Electric field induced charge transfer through single- and double-stranded DNA polymer molecules

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ABSTRACT: The charge transfer through single-stranded and double-stranded DNA polymer molecules has been the subject of numerous experimental and theoretical studies concerning their applications in molecular electronics. However, the underlying mechanisms responsible for their different electrical conductivity observed in the experiments are poorly understood. Here we use a self-consistent quantum molecular dynamics method to study the effect of an applied electric field along the molecular axis on charge transfer through single-stranded and double-stranded DNA polymer molecules with an injected electron or hole and assess the consequences for electronic applications. Charge transfer through both single-stranded and double-stranded DNA polymer molecules is predicted, regardless of the sign of the injected charge, the molecular

structure and the base sequence. The amount of charge transfer through a double-stranded DNA polymer molecule is slightly lower than through the corresponding two isolated single-strands as a result of the lower charge transport through the purine-pyrimidine base-stacking as compared with through DNA nucleobase-stacking. These results suggest that each DNA polymer strand can act as a molecular wire with both the sugar-phosphate backbone and the bases playing an important role in charge transfer, which opens new perspectives for molecular electronics applications.

KEYWORDS**:** Atomistic modelling, single- and double-stranded DNA, injected charge distribution, electric field effect, charge transfer, charged polaron mobility.

INTRODUCTION

The charge transfer through deoxyribonucleic acid (DNA) strands has attracted considerable attention during the past decade, because of its biological importance [1] and its potential applications in electrochemical sensors [2, 3] and molecular electronics [4, 5]. Motivated by these potential applications, a large number of theoretical and experimental studies have been carried out on charge transfer/transport in DNA molecules, which has been recently reviewed and analysed [6]. Experimental studies based on electrochemical DNA sensors [2] have shown that electrical conductivity of double-stranded DNA molecules is greater than single-stranded DNA molecules. Other experimental studies of electron transfer through DNA using electrogenerated chemiluminescence [7] suggested that single-stranded DNA strands with 15 bases long are not electronically conductive. However, the electrical characterization of self-assembled single- and double-stranded

DNA monolayers, without upper thiol end-groups and with 26 bases long, by a conductive atomic force microscope (AFM) [8] showed that electrical currents of approximately 2.5 nA and 0.6 nA flow through single-stranded and double-stranded DNA monolayers, respectively, for the applied bias of 3V. Therefore, the charge transfer properties through single- and double-stranded DNA molecules responsible for their conducting behaviour in the above experiments remain controversial.

Clearly, theoretical studies need to be done to unravel the underlying mechanism that manifests the difference in the charge transfer through single- and double-stranded DNA molecules suggested by the above experiments. Previous theoretical attempts [9] fail to consider the intra-strand interactions between the bases and sugar-phosphate groups for studying the charge transfer, which were shown to play an important role in charge transfer [10] and charge transport [11] of synthetic double-stranded DNA polymer molecules. In this work, we consider the contributions of covalently bonded phosphate groups with deoxyribose sugar and bases as well as non-bonded interactions to elucidate the difference in charge transfer properties between single- and double-stranded DNA polymer molecules. In order to address the intrinsic properties of DNA polymer molecules for charge transfer we do not consider any environment or electrical contacts related effects, which have been shown to affect charge transport in DNA-based devices [12, 13]. The dependence on the molecular structure and base sequence is also examined.

THEORETICAL METHODS AND COMPUTATIONAL DETAILS

In the present study, we investigated the charge transfer properties through four types of single-stranded DNA polymer molecules consisting only of Adenine (Poly(A)),

Thymine (Poly(T)), Cytosine (Poly(C)) and Guanine (Poly(G)) base and two types of double-stranded DNA polymer molecules consisting only of Adenine-Thymine (Poly(dA)-Poly(dT)) or Cytosine-Guanine (Poly(dC)-(Poly(dG)) base pair, with the molecular structures adopted in aqueous solution (B–form), as well as in their dry state (A–form).

