# Cooperative Effect in the Electronic Properties of Human Telomere Sequence

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The contribution of sequence elements of human telomere DNA to the interaction of DNA with electrons has been analyzed. By applying wavelength dependent low-energy photoelectron transmission and two-photon photoemission spectroscopy, we investigated the density of states of DNA oligomers with partial sequence elements of the human telomere assembled as monolayers on gold. The findings demonstrate the role of the resonance states in the DNA in accepting electrons and the effect of the sequence on these states. When guanine (G) bases are clustered together, the resonance negative ion state is stabilized, as compared to oligomers containing the same number of G bases but distributed within the sequence. The electron-capturing probability of the human telomere-like oligomer, a sequence with an additional single adenine (A) base adjacent to the G cluster, is dramatically enhanced compared to the other oligomers studied, most likely due to the enhancement of the density of states near the highest occupied molecular orbital.

## Introduction

Telomeres are repetitive DNA sequences found at the end of chromosomes that prevent loss of coding information during chromosome replication.[1,2] Although the exact telomere sequence as well as telomere length vary from one species to another, all telomeres are rich in guanine (G) bases. G bases are special among the natural bases of DNA by having the lowest oxidation potential.[3] It has been proposed that G clustering, found mainly in introns, may serve as a protector of coding sequences by drawing oxidation-induced damage to noncoding regions.[4] Recently we have shown that G bases are special not only by having the lowest oxidation potential among all DNA bases, but also as an excellent electron captor, facilitating transfer of the captured electron to a phosphate on the DNA backbone,[5,6] as was predicted theoretically[7] and observed also by Zheng et al.[8] This interaction of G-rich DNA oligomers with low-energy electrons (LEE) has been directly correlated with DNA damage.[9] In the present work, we investigated whether the unique telomere sequence has special electronic properties that may play a role in protecting chromosomes from damage by LEEs. Specifically we aimed at determining the energetics of anionic electronic states, which may serve as efficient acceptors of low energy or weakly bound electrons. We also discuss the emerging of new cooperative properties of specific sequences. These are not simply the additive properties of the isolated bases but result from the interaction between the bases in the oligomer.

In the past few years, it has been shown that electrons with nearly zero kinetic energy[10] or even electrons that are weakly bound to water molecules[11] (namely have negative energy) can induce dissociative electron attachment (DEA) in DNA. The study performed in water introduced the ability to investigate bound electrons and the biological relevance of these anion resonance states below the vacuum level. In the past, the negative ion states were studied by electron beam and mass spectroscopy methods for relatively small components of the DNA,[12−17] providing information on the low lying unoccupied orbitals and on electron-molecule resonances above the vacuum level. In this process, anion resonance states in the DNA serve as electron acceptors. However, only a few studies provide information on long chains of DNA not in the gas phase, including studies in the condensed phase,[18,19] and on oligonucleotide tetramers.[8,20,21] At present, very little is known about DNA oligomer's negative ion states located just below the vacuum level and almost no information is available on the effect of the DNA sequence on these states.

To address these questions experimentally, we devised an experimental setup that allowed us to investigate the interaction of electrons with DNA oligomers that are self-assembled as a monolayer on a gold substrate. Electrons are ejected from the sample either by a single or two-photon processes and their kinetic energy is determined, after passing through the DNA monolayer (Figure 1). In this setup, the electron's kinetic energy is determined by the work function and by the chosen laser wavelength that ejects the electrons from the sample. The electron capturing probability by the DNA can be determined as a function of the electrons' energy as well as the DNA oligomer's sequence. Using this system we were able to demonstrate that G bases possess the highest electron capturing probability and that the electronic properties of the bases were not affected significantly by the gold substrate since they were independent of the position of G bases relative to the gold substrate.[22]

The DNA within monolayers retains several of its biologically relevant properties as in solution.[23,24] The adsorbed oligomers were found to contain structural water molecules, even when placed in an ultrahigh vacuum chamber.[25] The distance between DNA molecules in a monolayer approaches values that are found within cells, opening up the possibility to study density effects that cannot be addressed in dilute solutions. In addition, the high density of the DNA molecules in the monolayer results in reduced amounts of counterions, as discussed in detail in ref 26. Thus, a monolayer configuration, being very different from the common gas-phase or solution experiments, provides a convenient and interesting strategy to study some aspects of the LEE-DNA interaction and retrieve biologically relevant

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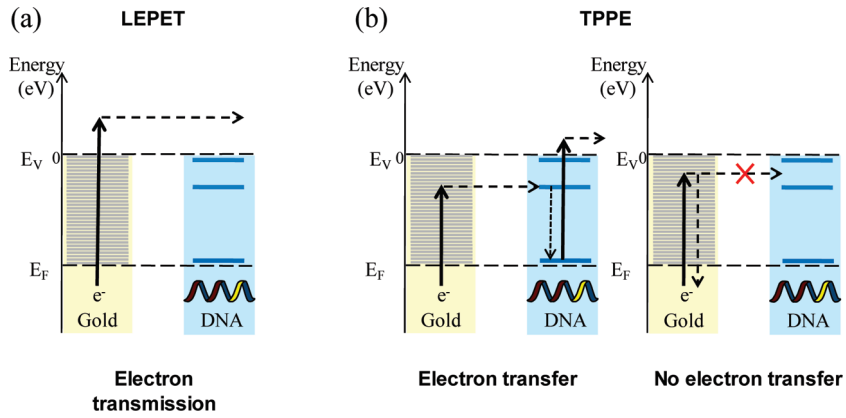


