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Excitation Spectra Argue for Threadlike Shape of DNA-Stabilized Silver Fluorescent Clusters

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Ⓢ Supporting Information

ABSTRACT: We calculate geometry and electronic excitation spectra of silver clusters containing 1−6 atoms bound to single DNA bases and also to dC_3 cytosine oligomer using density functional theory method. We show that planar shaped silver clusters complexed with the bases exhibit nearly forbidden the lowest transitions and weak fluorescence ability. Their calculated spectra do not appear to match experimentally observed fluorescence excitation spectra of silver clusters on DNA and other polymers. On the contrary, threadlike-shaped silver clusters reveal intense the lowest transition, energy of which depends on the chain bend. We show the equilibrium structures of Ag_3^+ cluster stabilized by oxygen atoms on phosphates and in the minor groove of dC_3 oligomer. The calculated excitation spectrum of Ag_3^+ cluster in the minor groove appears to be close to the experimental spectrum of green emitting clusters on cytosine oligomers.
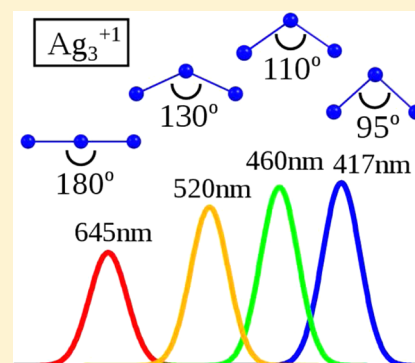
INTRODUCTION

Fluorescent noble metal nanoclusters (NCs) containing up to tens of metal atoms have been paid more and more attention as a special class of nanoobjects. Their electronic states may be treated as discrete energy levels leading to essentially different optical, electrical, and chemical properties from nanoparticles.[1] Different methods are used for the fabrication of fluorescent NCs in the presence of polymers as stabilizing agents.[2−6] In particular, DNA is most widely used in the synthesis of fluorescent silver nanoclusters (AgNCs) due to potential biocompatibility and high brightness of the AgNCs obtained. A series of DNA-based AgNCs with fluorescence from visible to near-infrared region have been synthesized.[7−12]

Despite the huge progress made over the past years in synthetic development of silver-based fluorescent clusters, an understanding of the structural origins of their emission properties tuning by modifications in DNA sequences remains elusive. Achieving a better understanding of the molecular level of the cluster−polymer interactions is critical for further development of DNA-based silver nanoclusters as fluorescent probes. In this respect, the data on the DNA binding sites as well as on the cluster sizes seem essential. K-edge EXAFS analysis evidently shows the presence of Ag_N/O ligations to DNA.[13] ESI mass spectra give the amount of silver atoms of about ten on oligonucleotides.[14] They also reveal a partial positive charge of fluorescent clusters.[14] It should be noted, however, that mass spectroscopy gives the overall mass and charge of clusters on one oligonucleotide. As the number of clusters per DNA molecule is not known, the size and the charge of one cluster may be overestimated.

A very few theoretical studies were concerned with the electronically excited states of Ag−DNA complexes. The time-dependent density functional theory (TD DFT) has been exploited to examine the complexes of few-atom neutral Ag clusters with DNA bases and their absorption spectra.[15] The calculations showed the presence of absorption bands at energies well below those of the isolated components in some cases.[15] Low-energy transitions of some complexes of clusters with cytosine showed a significant charge separation. Unfortunately, calculated absorption spectra do not seem to be close to the ones observed in various experimental studies of fluorescent Ag−DNA complexes. Generally, charge transfer transitions strongly affect by relative displacement of electronic levels of free components. In this respect, accuracy of calculations strictly depends on the computational model used in the TD DFT method. Another difficulty is that neither exact structure nor the charge is known in the case of Ag−DNA complexes. At present no calculations have been done for partially charged clusters. However, recent experimental data[14] clearly indicate significant positive charge on clusters. No calculations of the fluorescent states of the clusters have been performed so far. In the meantime, excited state dynamics determines the fluorescence spectra. Stokes shifts observed for Ag−DNA complexes appear to be significant,[7−12] suggesting a significant nuclear relaxation of the excited complexes. As it has been supposed,[16] large Stokes shifts might also be explained by a change in solvation shell due to significant change in dipole moment in excited state.