We start from the single- and double-stranded DNA polymer molecules with the standard A–form and B–form geometries shown in Figure 1. Each molecule considered in this work has 10 nucleotides per strand and the dangling bonds saturated by hydrogen atoms. We use the self-consistent quantum molecular dynamics method, implemented in the CHEMOS code [14, 15], to study the atomic charge distribution of the relaxed uncharged molecules with the lowest triplet ground state energy, and the effect of injecting an electron or hole on that charge distribution, both corresponding to a doublet state. The same theoretical method was also used to study the charge transfer from one end of the molecule to the other, with no net flow of charge, induced by a strong uniform electric field applied to the charged DNA polymer molecules along the directions shown in Figure 1.

Because of the strong level of electron-lattice coupling in DNA polymer molecules, it is necessary to perform self-consistent calculations of electronic wave functions and atomic positions in order to properly study the charge transfer in these molecules. The method used in this work solves simultaneously the Schrödinger equation for the entire system, using the semi-empirical molecular orbital theory which works at the CNDO (Complete Neglect of Differential Overlap) level within a minimum basis set [16, 17], for obtaining the electronic structure of an isolated DNA polymer molecule and Newton's equations for

obtaining the nuclear motion, using the forces calculated self-consistently at each time step, assuming that the initial velocities of all nuclei are zero. When an electric field is applied, the Hamiltonian of the DNA polymer molecule gets modified which affects not only the wave functions and energy of the molecule but also the force acting on each nucleus. Although nuclear motion and the effect of intrinsic fluctuations, resulting self-consistent inter-atomic interactions and the application of the external electric field, are included in the quantum molecular dynamics simulations performed in this work, no rescaling of nuclear velocities was done during the simulations in order to assure quantum molecular dynamics simulations at constant temperature. Therefore, the results present here are a useful approximation of probable behaviour at the temperature of zero Kelvin or at closely packed structures within a monolayer because thermal fluctuations are constrained by intermolecular interactions.

The reliability of this self-consistent approach based on the CNDO method to predict the right trends for the molecular properties of DNA and to give quantitative estimates for electric field induced charge mobility along the molecular axis of conjugated polymers, in very good agreement with the experiments, is thoroughly described in our previous publications [10, 18].

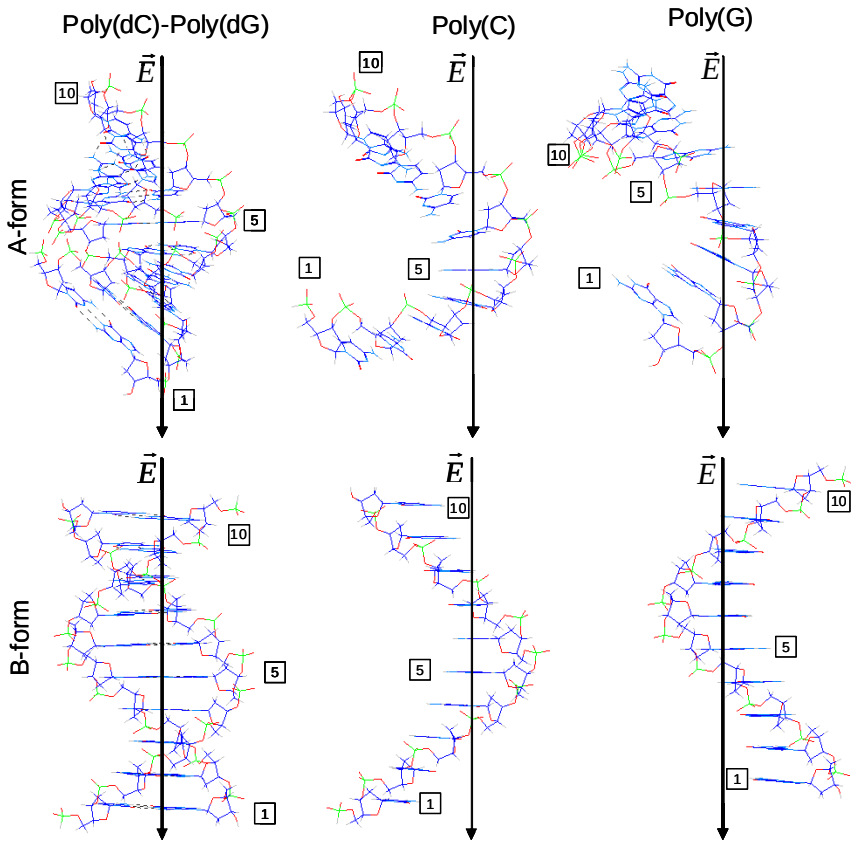

Figure 1. The types of molecular structure of single- and double-stranded DNA molecules considered in this work. All DNA polymer molecules have 10 nucleotides per strand. The arrows indicate the direction of the external electric field to be applied and the nucleotides (phosphate-sugar-base) are numbered for easier identification.