**Figure 1.** (a) A scheme of the LEPET studies. Electrons are ejected with a single photon from below the Fermi of the metal substrate to the vacuum. On the way, they pass through the self-assembled monolayer and some of them are captured by the layer. (b) Scheme of electrons pathway in the TPPE spectroscopy experiment. Electrons are excited in the metal substrate from below the Fermi level to states above the Fermi level and are able to be transferred to the monolayer when a resonance exists between the energy of the electrons excited in the gold by the first photon, and a negative ion state in the DNA. When no negative ion state is in resonance with the energy of the excited electrons, electron transfer is not efficient and electrons relax in the metal back to the Fermi level.

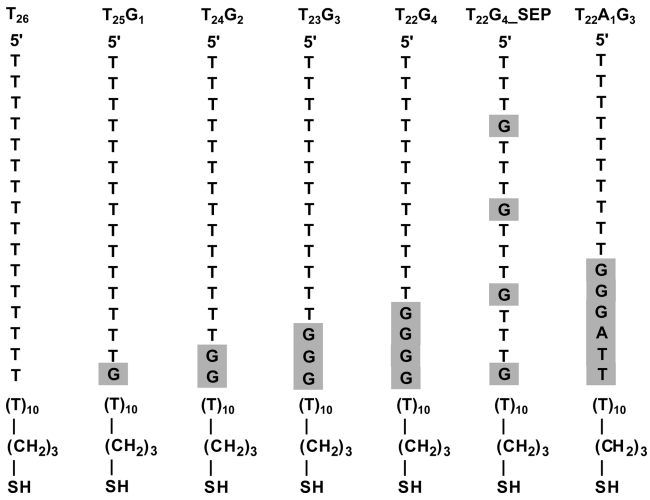


**Figure 2.** The seven oligomers studied. T, G, and A indicates thymine, guanine, and adenine, respectively. For all the DNA strands used, the first ten bases are T and are attached to the gold through a 3′ propyl-thiol group.

information on DNA-electronic states that cannot be probed by other means.

In the present work, we were able to probe the negative ion states located just below the vacuum level and the ionization potentials of different DNA oligomers, having either the human telomere sequence (TTAGGG) or different number of G bases, distributed along the oligomer or clustered together. The results presented here indicate that the human telomere sequence has electronic properties different than closely related sequences. Although the clustering of G bases was found to be an important factor contributing to these special features, the presence of an adenine (A) base in addition to the G bases seems to amplify the effect of the G bases leading to an enhancement of electron capturing. The effect is not simply the additive contribution of each base, but rather a cooperative effect resulting from the interactions among the bases in the sequence.

## Materials and Methods

Seven types of self-assembled DNA monolayers were prepared (Figure 2) according to standard procedures[23,27] by depositing 3′ thiolated 26-mers of DNA (Integrated DNA technologies, Inc.) on a clean gold substrate.[28] All sequences were chosen to contain 10 thymine (T) bases at the 3′ closest to the thiol modified end of the strand, as T was shown to have the weakest interactions with the Au substrate.[29] Radioactive $^{32}$P-labeled DNA oligomers were used to characterize the adsorption quantitatively.[22] For all the ssDNA oligomers, the monolayer density was found to be $N = (1.6 \pm 0.4) \times 10^{13}$ molecules/cm$^2$ (see Supporting Information). This density is in agreement with the expected calculated density of a close-packed monolayer based on the size of the molecules.

The experimental setup is the same as described in ref 5 and is based on ejection of photoelectrons from a gold substrate on which the ssDNA monolayers are adsorbed. In the low-energy photoelectrons transmission (LEPET) studies, the photoelectrons were ejected using a laser that operated at 10 Hz and energy of 50 pJ per pulse. In the case of the two photons photoelectrons (TPPE) studies, the laser pulse energy was kept below 1 $\mu$J. The samples were exposed to the laser beam for a total time of 20 $\mu$s to avoid UV radiation damage. The kinetic energy of the electrons that are emitted from the sample to the vacuum is measured by a time-of-flight spectrometer. Electrons that are not transmitted are captured in the layer and transferred back to the grounded metal substrate. Because of the short lifetime of the captured electrons and the low laser intensity and repetition rate, the monolayer does not get charged by electrons between two laser pulses. This was verified by observing a stable electron energy spectrum that does not vary with time. In all of the studies, the sample was biased by $-1$ V versus the detector.

**The LEPET.** In the LEPET studies (Figure 1a), electrons are ejected by a laser with energy higher than the work function of the sample. The photoelectrons are therefore excited from states below the Fermi level, to above the vacuum level ejected from the substrate and transmitted through the adsorbed film to the vacuum. The transmission properties provide information about the scattering cross section and its dependence on the film's organization, thickness, constituents, and the electrons' kinetic energy.[30] The LEPET signal depends therefore on the density of states of the system below the Fermi level, since it determined the number of excited electrons. The signal also depends on the transmission probability of these electrons through the adsorbed layer. The density of state information can be determined separately from the transmission probability by tuning the excitation laser wavelength as will be discussed in the Results.