Luminescence properties of Ag−DNA complexes are known to depend strongly on the base sequence. In fact, only special sequences in oligonucleotides provide formation of the fluorescent clusters.[8] It seems that local geometry of binding

sites on polymer provides a structure necessary to form fluorescent clusters. The nature of the lowest transitions in Ag−DNA complexes is in fact a key point in determining the fluorescent ability of the clusters because molecules are known to emit from their lowest electronic states according to Kasha's rule.[17]

The present study is aimed to address the following question: which shape of Ag clusters bound to single base or DNA strand would adequately reflect the main spectral features of Ag−DNA complexes such as high fluorescence quantum yield, high absorption cross section of the lowest transition, large Stokes shift, and high tunability of emission. Our calculations focus on neutral as well as charged Ag−DNA base complexes containing up to six Ag atoms. We performed DFT (density functional theory) optimization of the geometry of the cluster complexes with single bases as well as with DNA sugar−phosphate backbone and with carboxyl groups in DNA minor groove and then calculated their absorption transitions by the TD DFT method. We also analyze luminescent states of Ag−DNA complexes, i.e., the evolution from Franck−Condon state to nuclear optimized. Comparison of the calculated spectra of clusters of different shape with the fluorescence excitation spectra reported in the literature and analysis of the nature and oscillator strengths of the lowest transitions allow us to conclude that fluorescent clusters most likely possess threadlike structure stabilized by carboxyl groups on polymer.

■ THEORETICAL METHODS

Ground and excited state geometry optimization calculations for excitation spectra were performed using the DFT[18] approach as implemented in the GAMESS US program.[19] Silver atoms were represented through a LANL2DZ, relativistic effective core potential RECP with 28 inner electrons.[20] The other atoms were represented through a valence double-ζ polarized basis set 6-31g*.[21] For the full ground state geometry optimization we have used rPBE[22] functional. Geometry optimization of the free clusters and cluster−base complexes were performed without any restrictions in a vacuum. In the case of threadlike free clusters, one-dimensional nuclear gradient optimization was performed. We also examined binding of the silver clusters with short DNA oligomer dC$_3$, namely, the binding to sugar−phosphate backbone containing negative charged oxygen atoms and to carboxyl groups in the minor groove. The DNA sequence was constructed by use of X3DNA[23] program, and then Ag−DNA complex in the presence of Na$^+$ counterions was gradually optimized, with B-DNA structure being frozen. In the case of phosphate groups and DNA minor groove as binding sites PCM implicit solvent model was used. In all cases the force matrix was calculated to ensure that the global minimum on potential energy surface was found. The same rPBE functional has been used earlier for calculation of the excitation spectra of planar silver clusters bound to nitrogen bases.[15] In our work, to obtain the excitation spectra for charged and neutral complexes we used TD DFT[24,25] with B3LYP[26] functional and the same basis sets described above. We performed calculations of the excitation energies for singlet excited states of open and closed electronic shells in the case of different atomic sets up to excitation energy of 6 eV. B3LYP functional generally provides good results in calculations of electronic absorption spectra of coinage metals[27,28] and also purine and pyrimidine nucleic bases.[29] Hence, one can expect reasonable results in the calculation of the optical properties of their complexes. Practically, for most

complexes with single DNA bases we observed charge transfer character of low-energy transitions. It is known that B3LYP functional can inadequately predict energy of such transitions.[30] In this case, the use of range-separated CAMB3LYP[31] functional might improve description of such absorption bands. However, a preliminary calculation of the excitation spectra of free DNA bases using CAMB3LYP functional showed significant underestimation of energy of the low-lying transitions. In spite of such underestimation of transition energies in the case of free bases, one might expect that the use of CAMB3LYP functional for cluster−base complexes would provide adequate picture. But we cannot be quite sure as we have no ability to compare the calculation results with the experimental data because of their absence in the case of Ag cluster complexes with single bases. Keeping the above point in mind, we focus on the trend in the spectra rather than absolute values of energies. Optimizations of excited states[32] were further performed with use of CAMB3LYP functional as it provided better analytical gradient convergence in optimization of electronic structures with charge-separated states. For illustration of the structures, orbitals involved in transitions and excitation spectra we used the Chemcraft software.[33] The excitation spectra are convoluted with a Gaussian with a full width at half-maximum of 0.2 eV. Orbitals are represented with a contour value of 0.03.

