines the DOS of the neutral cluster and the completely charged complex, respectively. Moreover, in the same figure, the projected density of states (PDOS) over atoms that form the DNA and Ag moieties are shown in red and blue lines.

The electronic structure of this system and its effect on the photodynamical properties of $((C_2Ag)_6)$ was extensively discussed in our previous report.[26] Briefly, four feature zones can be distinguished in the DOS (depicted in Figure 2a with dashed lines and roman numerals). The first one (I) consists of a manifold of states mainly arising from a large contribution of states coming from the DNA moiety with an almost negligible contribution of the Ag moiety. The second feature zone (II) consists of a broad manifold where a significant mixture of states from DNA and Ag occurs. The third feature zone (III) occurs near the Fermi energy and consists in a series of four narrow groups of states, three of which fall at slightly lower energies than the Fermi level, and a fourth one, above it. One important characteristic to highlight about zone (III) is that states within this zone, which include the HOMO and LUMO orbitals of the structure, are well separated in energy from the other manifolds. In the fourth feature zone (IV), several manifolds of states occur, and an alternation in the preponderance of the contribution between DNA and silver moiety states can be observed. Figure S1 shows that as the charge of the complex increases from 0 to 4, a gradual shift of the manifolds of states to higher energies can be observed, but there are no major modifications of the described characteristic features of the DOS of the neutral cluster.[26] This rigid electronic structure shift implies that charging the system consists mostly on the depopulation of otherwise occupied states and to a lesser extent in an expansion of the energy range these states span. Nevertheless, abrupt changes in the electronic structure are observed when the charge of the system reaches the same value as the number of silver atoms present. This modifications can be clearly observed in Figure 2a and 2b among which we can point out three important differences. First, a new manifold of states is observed for $((C_2Ag)_6^{+6})$ at the Fermi energy, caused by the close proximity of occupied states from DNA moiety and unoccupied s states from Ag moiety. Secondly, the contribution of unoccupied states from the DNA moiety appears ~2 eV higher in energy for the ionic complex. And thirdly, the overlap between DNA states and the d states from Ag ions decreases considerably and spans over a wider energy region, just one sharp overlap region between this two moieties remains present at ~ -1.3 eV. This is a clear manifestation of a change in the bonding features between the two moieties upon chemical reduction. Figure S2 presents the charge density difference with respect the neutral cluster for all states of charge. It can be clearly seen that as the total charge of the system increases, the positive charge density is delocalized along
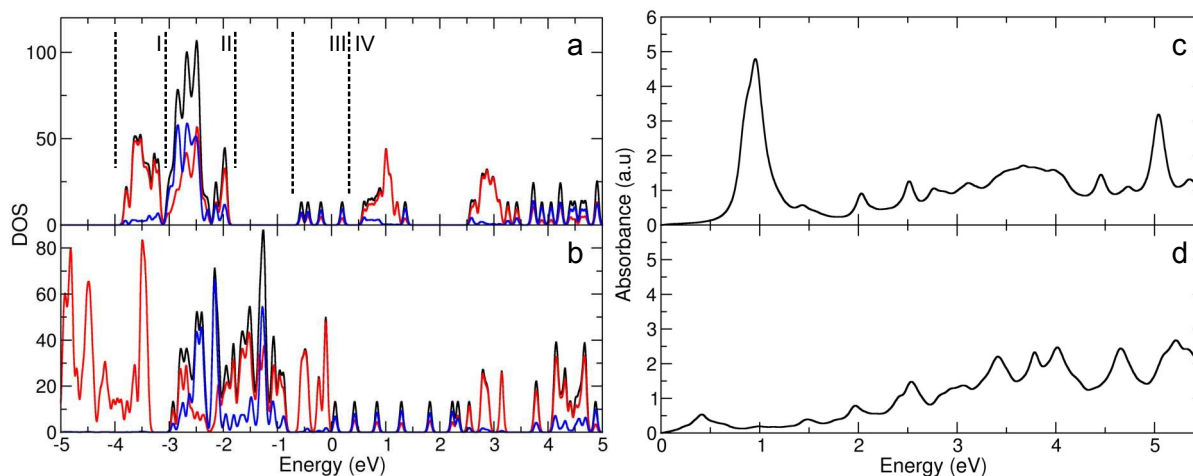
Fig. 2 (**a** and **b**) Black lines show the obtained DOS for $((C_2Ag)_6)$ and $((C_2Ag)_6^{+6})$ respectively. Furthermore, the PDOS of the DNA and Ag atoms are shown in red and blue lines. (**c** and **d**) Show the obtained absorption spectra for $((C_2Ag)_6)$ and $((C_2Ag)_6^{+6})$ respectively.