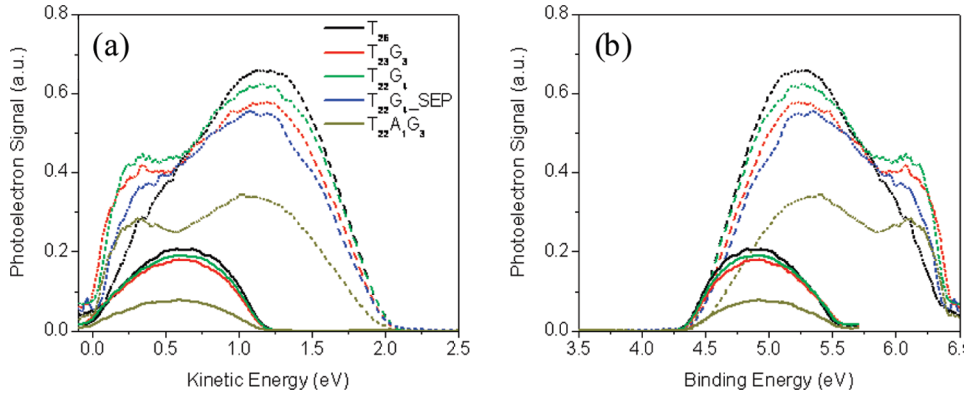


**Figure 3.** LEPET spectra obtained with 6.42 eV photons (dashed lines) and 5.51 eV photons (solid lines). The photoelectrons' signal is presented as a function of either their kinetic (a) or binding energy (b).

**The TPPE.** In TPPE spectroscopy, photons with energy lower than the work function of the system are used. The "pump" photons interact with electrons below the Fermi level in the substrate and excite them to states above the Fermi level. If the lasers used are not very intense and the laser pulse is relatively long, the electrons excited by these first photons can relax either back to states in the substrate below the Fermi level or be transferred through a resonance with a state in the monolayer (Figure 1b) to originally unoccupied negative ion states on the organic film, forming transient ions. The second "probe" laser pulse, having also photons with energy below the work function of the substrate, is able to eject the electrons from these transient ion states on the organic film to above the vacuum level. The measured kinetic energy of these electrons provides information on the binding energy of the electron, namely on the energy of the transient ion states relative to the vacuum level. These ion states are "transient" because they are located above the Fermi level of the system and electrons in these states can relax back to the metal substrate. The intensity of the TPPE signal depends on the transfer probability of electrons from the initially excited substrate to the DNA monolayer and on the lifetime of the transient ion states in the DNA.

In the present setup, we used two photons from the same laser pulse to induce the TPPE process. Because of the relatively long laser pulse (10 ns) and the low intensities, there is no contribution to the signal from a two-photon coherent process. Because of the energy conservation, the kinetic energy of electrons resulting from such a coherent process would be $E = 2h\nu - \Phi$, when $h\nu$ is the photon energy and $\Phi$ is the sample's work function. We obtain no signal at this energy, which means that in the TPPE process, once the electrons are excited by the first photon, they relax to some long-lived state from which they are excited by the second photon. In order for these intermediate states to be long-lived, they must be localized on the monolayer. Hence, the kinetic energy ($E_k$) of the electrons reflects their binding energy in the monolayer so that $E_b = |E_k - h\nu|$ when $h\nu$ is the photon energy.

When the photon energy in the TPPE experiment is varied, the electrons in the substrate are excited to different energies above the Fermi level. The efficiency of the transfer of these electrons to the DNA monolayer depends on the existence of resonance states in the DNA that will act as acceptor states. Hence, by tuning the laser energy we are able to energetically position the DNA negative ion states below the vacuum level. Once the electrons are transferred to the DNA, they relax from the resonance ion state to the lowest unoccupied molecular orbital (LUMO). The electrons in the LUMO are either ejected by the second laser pulse or relax back to the metal substrate.

## Results

We have assembled several homogeneous monolayers of DNA oligomers (Figure 2) on gold substrates. The sequences were chosen to evaluate the contribution of the G bases, their clustering level, and the role of an additional A base on the electron capturing probability. The sequence that includes the A base is a telomere-like sequence. The DNA monolayers were analyzed both by low-energy photoelectron transmission (LEPET) and by two-photon photoemission (TPPE) (see Figure 1 and Materials and Methods).

**LEPET.** Figure 3 shows the LEPET[30] spectra for electrons that are ejected either by 6.42 or 5.51 eV photons from gold-coated DNA oligomers. The spectra can be represented either as a function of the kinetic or initial binding energy of the electrons (Figure 3a,b respectively). The high energy cutoff in the spectra corresponds to electrons near the Fermi level. Their kinetic energy is given by $E_k = h\nu - \Phi$, where $h\nu$ is the photon energy and $\Phi$ is the sample's work function. The low-energy cutoff in Figure 3b directly represents the work function that was found to be $4.3 \pm 0.1$ eV.[31] This value was similar for all oligomers, indicating that the ssDNA are interacting with the gold substrate only through the S−Au bond. The spectra obtained with the 6.42 eV photons, can be qualitatively described as having two characteristic peaks whose maximal kinetic energies are at 1.2 and 0.3 eV (Figure 3a, dashed lines). The peak at 1.2 eV is similar in shape for all ssDNA sequences studied, but its intensity varies. The monolayer consisting of $T_{26}$ showed the highest peak intensity while that made from the $T_{22}A_1G_3$ oligomer (human telomere) had the lowest. In contrast, the peak at 0.3 eV did not appear in the spectra of monolayers consisting of sequences $T_{26}$, $T_{25}G_1$, and $T_{24}G_2$ (see Supporting Information Figure S2) but was present for all sequences containing three G bases or more. The intensity of this peak has clear sequence dependence (Figure 4).