■ RESULTS AND DISCUSSION

Free Clusters and DNA Bases. First, we checked if the computational approach was adequate to describe the spectra of isolated clusters and DNA bases. In the literature there are numerous investigations of optical properties of nitrogenous bases of DNA involving the different approaches of quantum chemistry.[29,34,35] In present work we performed geometry optimization and calculation of the excitation spectra by DFT method for DNA bases using the basis and the functional that we further used for calculations of the complexes. Our calculations agree well with previous theoretical and experimental spectra. The obtained results are shown in Table S1 in comparison with other studies.

To ensure that the same approach correctly described the clusters, we also calculated optical spectra of free Ag clusters and compared the obtained results with the experimental absorption spectra reported in the literature. Optimization of the silver clusters geometry in the same manner for Ag^0_n and Ag$^+$Ag$^0_{(n-1)}$ structures, where n = 1−6, was performed without any restriction on symmetry. The lowest energy configurations were then chosen to calculate the absorption spectra. Both the charged and neutral optimized silver clusters containing up to six atoms in size appear to possess a planar symmetry that agrees well with previous calculations[27,36,37] (Chart 1).

Further calculations of optical properties were carried out for the optimized structures by the TD DFT method described above. The results of calculations for free planar neutral and charged clusters are presented in Table S2 along with comparison with the experimental absorption spectra.[27,36,37] Comparison of excitation spectra of free planar clusters shows a good agreement with literature data on low-temperature absorption spectra that allows us to use the chosen approach for further calculations of complexes of Ag clusters with DNA.

A special feature of the luminescence excitation spectra of Ag clusters stabilized by polymer matrix reported in the literature[10,14,16] is a strong the lowest energy transition in the visible or near-UV range as well without any other significant

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Chart 1. Optimized Structures of Charged and Neutral Silver Clusters
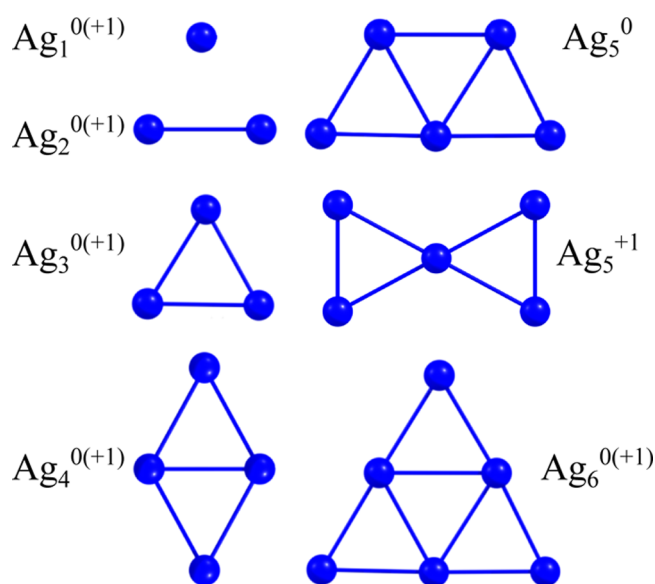
transitions up to far-UV. As for the clusters on DNA, all the fluorescent complexes exhibit a single low-energy band of high intensity along with some weak transitions and also DNA absorption band at about 5 eV.[10,14] Evidently, any relevant structure of cluster must possess that feature in its excitation spectrum. Among the planar clusters, the only structures that might fit that criterion are the series of 1 and 2 silver atoms in the different oxidized states (Figure 1).
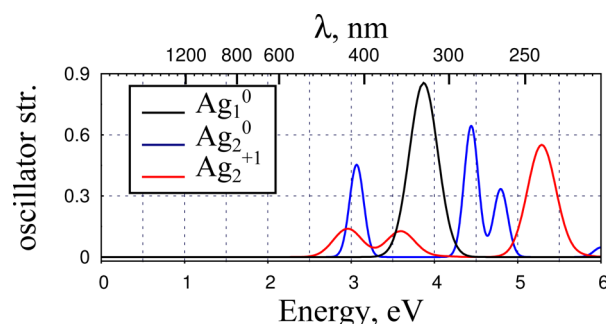
Figure 1. Excitation spectra of Ag_1^0, Ag_2^0, and Ag_2^{+1}.