RESULTS AND DISCUSSION

Figure 2 shows the results obtained for the distribution of the negative injected charge per nucleotide throughout the molecular axes depicted in Figure 1. The analyses of these results show interesting features. One is that the injected electron is distributed differently throughout the molecular axis of the same polymer strand for single- and double-stranded DNA molecules, regardless of the molecular structure and the type of base. Another

important aspect is that the maximum charge stored per nucleotide does not change significantly for single- and double-stranded DNA molecules. One striking result is that charge injection is most strongly localized for single-stranded DNA molecule of A–form consisting only of cytosine base. Similar features are found when an electron is removed from these DNA molecules.

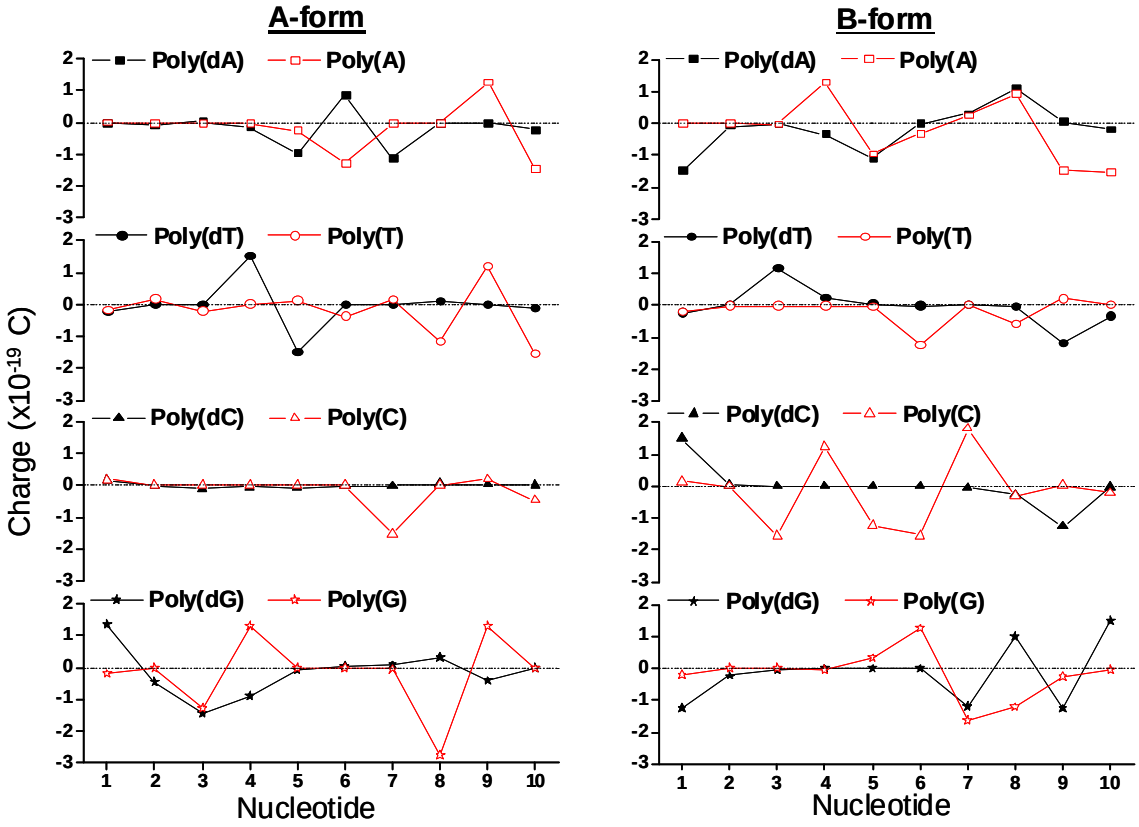

Figure 2. Change in the charge of the nucleotides of each strand when one electron is added to the single- and double-stranded DNA molecules shown in Figure 1. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye.