To elucidate the origin of the sequence dependence effects in the LEPET spectra, we must realize that the spectrum, $S(E)$, is a result of two parameters, the electron energy distribution, $P(E_b)$, which reflects the density of states of the system below the Fermi level, and the probability of the excited electrons to be transmitted through the self-assembled monolayer, $T(E)$. As discussed in ref 30

$$S(E) = P(E_b)T(E) \quad (1)$$

where $E$ is the final kinetic energy of the electrons as measured in the setup and $E_b$ is the binding energy of the electrons, namely

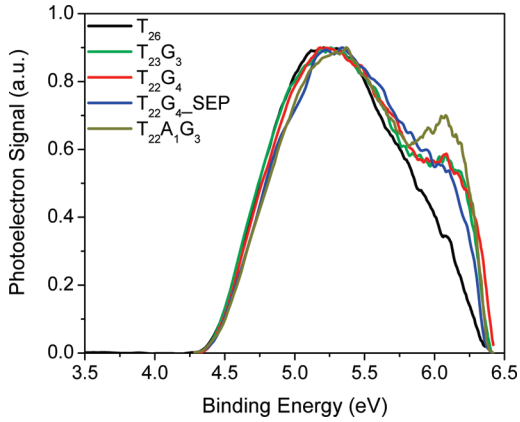


**Figure 4.** The LEPET spectra, obtained with 6.42 eV photons, of each oligomer after normalization to peak at −1 eV below the Fermi energy, which corresponds to the thiol-gold bond. Notice the peak at ∼6.25 eV that results from the HOMO of the oligomers and is the largest for the oligomer containing the human telomere sequence.

the initial state from which they were excited to above the vacuum level. The contribution of each of the two different terms in eq 1, $P(E_b)$ and $T(E)$, can be extracted by comparing the spectra obtained with two different photon energies. The photon with the lower energy ejects only a subpopulation of the electrons (Figure 3a solid lines) that are ejected by the high energy photon (dashed lines Figure 3a). Figure 3a clearly shows that the relative intensities in the spectra corresponding to the different oligomers change dramatically upon a change in the photon energy. For example, $T_{26}$ had the lowest intensity of all sequences at electron energy of 0.3 eV when 6.42 eV photons were used, but when using 5.51 eV photons it had a similar intensity at 0.3 eV as the $T_{23}G_3$ and $T_{22}G_4$ sequences. The fact that the intensities of the 0.3 eV peak vary when using different photon energies indicates that the difference must stem from variation in $P(E_b)$. If the origin of the difference between the spectra of the different oligomers was due to electron transmission through the monolayers, $[T(E)]$, no difference in relative intensities for the different oligomers was expected to be observed upon changing the photon energy. When the LEPET spectra are represented as a function of $E_b$ instead of $E_k$ (Figure 3b), the relative intensities in the spectra are similar when using either 5.51 and 6.42 eV photons, indicating that $P(E_b)$ is the function governing the spectra. By comparing the results obtained using two wavelengths, we realize that the peak at binding energy of 1.2 eV in Figure 3b is a result of the transmission probability, $T(E)$, through the monolayer, and not the effect of the density of states, $P(E_b)$. Hence, in Figure 4 the spectra obtained with the 6.42 eV photon, shown in Figure 3b, were normalized so as to coincide at 1.2 eV. Clearly, a difference in the peak intensity at about 6.25 eV below the vacuum level is evident for the oligomers containing G bases, as compared to the all T oligomer. In the case of the human telomere sequence, this peak is further enhanced. We therefore conclude that the peak at kinetic energies of 0.3 eV in the LEPET spectra (Figure 3a), which refers to a state with a binding energy of about 6.25 eV (Figure 4), corresponds to the ionization potential (IP) of the G bases and that the addition of an A base increases the density of states at this energy. Namely, there is a cooperative effect in the density of states at the highest occupied molecular orbitals (HOMO) and the interaction among the bases in the sequence A-G-G-G plays an important role in defining the electronic structure of the oligomer. This observation is consistent with previous calculations showing that stacking of G bases significantly lowers their IP.[32]

The second peak at kinetic energies of 1.2 eV in the LEPET spectra (Figure 3a) refers to a state located 5.2 eV below the vacuum level, which is ∼0.9 eV below the Fermi level. Previous studies associated a state located at 1.1 eV below the Fermi level to thiols adsorbed on gold.[33] In addition, calculations have shown that chemisorption of thiols can result in the formation of a metal/molecule band close to this energy.[34−36] We therefore suggest that the band seen in the present spectra, which is common to all oligomers studied, stems from their 3′ thiol binding to the gold surface. The intensity of this peak depends on the transmission probability through the ssDNA layer.