In this regard we distinguish a group of threadlike-shaped clusters up to eight atoms having an elongated shape, so that each atom is bound to only one or two neighbors. The principal difference between the planar and threadlike clusters lies in their ability to self-formation in free conditions. The formation of elongated forms of clusters necessarily involves several binding sites on polymer in contrast to planar shapes. In such model, positioning of binding sites on polymer chain determine the geometry parameters and absorption spectra of threadlike clusters. We constructed different chains up to eight Ag atoms with imposed constraints on the bending angles. Then we calculated excitation spectra for the optimized threadlike clusters. The spectra for strictly linear chains of silver atoms of different charge are shown in Figure 2. The spectra calculated for one-dimensional chains of the neutral and single-charged clusters agree well with that ones obtained earlier.[38]
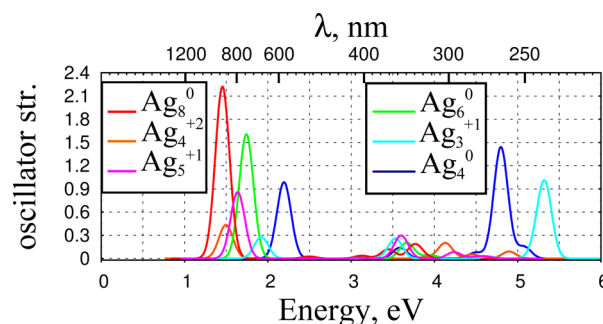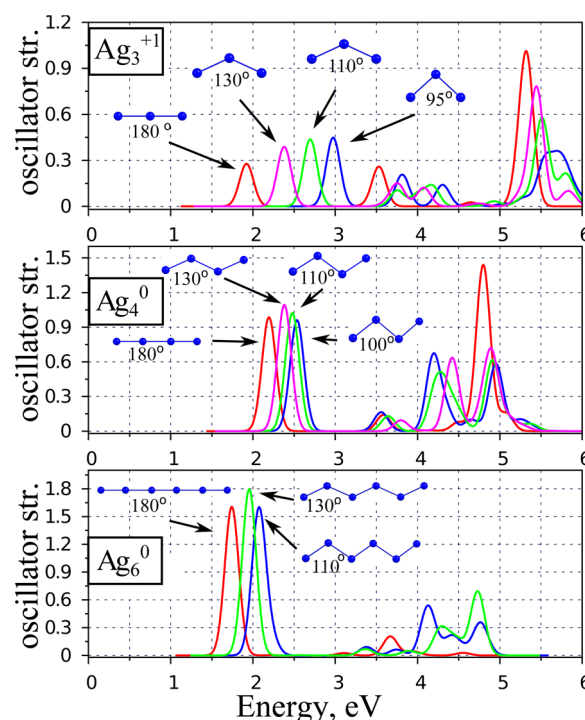

Figure 2. Excitation spectra for threadlike clusters up to eight Ag atoms.

It appears that just by changing the bend angle in the chain of atoms, one can get the different low-energy peaks which cover the entire visible region (∼1.7−3 eV) in the excitation spectra (Figure 3).

Figure 3. Excitation spectra for threadlike Ag_3^{+1}, Ag_4^0, and Ag_6^0 clusters with the different bend angles.

DNA Base−Cluster Complexes. Silver clusters are supposed to bind to the DNA bases and not to the sugar−phosphate backbone[13,15] in a common model. As a first approximation of structural and optical properties of the Ag−DNA complexes, a model of interaction of clusters with nitrogenous bases can be considered. In the present study we treat adenine, guanine, and cytosine composing most sequences of ss-DNA on which fluorescent clusters were synthesized. The mechanism of interaction of the clusters with DNA as well as their structure remains unknown. Generally, N3 atom in the pyrimidine ring of cytosine and N atoms in the purine rings of guanine and adenine are considered to be the most probable binding sites.[9,15] For adenine and guanine, no principal difference between N atoms in the ring was noted.[15] In our first model we consider complexes of planar clusters bound to