the silver wire, with strongest charging occurring at the ends, as can be expected from purely electrostatic considerations. Charging of the wire causes a polarization of the cytosine molecules, with a negative compensating charge localized mainly over the Nitrogen atoms involved in the Ag-N interaction. This evolution of the difference of total charge density reveals a gradual shift of the silver-cytosine interaction from a "covalent character" to an "electrostatic character", and explains the change from a localized bonds picture to a de-localized and non-specific interaction as observed in the DOSs shown in Figures 2a and 2b.

In order to asses the effect of the above described modifications in the electronic landscape on the photophysics of $((C_2Ag)_6)$, the absorption spectra as function of charge was simulated. Figure S3 presents the simulated spectra for all states of charge considered in this work and Figures 2c and 2d, the obtained spectra for the neutral cluster and completely ionic complex, respectively. As was described elsewhere[26] the absorption spectra obtained for the neutral cluster (Figure 2c) presents a reasonable correlation with what is expected from existing experimental and theoretical reports,[8,12,14,31] regarding the presence of a band in the UV region at almost the same energy than the UV absorption of isolated cytosine and cytosine strands ($\sim$4.6 eV),[10] as well as the presence of a new low lying sharp absorption band ($\sim$1 eV) related with the longitudinal plasmon like excitation of the silver rod,[14,30] in agreement with TD-DFT based reports.[32,39] As can be seen from Figure S3, and Figure 2c and 2d, as the state of charge of the system increases, the principal features described for the neutral cluster stand. In accordance with previous reports based on TDDFT calculations of naked silver wires absorption spectra,[39] a gradual red shift of the longitudinal plasmonic band is observed as the total charge grows. When the charge reaches +6, the absorption spectrum presents several differences compared to the corresponding spectra of the neutral cluster. The main one being the sharp decrease of the absorption intensity of the longitudinal plasmonic band as the charge of the system increases, in accordance with the disappearance of the longitudinal resonance of

isolated silver wires.

In order to gain insight on the photodynamics triggered after light absorption, electron dynamics simulations were carried out as this methodology has proved to provide a deep understanding of the electronic excitation through the calculation of relevant time dependent properties like molecular orbital population and time dependent charges.[16,17,19,21–23,26] A sinusoidal time-dependent electric field, tuned with the absorption maximum in the UV region of both $((C_2Ag)_6)$ and $((C_2Ag)_6^{+6})$ was applied. The polarization direction of the field was chosen to match the transition dipole moment vector for each cluster at the absorption maximum. In order to provide a meaningful representation of the obtained results, the evolution of the molecular orbital population during light irradiation (with reference to the ground state population) is presented in a 2D representation as function of time and the energy of each eigenstate. In this 2D representation, (hereafter called "*DynPop*" from "dynamical population") the color map represents the change (increase or decrease) of each state's population as a function of time, compared with the corresponding population of the unperturbed ground state.

For the neutral cluster $((C_2Ag)_6)$ the obtained "*DynPop*" irradiating at 5.1 eV (Figure 3) confirms one of the central conclusions of our previous publication[26], regarding the relationship between the electronic structure and the photophysical properties of this system. Briefly, as can be observed, depopulated states correspond to states from feature zone (I) with a major contribution of DNA states. The populated states are located in feature zone (IV). It can be observed that isolated Ag "spectator" states in region (III) are clearly separated in energy and electronically decoupled from, groups (I), where electrons are promoted from, and group (IV), where electrons are promoted to. These states provide a "gap" akin to that in semiconducting quantum dots, and might be the key to explain the cause for fluorescence in these systems.