Previously, we have shown that the electron capturing probability was linearly dependent on the number of G bases.[5,6] Our current results show a decrease in the peak intensity when adding 3G bases or more, but no dependence on G content was observed for oligomers with less than 3G bases (see Supporting Information Figure S2). This could be because in the present study we investigated a 26mer ssDNA, while in the former 15mer ssDNA were used. Hence, the effect of one or two G bases on the transmission probability through the longer oligomers might be too small to be detected. When conducting the TPPE experiment (see below), which is more sensitive than LEPET, the effect of each additional G on the electron capturing was observed. By adding a single A base to the 3G cluster, the sequence of the human telomere clearly exhibits the highest electron capturing probability relative to all other oligomers studied.

**TPPE.** In general, the TPPE[37−40] signal depends on the transition probability ($k_T$) of the electrons from the metal to the layer and on the lifetime of the electrons residing on the LUMO of the monolayer. This lifetime depends on the relaxation rate ($k_R$) of the electrons back to the metal. Hence, an intense TPPE signal means that either the excited electrons were transferred to the layer very efficiently ($k_T$ is large) or that the lifetime of the electron in the originally unoccupied states (LUMO) was very long ($k_R$ is small), allowing for a large transient population. If the intensity of the TPPE signal varies as a function of photon energy, but the binding energies of the ejected electrons remain the same, then one can conclude that the injection rate, $k_T$, of electrons from the metal substrate to the monolayer varies, indicating a variation in density of states in the adsorbed molecules as a function of energy.

Figure 5a presents the TPPE spectra observed for DNA layers composed of different oligomers applying photon energy of 4.27 eV, which is just below the work function of the samples. The peaks in all of the spectra look very similar for all oligomers. This indicates that the states on the monolayer (LUMO) from which electrons are ejected by the second photons are the same for all oligomers, and hence the binding energies of the electrons to the DNA molecules in the monolayer are sequence independent. Therefore, the electron lifetime and hence $k_R$ are the same for all oligomers, and the relative intensities of the spectra must result from the variation in $k_T$ among the different oligomers. On the basis of Figure 5a, it is then concluded that $k_T$ increases as the number of G bases in the sequence increases and that an addition of an A base to form the human telomere sequence increases $k_T$ dramatically.

This notion is consistent with the significant change in relative intensities of the TPPE spectra upon a change in the photon energy from 4.27 to 4.13 eV (compare Figure 5a,b). At photon energy of 4.27 eV, the $T_{22}G_4$_SEP spectrum had the strongest signal compared to the $T_{23}G_3$ and $T_{22}G_4$ sequences but at photon energy of 4.13 eV, the strongest signal was observed for the

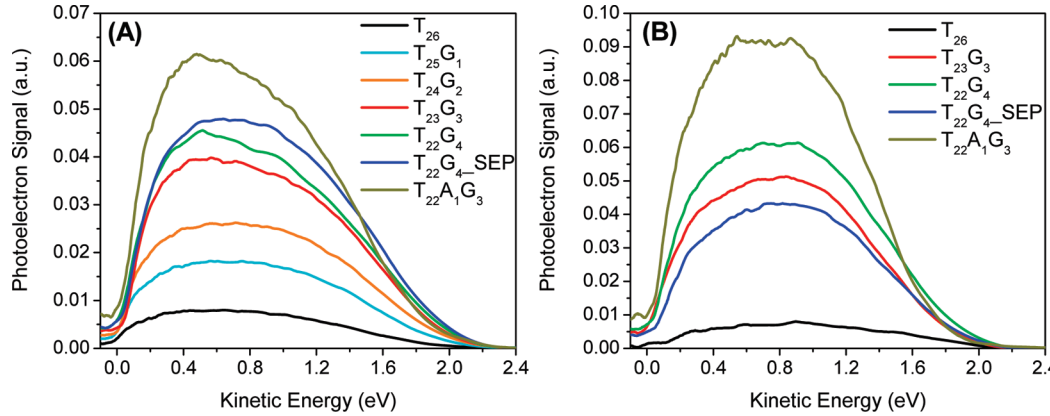


**Figure 5.** TPPE spectra obtained using photons energy of 4.27 eV (A) and 4.13 eV (B).

$T_{22}G_4$ sample. The signal intensity from $T_{22}G_4$_SEP decreased below that of the $T_{23}G_3$ sample.

By changing the photon energy that excites the electrons in the substrate, we were able to probe the energies of the anion states in the DNA. Since, as discussed above, the LUMO is the same for all oligomers, the LUMO lifetime ($k_R$) cannot explain the variations in intensity among the different samples, or the changes in the TPPE spectra intensity as a function of photon energy. Therefore, the variation in relative intensities as a function of wavelength must depend on the probability ($k_T$) of injecting the electrons into the DNA. This electron transfer probability at a given excitation energy is correlated with the presence of negative ion states in the DNA monolayer at the same energy.

Figure 1b depicts the electron transfer process occurring when the gold substrate is excited by a photon with energy below the work function. If there is a negative ion state in the DNA in resonance with the excitation energy, the electron will be transferred efficiently. However, if such a state does not exist the transfer will be slow. The results in Figure 5 indicate that at energy of about 0.17 eV below the vacuum level, the transfer probability, in the case of the $T_{22}G_4$_SEP sample, was lower compared to the transfer probability for $T_{22}G_4$, $T_{23}G_3$. However, at 0.03 eV below the vacuum level there is a negative ion state in the oligomer containing the separate Gs, which does not exist for the clustered Gs. We therefore conclude that when the G bases are clustered the negative ion state is stabilized significantly, by 140 meV, as compared to separated G bases. A similar effect was observed previously when the anion states of ssDNA containing 8-oxo-7,8-dihydroguanosine (8-oxoG) were mapped, showing that the anion state of 8-oxoG was located lower in energy than for nonoxidized G bases.[22]

For all wavelengths and intensities used in the TPPE experiments, no signal was observed for a clean gold substrate. Ensuring that the signal obtained was only due to the presence of the various DNA monolayers absorbed on the gold.