N3 atom of cytosine and to N7 atoms of guanine and adenine. The lowest energy configurations of the cluster complexes with single bases were found (Chart S1 illustrates the complexes with adenine as example). The excitation spectra of single Ag atom bound to the bases are shown in Figure 4.
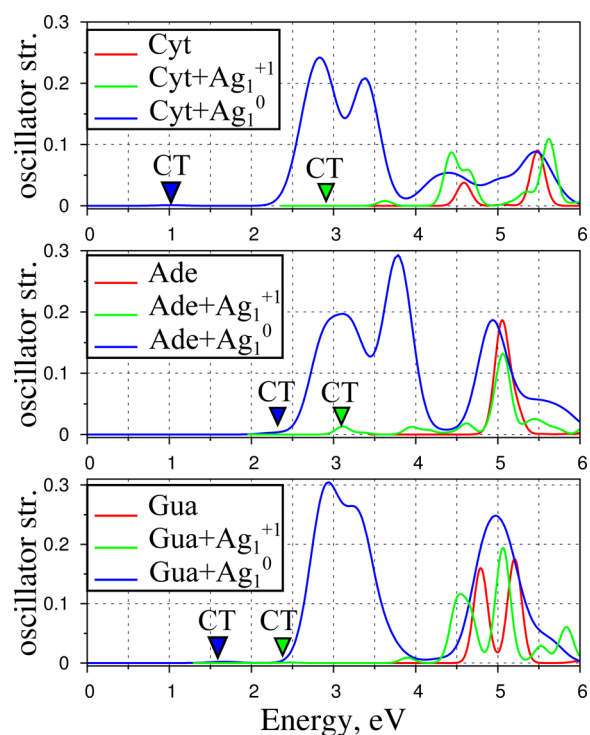

Figure 4. Excitation spectra for Ag_1^0 and Ag_1^{+1} bound to DNA bases. Blue and green triangles indicate the lowest energy transitions having charge-transfer character in the corresponding complexes.

Common features are noticeable for all the bases. In the case of neutral complexes, the maximum of the absorption band of free silver atom at 3.87 eV in the absorption spectra is split into a few red-shifted peaks of lower intensity that lie above 2.5 eV. The lowest energy transitions (marked in Figure 4) corresponding to the transitions between highest occupied molecular orbital (HOMO) or single occupied molecular orbital (SOMO) and lowest unoccupied molecular orbital (LUMO) have nearly zero intensity in all cases. Detailed examination of orbitals involved in this transition can explain its practically forbidden character (Chart 2).

In all cases, the HOMO (SOMO) state is even relative to the base plane, and the LUMO is odd that results in diminishing of transition dipole components parallel to the plane of the base and cluster. In addition, one can see a very little overlap between the orbitals. Complexes of the bases with both neutral and charged Ag atoms exhibit charge transfer character of the lowest energy transitions. The only difference is that an electron transfer in the charged complexes occurs from the bases toward the positive silver ion (Chart 2) contrary to the neutral complexes for which an electron shifts from silver atom to the base (Chart 2). Moreover, we found no strong intensity bands in the spectrum of charged complexes in the visible region.

The excitation spectra of the complexes of Ag_2 cluster with the bases are shown in Figure 5.

Chart 2. Illustration of the HOMO (SOMO)−LUMO Transitions of Ag_1^0 and Ag_1^{+1} Bound to DNA Base
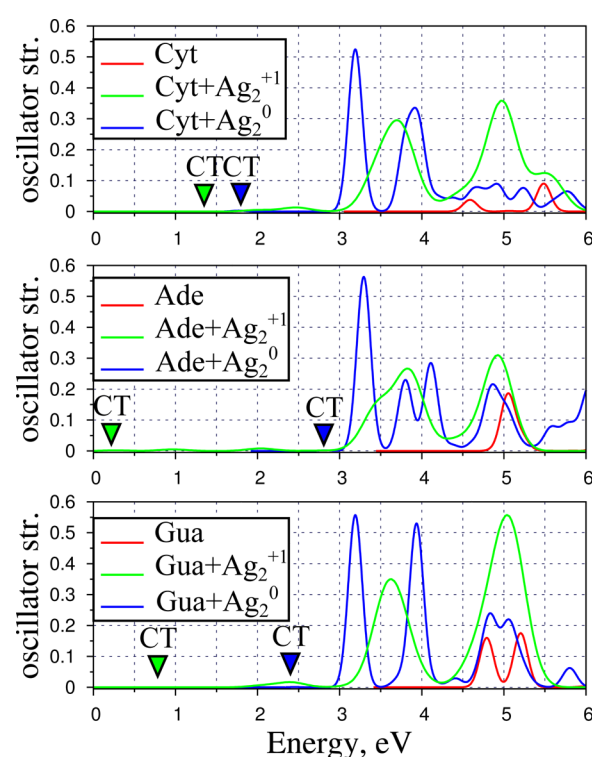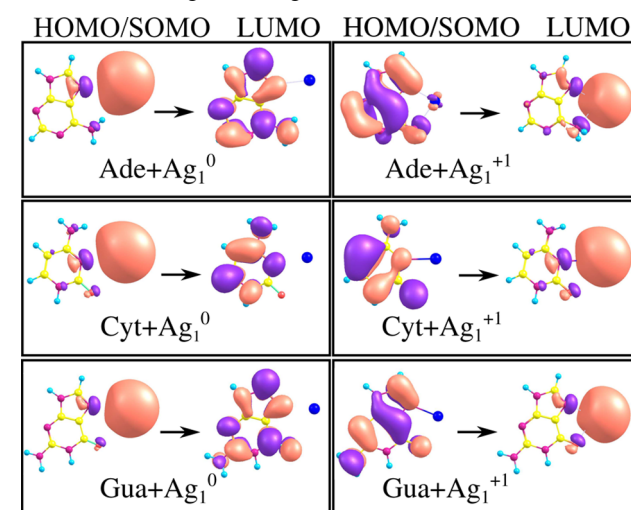