When a strong uniform electric field is applied to the charged single- and double-stranded DNA polymer molecules along the directions depicted in Figure 1, there is a transfer of the injected charge towards the molecular end favoured by the applied electric field and an additional electron transfer along each DNA strand in the opposite direction to the applied field, leading to a gradient of charge distribution in the presence of external field (see Figure 3). Both charge transfers take place before the nuclei are allowed to move. The amount of positive and negative charge stored at both ends of each DNA strand depends on the type of DNA molecule, its molecular structure and type of bases.

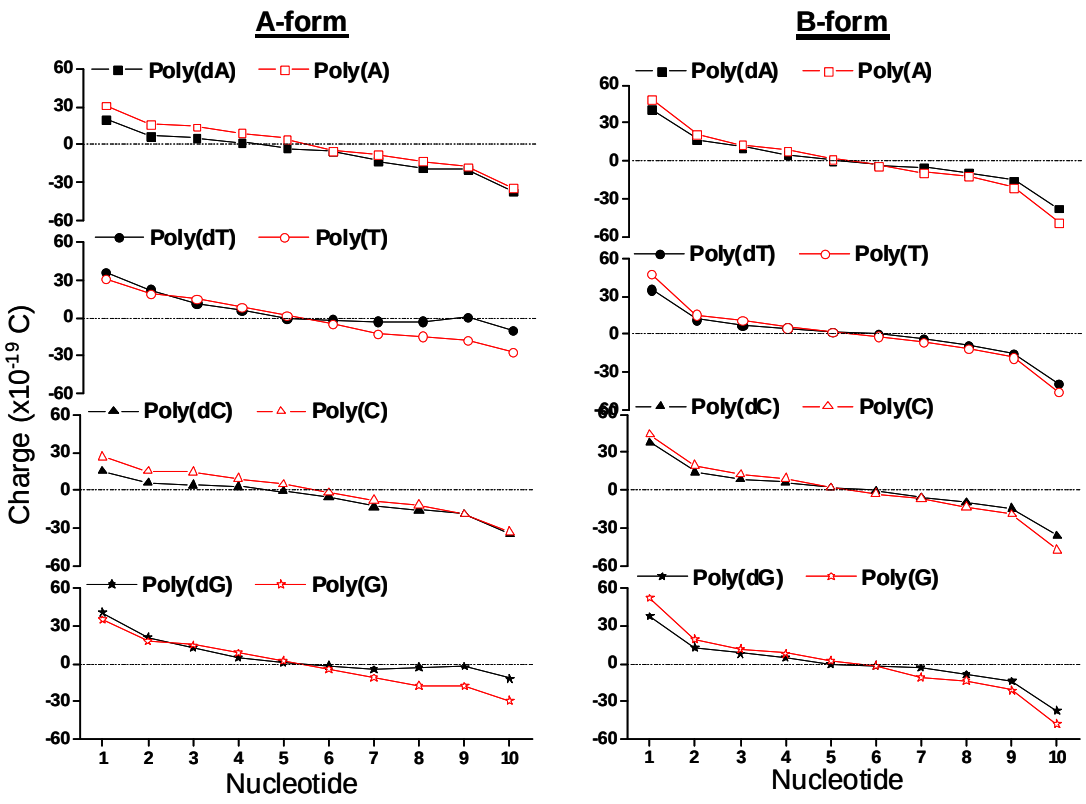

Figure 3. The effect of the applied electric field on the distribution of the injected electron into the single- and double-stranded DNA molecules, for each molecular strand in A- and B-forms and an external applied electric field of 100 MV/cm along the direction shown in Figure 1. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye.