## Discussion

It is known that LEEs are the dominant secondary species created by high-energy photons or particles.[41] Electrons with energy lower than the ionization potential of the DNA have been shown to cause single and double strand breaks[42] by interacting with the DNA via electronic states located above the vacuum level. It was found that electrons with nearly zero kinetic energy[10] or even electrons that are weakly bound to water molecules (namely have negative energy)[11] can induce DEA in DNA. These observations imply that part of the radiation-induced DNA damage that had been attributed to hydroxyl radicals, might be actually caused by electrons.[43] For the low kinetic energy or weakly bound electrons to be effective in the DNA damage process, their energy must be in resonance with negative ion states located on the DNA (see Figure 1b).

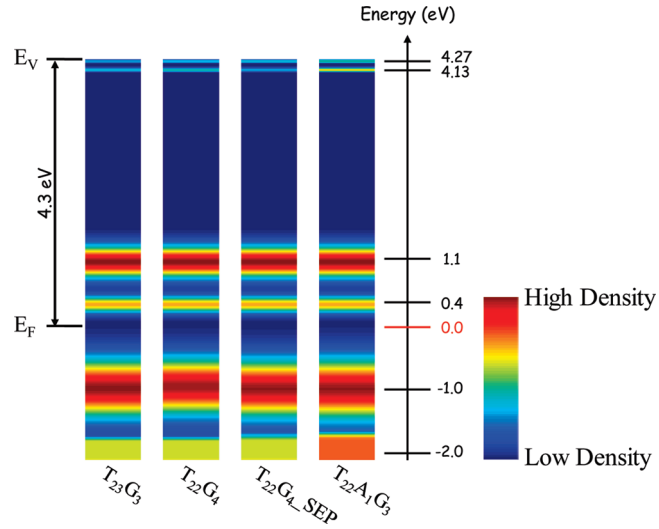


**Figure 6.** A scheme of the relative density of states based on the LEPET and TPPE experiments for four types of monolayers. The high densities near the vacuum energy ($E_V$) correspond to negative ion states and were normalized to the density of states obtained for the $T_{26}$ oligomer.

Figure 6 summarizes schematically the results obtained from the LEPET and the TPPE experiments. Notice the negative ion states, as derived from the TPPE measurements. The intensity scale of these states in the figure refers to the ratio between the electron transition probability from the gold to the DNA for a given sequence as compared to the $T_{26}$ oligomer. The LUMO energy is independent of the oligomer sequence. This finding is consistent with past studies, and strengthens the notion that once captured by the bases, the electrons are transferred to the backbone of the DNA and reside there.[21,44] Figure 6 highlights our conclusion that the TPPE signal for the human telomere sequence (TTAGGG) is the strongest than that of all other oligomers, indicating a higher electron transfer probability, which implies a higher density of anion resonance states.

Two types of cooperative effects were found in the present study. (i) When the G bases are clustered together, the negative ion state is stabilized by 140 meV, as compared to separated G bases. Hence, there is a clear effect of the G-G interaction on the electronic properties of the oligomer. (ii) While in general the ionization potential is reduced with the increasing number

of G bases, we found that the density of states of the HOMO for oligomers containing an A base adjacent to a clusters of three G bases was significantly increased as compared to four G bases either clustered or distributed along the oligomer. The addition of an A base that converts the sequence to that of the human telomere enhanced the effect of G clustering, resulting in a sequence with a special affinity to electrons, either free or weakly bound.

The ionization energy decreases when the T bases are replaced by G bases to ~6.25 eV, as deduced from the LEPET experiments, and was found to be lower than that reported for isolated DNA bases investigated both theoretically[45−47] and experimentally in the gas phase.[48−51] We attribute the low value of the IP to the interaction among the G bases that results in stabilization of the cation states. Indeed the calculations of the IP values show a systematic decrease in IP as the number of interacting G bases increase.[45,52,53]

The human telomere sequence, $T_{22}A_1G_3$, differs from the $T_{22}G_4$ and $T_{23}G_3$ sequences by a single A base. However, this change is enough to enhance both the capturing probability of electrons and the transfer probability of electrons below the vacuum level from the substrate to the DNA. Past work showed that the capturing probability of A by itself is lower than that of G,[5,6] hence the A base by itself cannot explain the large effect observed. It is also not expected that a single A base will change the structure of the oligomer or of the monolayer, since the radioactive characterization of the monolayers indicated clearly that it does not affect the density of molecules on the surface. Therefore, we conclude that the electronic interaction between the A and G bases affects the energetics of the system and hence the capturing probability of electrons. As indicated previously, it seems that when several G bases are clustered together and are interacting with an A base, charge is transferred from the G to the A, making the G slightly positively charged. This is consistent with the G bases having the lowest IP of all bases. As a result of being partially positively charged, the G bases can now capture electrons. Hence, they serve as a door-way for electron capturing. Once electrons are captured on the G bases, they can be transferred to the backbone where they reside and form transient ions.[21]