Figure 5. Excitation spectra for Ag_2^0 and Ag_2^{+1} bound to DNA base. Blue and green triangles indicate the lowest energy transitions in the corresponding complexes.

In all cases for the charged and neutral complexes the lowest excited states exhibit charge transfer character with very low oscillator strengths of the corresponding electronic transitions. Like the complexes with a single silver atom, the lowest energy transitions correspond to the charge transfer from neutral Ag_2^0 cluster to DNA bases and from the bases toward the charged Ag_2^+ cluster (Chart 3). For all the neutral clusters, the main peaks of Ag_2^0 around 4.44 and 4.79 eV are greatly diminished in the complexes, although new peaks around 4 eV appear. The peak around 3.07 eV is blue-shifted by roughly 0.15 eV. For all the charged complexes, the peaks of free Ag_2^+ around 2.96 and

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Chart 3. Illustration of the HOMO (SOMO)−LUMO Transitions for Ag_2^0 and Ag_2^{+1} Bound to DNA Base
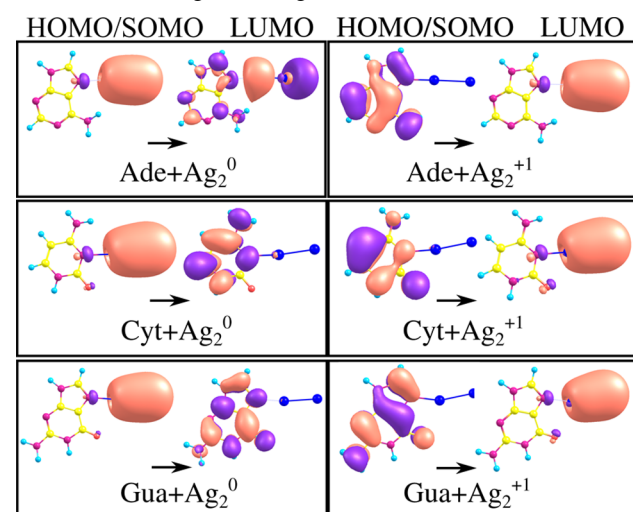
3.59 eV are blue-shifted so that they lie above 3.3 eV in the complexes.

In a previous study,[15] no charge transfer transitions were noted in the complexes of Ag_1 and Ag_2, although they were marked in the larger complexes with cytosine. Such a discrepancy might be connected with the different functionals used in the studies. It should be noted that TD DFT does not always describe well charge transfer transitions. Unfortunately, high level quantum chemistry calculations would be too demanding for the studied complexes.

As noted above, planar forms consisting of more than two silver atoms do not seem to be candidate clusters for fluorescent complexes due to low intensity of the lowest energy transitions. Nevertheless, we calculated the spectra of neutral and charged planar clusters containing 3−6 Ag atoms bound to the bases (Figure S1). With increasing in number of Ag atoms, deviations in main peak positions and their relative intensities in the complexes compared to free clusters tend to diminish. For the complexes of Ag_4−Ag_6 clusters with adenine and guanine, the lowest energy transitions associated with HOMO (SOMO)−LUMO orbitals are localized mostly at the clusters (Chart S2), although, some contribution of the bases is noticeable. In contrast, for cytosine in the same range of Ag atoms there is observed a charge transfer toward the base. Cytosine in all the clusters serves as an acceptor of electron density. In principle, that lies in agreement with the fact that pyrimidine bases possess higher affinity compared to purine ones.[39]

In attempt to estimate the fluorescence Stokes shift for cluster−base complexes, we performed optimization of excited states using CAMB3LYP analytical nuclear gradient code for closed electronic shell structures. According to Kasha's rule,[17] fluorescence is expected to come from the lowest excited state. Hence we focus on the gap associated with HOMO−LUMO energy difference. The relaxed and unrelaxed energy gaps for corresponding orbitals are presented in Table 1.