Before we can relate the amount of charge transfer along each DNA strand, induced by the strong applied electric field, with the charge transfer characteristics or conductivity of single- and doubled-strand DNA polymer molecules, we need to test the reliability of the self-consistent quantum molecular dynamics approach based on the CNDO method in predicting the different charge transfer characteristics of molecular systems, where atomic positions and electronic structure as coupled problems, in the presence of a strong electric field, such as conjugated polymer strands.

As we have shown previously [18] when one electron (or hole) is injected into a straight polymer strand with 16 monomer units of poly(*para*-phenylene vinylene (PPV) and its derivative poly(2,5-dimethoxy-*para*-phenylene vinylene) (DMeO-PPV), there is a charge rearrangement of the polymer backbone atoms which is accompanied by a change in its dimerisation pattern (defined by the absolute value of the difference between adjacent carbon-carbon bond length at each carbon atom). In the absence of an applied electric field, the polaron-type charge-induced defects formed are localized at the central region of the conjugated polymer strand, regardless of the sign of the injected charge and the polymer chemistry. When the strength of the applied electric field, along the molecular axis, is just below the threshold value needed to induce coherent transport of the injected charge (the strength of the applied electric field for which the coupling between the injected charge and the induced structural defect on the polymer backbone is broken and the injected charge moves to the strand end favoured by the applied electric field before nuclear motion occurs), we predicted that PPV has a negative polaron-type mobility along the conjugated polymer strand approximately four times larger than DMeO-PPV. Figure 4 shows the effect of an external applied electric field of 100 MV/cm, along the

molecular axis of PPV and DMeO-PPV, on the distribution of the injected electron into these molecules.

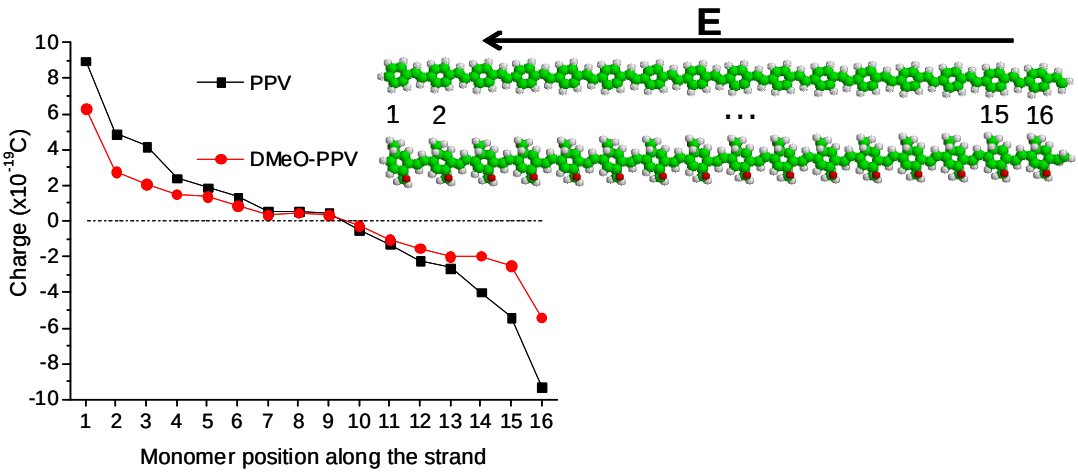

Figure 4. The effect of the applied electric field on the distribution of the injected electron into straight conjugated polymer strands with 16 repeated monomer units of poly(*para*-phenylene vinylene) (PPV) and poly(2,5-dimethoxy-*para*-phenylene vinylene) (DMeO-PPV), for an external applied electric field of 100 MV/cm along the direction shown by the arrow. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye. The repeated monomer units are numbered for easier identification.

When a strong electric field was applied to negative charged PPV and DMeO-PPV strands, we found the disappearance of the localised injected charge at the strand end favoured the external applied field. This was observed for field strengths significantly higher than the threshold value for coherent charge transport along the conjugated polymer strands, before the nuclei motion is allowed, and the formation of a gradient of charge distribution similar to those obtained for both single- and doubled-strand DNA

polymer molecules in the presence of a strong electric field, with each strand in the B-form (see right-end side of Figure 3). Moreover, the amount of charge transfer through the PPV strand is significantly larger than through the DMeO-PPV, which seems to be correlated with the difference in charge transport mobility along the molecular strands of both polymers. Therefore, the results shown in Figure 3 suggest that charge transfer through a double-stranded DNA molecule is significantly larger than through a single-stranded DNA molecule with the same length, molecular structure and base sequence, because both strands of the double-stranded DNA molecule contribute to the charge transfer, which is in agreement with the experiments using electrochemical DNA chips [2].