In summary, the present work dissected the contribution of sequence elements of the human telomere to its negative ion states and to electron capturing. We found that a major feature affecting the telomeres density of states is the high content of G bases and their clustering level. Most importantly, having an A base enhances the effect of G clustering, resulting in a sequence with a special affinity to electrons, either free or weakly bound. It is well-known that the DNA in the cell is tightly packed in a complex 3D architecture. Hence, the telomere may affect the electron capturing of DNA regions that might be very far on the linear genome sequence but in its spatial vicinity. Hence, it is likely that the evolutionary process has selected this specific sequence, containing three clustered Gs with an adjacent A, because of its unique electronic properties, to help maintain chromosomes by directing electron damage to these noncoding regions.

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**Supporting Information Available:** Sample preparation, additional figures, and additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Blackburn, E. H. *Cell* **2001**, *106*, 661–673.
(2) Cech, T. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 34–43.
(3) (a) Steenken, S.; Jovanovic, S. V. *J. Am. Chem. Soc.* **1997**, *119*, 617–618. (b) Milligan, J. R.; Aguilera, J. A.; Ward, J. F. *Int. J. Radiat. Biol.* **2001**, *77*, 1195–1205.
(4) Heller, A. *Faraday Discuss.* **2000**, *116*, 1–13.
(5) Ray, S. G.; Daube, S. S.; Naaman, R. *Proc. Nat. Acad. Sci. U.S.A.* **2005**, *102*, 15–19.
(6) Ray, S. G.; Daube, S. S.; Cohen, H.; Naaman, R. *Isr. J. Chem* **2007**, *47*, 149–159.
(7) (a) Barrios, R.; Skurski, P.; Simons, J. *J. Phys. Chem. B* **2002**, *106*, 7991–7994. (b) Berdys, J.; Skurski, P.; Simons, J. *J. Phys. Chem. B* **2004**, *108*, 5800–5805. (c) Berdys, J.; Anusiexicz, I.; Skurski, P.; Simons, J. *J. Am. Chem. Soc.* **2004**, *126*, 6441–6447.
(8) Zheng, Y.; Cloutier, P.; Hunting, J. D.; Sanche, L.; Wagner, R. J. *J. Am. Chem. Soc.* **2005**, *127*, 16592–16598.
(9) Solomun, T.; Seitz, H.; Sturm, H. *J. Phys. Chem. B* **2009**, *113*, 11557–11559.
(10) (a) Abdoul-Carime, H.; Langer, J.; Huels, M. A.; Illenberger, E. *Eur. Phys. J. D* **2005**, *35*, 399–404. (b) König, C.; Kopyra, J.; Bald, I.; Illenberger, E. *Phys. Rev. Lett.* **2006**, *97*, 018105/1−018105/4.
(11) Wang, C. R.; Nguyen, J.; Lu, Q. B. *J. Am. Chem. Soc.* **2009**, *131*, 11320–11322.
(12) Ptasińska, S.; Denifl, S.; Scheier, P.; Illenberger, E.; Mark, T. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 6941–6943.
(13) Ptasińska, S.; Denifl, S.; Mróz, B.; Probst, M.; Grill, V.; Illenberger, E.; Scheier, P.; Märk, T. D. *J. Chem. Phys.* **2005**, *123*, 124302/1−124302/8.
(14) Denifl, S.; Ptasińska, S.; Probst, M.; Hrušák, J.; Scheier, P.; Märk, T. D. *J. Phys. Chem. A* **2004**, *108*, 6562–6569.
(15) Denifl, S.; Ptasińska, S.; Cingel, M.; Matejcik, S.; Scheier, P.; Märk, T. D. *Chem. Phys. Lett.* **2003**, *377*, 74–80.
(16) Abouaf, R.; Pommier, J.; Dunet, H. *Int. J. Mass Spectrom.* **2003**, *226*, 397–403.
(17) Hanel, G.; Gstir, B.; Denifl, S.; Scheier, P.; Probst, M.; Farizon, B.; Farizon, M.; Illenberger, E.; Märk, T. D. *Phys. Rev. Lett.* **2003**, *90*, 188104/1−188104/4.
(18) Pan, X. L.; Sanche, L. *Chem. Phys. Lett.* **2006**, *421*, 404–408.
(19) Ptasińska, S.; Sanche, L. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1730–1735.
(20) Ptasińska, S.; Sanche, L. *J. Chem. Phys.* **2006**, *125*, 144713/1−144713/9.
(21) Ptasińska, S.; Sanche, L. *Phys. Rev. E* **2007**, *75*, 031915/1−031915/5.
(22) Markus, T. Z.; Daube, S. S.; Naaman, R.; Fleming, A. M.; Muller, J. G.; Burrows, C. J. *J. Am. Chem. Soc.* **2009**, *131*, 89–95.
(23) Aqua, T.; Naaman, R.; Daube, S. S. *Langmuir* **2003**, *19*, 10573–10580.
(24) Kaufman, R.; Peled, D.; Naaman, R.; Daube, S. S. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2320–2324.
(25) Swarts, S. G.; Sevilla, M. D.; Becker, D.; Tokar, C. J.; Wheeler, K. T. *Radiat. Res.* **1992**, *129*, 333–344.
(26) Ray, S. G.; Cohen, H.; Naaman, R.; Rabin, Y. *J. Am. Chem. Soc.* **2005**, *127*, 17138–17139.
(27) Petrovykh, D. Y.; Kimura-Suda, H.; Whitman, L. J.; Tarlov, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 5219–5226.
(28) Ron, H.; Matlis, S.; Rubinstein, I. *Langmuir* **1998**, *14*, 1116–1121.
(29) Kimura-Suda, H.; Petrovykh, D. Y.; Tarlov, M. J.; Whitman, L. J. *J. Am. Chem. Soc.* **2003**, *125*, 9014–9015.
(30) Naaman, R.; Sanche, L. *Chem. Rev.* **2007**, *107*, 1553–1579.
(31) The work function is calculated by $\Phi = h\nu - E_k^{max}$, where $E_k^{max}$ is the highest kinetic energy observed, which is equal to 2.1 ± 0.1 eV for all Au-ssDNA studied.
(32) Cauët, E.; Liévin, J. *Adv. Quantum Chem.* **2007**, *52*, 121–147.
(33) Alloway, D. M.; Hofmann, M.; Smith, D. L.; Gruhn, N. E.; Graham, A. L.; Colorado, R., Jr.; Wysocki, V. H.; Lee, T. R.; Lee, P. A.; Armstrong, N. R. *J. Phys. Chem. B* **2003**, *107*, 11690–11699.
(34) Di Felice, R.; Selloni, A.; Molinari, E. *J. Phys. Chem. B* **2003**, *107*, 1151–1156.
(35) Perebeinos, V.; Newton, M. *Chem. Phys.* **2005**, *319*, 159–166.
(36) Heimel, G.; Romaner, L.; Bredas, J. L.; Zojer, E. *Surf. Sci.* **2006**, *600*, 4548–4562.
(37) Bokor, J.; Storz, R.; Freeman, R. R.; Bucksbaum, P. H. *Phys. Rev. Lett.* **1986**, *57*, 881–884.
(38) (a) Ge, N.-H.; Wong, C. M.; Harris, C. B. *Acc. Chem. Res.* **2000**, *33*, 111–118. (b) Harris, C. B.; Ge, N. H.; Lingle, R. L., Jr.; McNeil, J. D.; Wong, C. M. *Annu. Rev. Phys. Chem.* **1997**, *48*, 711–744. (c) Wong, C. M.; McNeill, J. D.; Gaffney, K. J.; Ge, N.-H.; Miller, A. D.; Liu, S. H.; Harris, C. B. *J. Phys. Chem. B* **1999**, *103*, 282–292.
(39) (a) Wang, H.; Dutton, G.; Zhu, X. Y. *J. Phys. Chem. B* **2000**, *104*, 10332–10338. (b) Vondrak, T.; Cramer, C. J.; Zhu, X. Y. *J. Phys. Chem.*