We take into consideration free neutral silver clusters including 2, 4, and 6 atoms, free charged silver clusters including 3 and 5 atoms, and charged cluster−base complexes with adenine, guanine, and cytosine including 1, 3, and 5 silver atoms. All of these structures have an even amount of electrons that allows us to use analytical nuclear gradients in the context to the singlet excited state. We found that only Ag_3^+ cluster bound to nucleic bases was able to emit. The rest complexes exhibit a zero gap in their relaxed excited state which might be referred to as conical intersection of ground and singlet excited states on the potential energy surface. Such behavior should lead to effective nonradiative internal conversion causing the absence of emission. Moreover, in the case of single Ag^+ we observed conical intersections accompanied by breaking the Ag−N7 bond. The difference between unrelaxed and relaxed gaps varies from 0.3 to 1.3 eV, which is comparable with the magnitudes of Stokes shift observed for clusters on DNA.[10]

In overall, Ag clusters complexed with the bases through N atom ligation exhibit additional low-energy transitions in comparison with the corresponding free clusters. The lowest electronic transitions regardless of their nature (local or charge-transfer character) appear to be weak in comparison with higher transitions in Ag−base complexes. This fact is a key feature of the studied complexes. As the rate of the emission transition is proportional to oscillator strength, it means that all the studied complexes possess relatively low radiative rate, and thus, the contribution of nonradiative transitions to deactivation of excited state increases that might lead to relatively low fluorescence quantum yield. In addition, for some cluster−base complexes, a very effective conical intersection is observed indeed. Thus, the main features of the studied complexes point in fact at their low emitting ability. Therefore, it is not surprising that their calculated excitation spectra do not match the experimentally observed fluorescence excitation spectra of Ag−DNA complexes.

Cluster Complexes with DNA Backbone and DNA Minor Groove. Promising excitation spectra of the threadlike clusters and the unsatisfactory results for planar clusters bound to single DNA bases promoted us to consider other patterns of binding silver atoms to DNA. We examined the binding of threadlike Ag_3^{+1} cluster to oxygens on phosphates and carboxyl

Table 1. Relaxed and Unrelaxed Energy Gaps (in eV) for Singlet Excitation States of the Planar Silver Clusters and the Cluster−Base Complexes

N	Ag_n^0		$Ag^+Ag_{(n-1)}^0$		Ade-$Ag^+Ag_{(n-1)}^0$		Cyt-$Ag^+Ag_{(n-1)}^0$		Gua-$Ag^+Ag_{(n-1)}^0$	
	U^a gap	R^b gap	U^a gap	R^b gap	U^a gap	R^b gap	U^a gap	R^b gap	U^a gap	R^b gap
1	3.594		5.067		4.395	CI	4.176	CI	3.798	CI
2	3.066	2.947	2.958		2.726		2.725		2.654	
3	0.647		4.023	1.897	3.727	2.364	3.729	3.391	3.737	3.352
4	1.123	CI	1.467		1.911		1.918		1.94	
5	1.449		2.687	1.656	2.901	CI	2.666	CI	2.741	CI
6	2.241	CI	0.786		1.538		0.767		1.22	

^{a}Unrelaxed gap. ^{b}Relaxed gap; CI = conical intersection.

groups in the minor groove of dC$_3$ oligonucleotide. It is known that small fluorescent silver clusters of 2−5 Ag atoms in size may be effectively formed on acrylate polymers containing carboxyl groups.[6,16] On the other hand, practically all DNA-stabilized fluorescent clusters are formed on carboxyl-containing cytosine-rich oligonucleotides.[11] These facts encouraged us to treat oxygen atoms as a target for binding of Ag atoms. It should be taken into account that transitions associated with a lone pair of electrons on the oxygens and used to be calculated *ab initio* in vacuum[40,41] can exhibit strong solvatochromism. Therefore, we used PCM solvation model[42] to correct spectra for solvent effects.