In order to study the effect of inter-strand interactions in charge transfer through double-stranded DNA molecules with A- and B- form, we compare in Figure 5 the amount of charge stored in each nucleotide pair of double-stranded DNA molecule with the sum of the charge stored in two isolated single-stranded DNA molecules with the same base sequence and molecular structure for the same applied electric field. These results suggest that charge transfer through a double-stranded DNA molecule is slightly lower than through the corresponding two isolated single-stranded DNA molecules, regardless the type of molecular structure and the type of base pairs, which is in agreement with conductive AFM measurements through a packed monolayer of single- and double-stranded DNA molecules with a complex base sequence [8], because the number of DNA strands connecting the conducting AFM tip and the substrate should be similar in both cases.

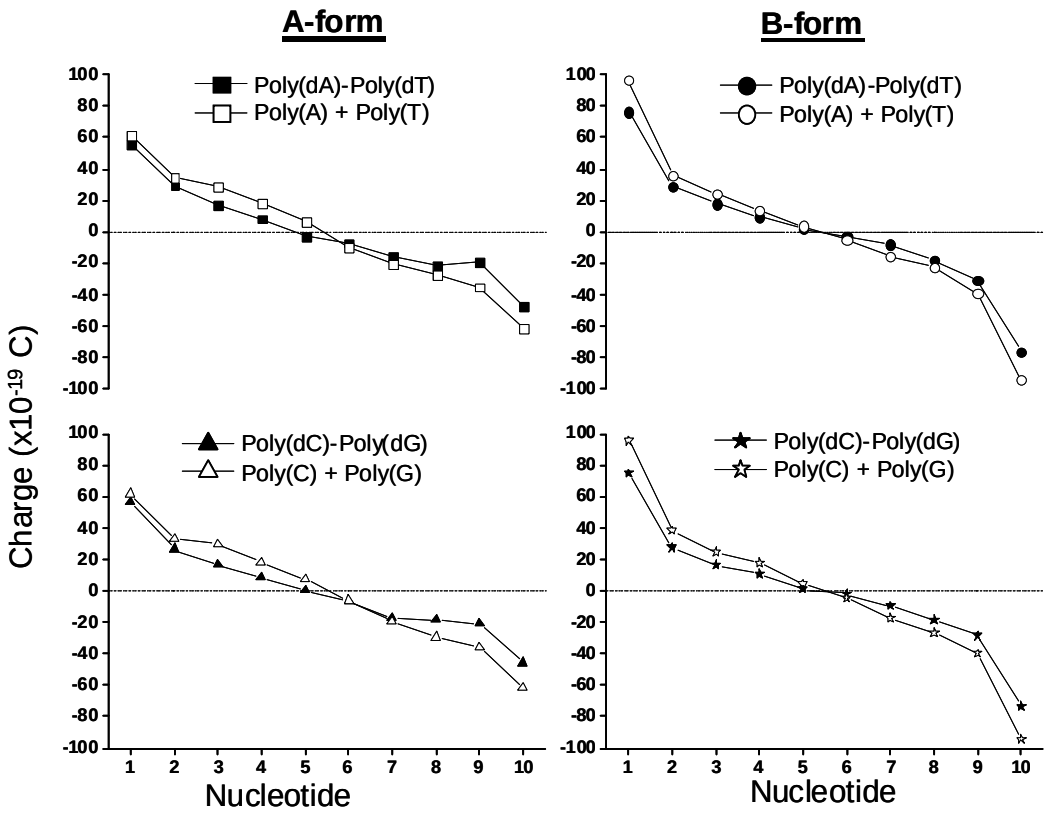

Figure 5. The comparison between the effect of the applied electric field of 100 MV/cm on the distribution of the injected electron into double-stranded DNA molecules and the two isolated single-stranded DNA molecules with the same base sequence and molecular structure. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye.