*B* **1999**, *103*, 8915–8919. (c) Szymanski, P.; Garrett-Roe, S.; Harris, C. B. *Prog. Surf. Sci.* **2005**, *78*, 1–39.

(40) Zhu, X. Y. Electron transfer at molecule-metal interfaces: a two-photon photoemission study. *Annu. Rev. Phys. Chem.* **2002**, *53*, 221–247.

(41) ICRU Report (International Commission on Radiation Units and Measurements), ICRU: Washington, DC, 1979; Vol. 31.

(42) Boudaïffa, B.; Cloutier, P.; Hunting, D.; Huels, A. M.; Sanche, L. *Science* **2000**, *287*, 1658–1660.

(43) Sanche, L. *Nature* **2009**, *461*, 358–359.

(44) (a) Simons, J. *Adv. Quantum Chem.* **2007**, *52*, 171–188. (b) Anusiewicz, I.; Berdys, J.; Sobczyk, M.; Skurski, P.; Simons, J. *J. Phys. Chem. A* **2004**, *108*, 11381–1138.

(45) Cauët, E.; Dehareng, D.; Liévin, J. *J. Phys. Chem. A* **2006**, *110*, 9200–9211.

(46) Crespo-Hernández, C. E.; Arce, R.; Ishikawa, Y.; Gorb, L.; Leszczynski, J.; Close, D. M. *J. Phys. Chem. A* **2004**, *108*, 6373–6377.

(47) Sevilla, M. D.; Besler, B.; Colson, A. O. *J. Phys. Chem.* **1995**, *99*, 1060–1063.

(48) Hush, N. S.; Cheung, A. S. *Chem. Phys. Lett.* **1975**, *34*, 11–13.

(49) Orlov, V. M.; Smirnov, A. N.; Varshavsky, Y. M. *Tetrahedron Lett.* **1976**, *17*, 4377–4378.

(50) Choi, K. W.; Lee, J. H.; Kim, S. K. *J. Am. Chem. Soc.* **2005**, *127*, 15674–15675.

(51) Jochims, H. W.; Schwell, M.; Baumgärtel, H.; Leach, S. *Chem. Phys.* **2005**, *314*, 263–282.

(52) Sugiyama, H.; Saito, I. *J. Am. Chem. Soc.* **1996**, *118*, 7063–7068.

(53) Prat, F.; Houk, K. N.; Foote, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 845–846.

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