Chart 4 shows equilibrated structures with corresponding HOMO−LUMO transitions for Ag$_3^{+1}$ cluster bound to sugar−

Chart 4. Structure of Ag$_3^{+1}$ Bound to Sugar−Phosphate Backbone (a) and to Minor Groove (b) of dC$_3$ Oligonucleotide[a]
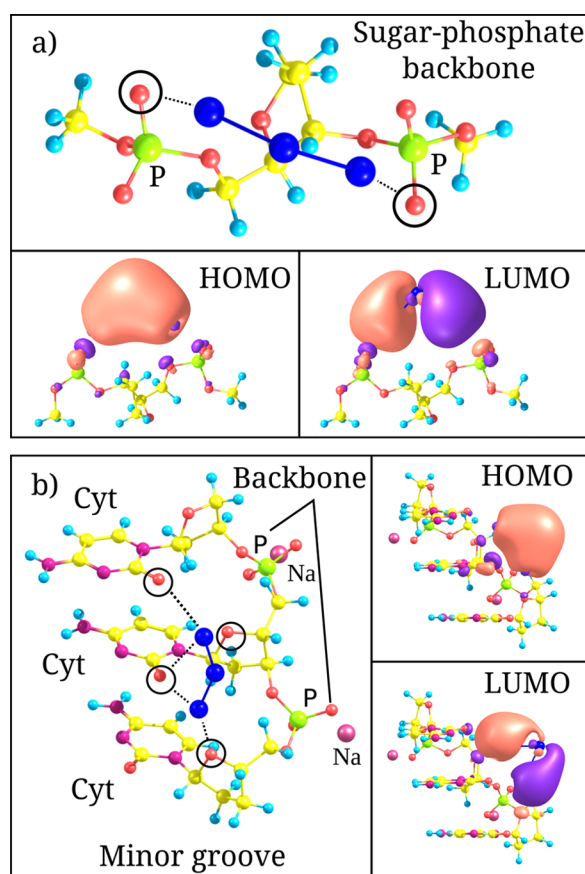
[a]Black circles mark the oxygens stabilizing silver atoms.

phosphate backbone and for the same cluster bound to minor groove of dC$_3$ oligomer. In both cases, it is clearly seen that HOMO−LUMO orbitals are mostly located on the cluster. As a consequence, excitation spectra shown in Figure 6 in both cases exhibit the lowest energy transitions of high intensity. The spectrum of the cluster in minor groove appears to be very close to the excitation spectrum obtained for the clusters synthesized on cytosine containing oligonucleotides emitting near 500 nm.[10]
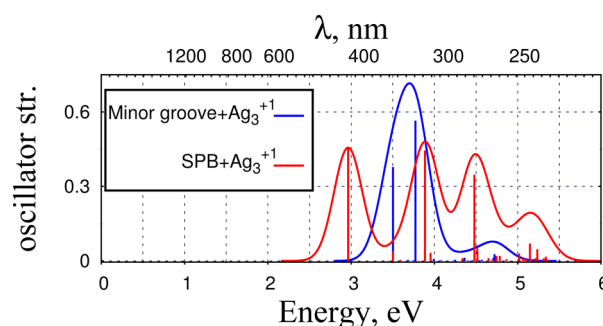

Figure 6. Excitation spectra for Ag$_3^{+1}$ bound to sugar−phosphate backbone (SPB, blue line) and to minor groove of dC$_3$ oligonucleotide (minor groove, red line). The spectra are convoluted with a Gaussian with a fwhm of 0.4 eV, the value observed in experimental spectra.[14]

CONCLUSIONS

This study shows that planar Ag clusters bound to nitrogen atoms of DNA bases possess weak the lowest energy absorption transitions and hence low emitting ability. Their absorption spectra do not match the excitation spectra of the emitting clusters. On the contrary, threadlike-shaped Ag structures exhibit excitation spectra similar to those observed for fluorescent polymer-stabilized Ag clusters. What is more, it appears that a very slight bend in Ag chain causes a strong shift of absorption band. Thus, threadlike Ag structures containing a very few atoms being stabilized by polymer chain may provide large variety of emitting species. Such variety might be provided by a slight change in the local polymer structure which depends on the base sequence in the DNA case. The clusters containing only three Ag atoms may cover all visible range. We show examples of DNA-stabilized structures of threadlike cluster containing three Ag atoms. The excitation spectrum of the cluster in minor groove is very close to the fluorescence excitation spectrum of the green emitting clusters on cytosine-containing oligonucleotides. We hope this result could promote further efforts in finding structures of emitting clusters.

ASSOCIATED CONTENT

S **Supporting Information**

Comparison tables of main peak position in excitation spectra for free nucleic bases and planar silver clusters; results concerning cluster−base complexes and corresponding excitation spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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