Unlike the neutral cluster, for the completely ionic system $((C_2Ag)_6^{+6})$ the "*DynPop*" (Figure 4) obtained when the system is irradiated at 4.6 eV shows that at the beginning of the simu-
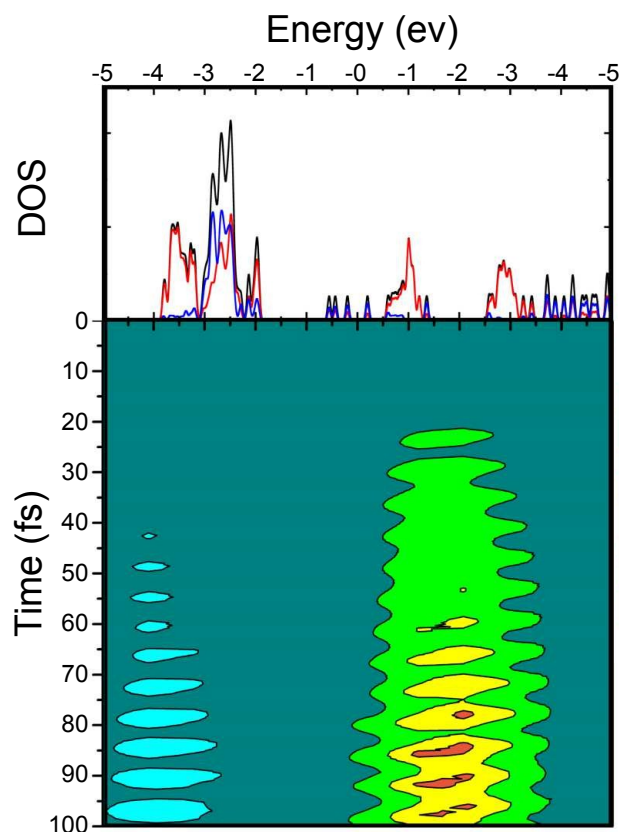
Fig. 3 Evolution of the molecular orbital population during light irradiation at 5.1 eV (with respect to the ground state population) as function of time and the energy of each eigenstate ("*DynPop*") for $((C_2Ag)_6)$. The color map represents the change (increase or decrease) of each state's population as a function of time, compared with the corresponding population of the unperturbed ground state. In order to aid interpretation of the result, the "*DynPop*" is plotted next to the DOS.
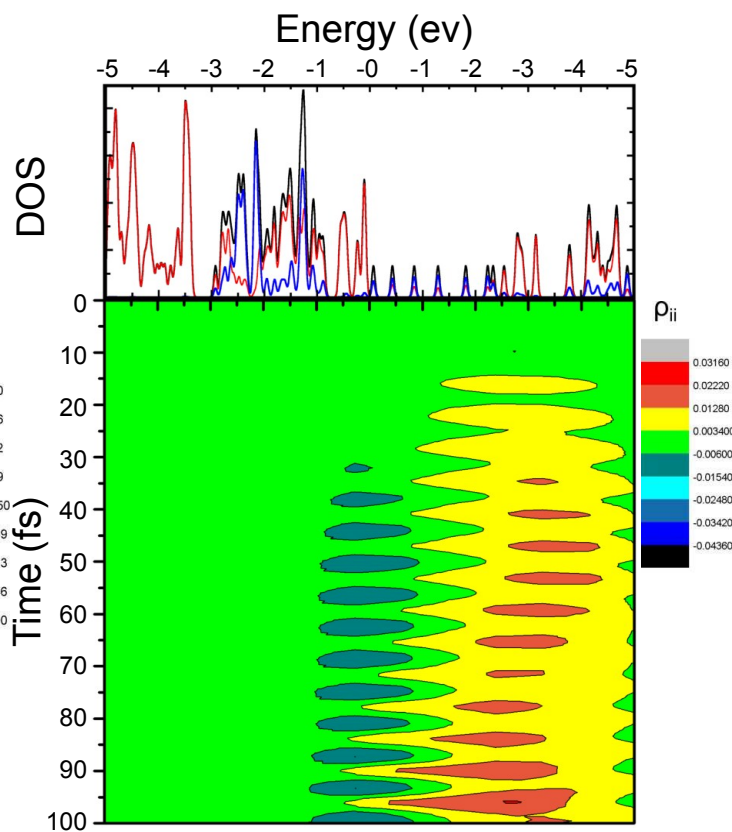
Fig. 4 Evolution of the molecular orbital population during light irradiation at 4.6 eV (with respect to the ground state population) as function of time and the energy of each eigenstate ("*DynPop*") for $((C_2Ag)_6^{+6})$. The color map represents the change (increase or decrease) of each state's population as a function of time, compared with the corresponding population of the unperturbed ground state. In order to aid interpretation of the result, the "*DynPop*" is plotted next to the DOS.

lation the populated states fall ~ 3.5 eV above the Fermi energy, but the wavepacket evolution leads to the population of low lying s states coming from Ag atoms. After an few tens of femtoseconds the "*DynPop*" plot shows that populated and depopulated states span over a wide energy region and fall just above and below the Fermi energy without any "gap" between them that can enable electronic decoupling. In light of the comparison between the "*DynPop*" plots shown in Figures 3 and 4, our proposal is that the abrupt electronic structure modifications that occur when the total charge of the system reaches the number of silver atoms (mainly the absence of states from feature zone (III) in $((C_2Ag)_6^{+6})$) substantially modifies the wavepacket evolution leading to gapless and coupled populated and depopulated manifold of states. The rise of state manifold (III) above the Fermi energy is the basis of the mechanistic pathway that causes the ultrafast quenching that precludes completely ionic complexes to fluoresce.

Furthermore, recent reports strongly suggest that in this kind of systems, DNA base paring does not conserve the standard antiparallel orientation, but instead interacts in a parallel motif, enabling a transoid interaction in the (C_2Ag) pair. This interaction motif enhances the base pair stabilization trough the formation

of hydrogen bonds.[34,37,38,40,41] Therefore, the same study presented here was reproduced for the $((C_2Ag)_6)$ structure generated with a transoid geometry. Figure S4 present the comparison of the DOS, absorption spectrum and "*DynPop*" of the neutral and completely ionic transoid $((C_2Ag)_6)$. As can be observed, and in a similar way to the results presented in Ref 26, the photodynamical properties described above are qualitatively preserved beyond the cisoid/transoid isomerism.

Within the present report we have addressed the charge dependent switching between dark and bright states in DNA-protected silver emitters, based on the simulation of electronic dynamics under UV irradiation form a model system $((C_2Ag)_6)$. Particularly, focus was made on the absence of fluorescence from completely ionic DNA-protected silver complexes. The main result points to the fact that, as the charge of the cluster increases, a gradual change in the nature of the bonding from a "covalent" to "iondipole" occurs between cytosine and silver. This strong change of the of the bonding nature explains the electronic structure modifications that are observed when the total charge of the system reaches the number of silver atoms. Mainly, the absence of decoupled states close to the Fermi energy, observed for the other states of charge. This changes in the electronic landscape substan-

tially modifies the wavepacket evolution upon excitation leading to gapless and close lying populated and depopulated manifolds of states. Our proposal is that the rise of state manifold (III) above the Fermi energy is the basis of the mechanistic pathway that causes the ultrafast quenching that precludes the completely ionic clusters to fluoresce. Moreover, the new results on the dynamical evolution following the excitation in the UV band for charged clusters, which clearly show overlapping energies between hole and electron wave-packets we believe strengthens the thesis presented in [26] on the fact that the pseudo-gap present in the neutral or partially reduced systems can be the explanation for the fluorescent nature of these systems.

acknowledgements

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