In order to understand the effects of both nucleotide fragments, consisting of the sugar-phosphate backbone and the DNA bases, on charge induced by a strong electric field transfer through double-stranded DNA polymer molecules and through the corresponding two isolated single-stranded DNA molecules induced by a strong electric field, we will consider only DNA polymer molecules with the B–form geometry. In Figure 6, we

compare the results obtained for the DNA polymer molecules considered in this work with the corresponding nucleic acid base-stacking (in these cases the sugar-phosphate backbone of the DNA strands are not included in the calculations).

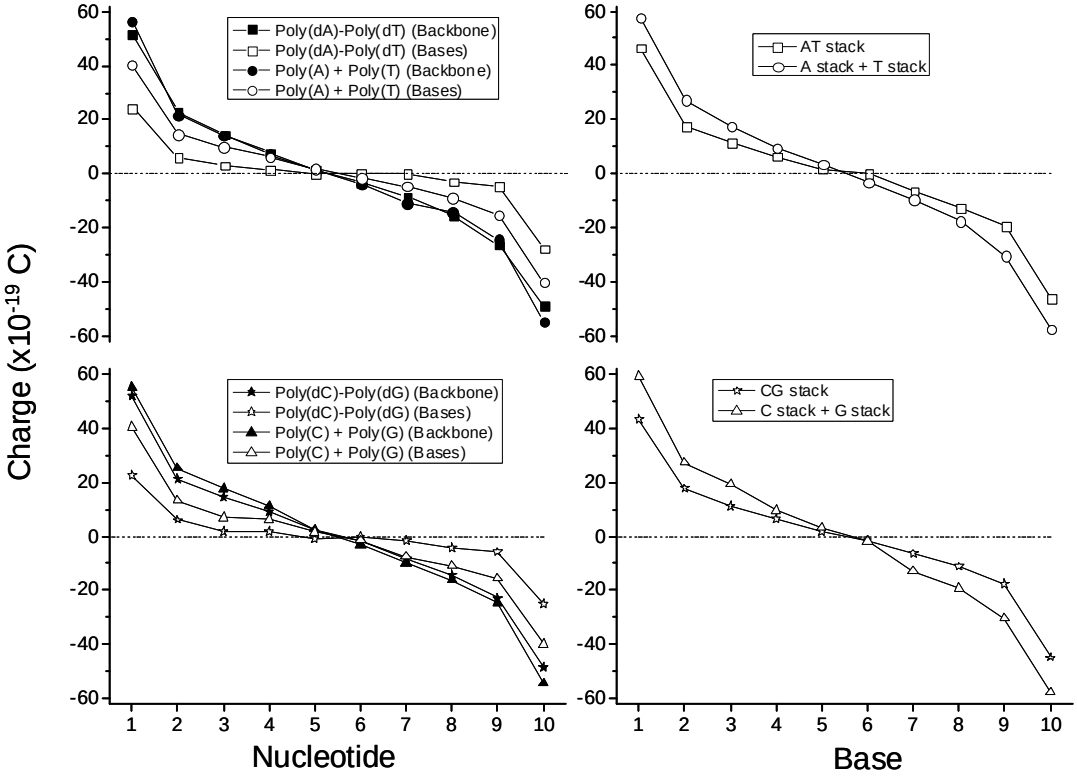

Figure 6. The comparison between the effect of the applied electric field of 100 MV/cm on the distribution of the injected electron into the sugar-phosphate backbone and the DNA bases of double-stranded DNA polymer molecules and the two isolated single-stranded DNA polymer molecules with the same base sequence (left-hand side) and the corresponding nucleic acid base-stacking (right-hand side), both with the B-form geometry. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye.

When a strong electric field is applied to both DNA polymer molecules (single- and double-stranded oligomers) and the corresponding nucleic acid base-stacking, a gradient of charge distribution similar to those obtained for conjugated polymer strands is formed, before the nuclei motion is allowed, as result of coherent charge transfer through the

DNA polymer molecules and nucleic acid base-stacking. Although, the charge transfer through the sugar-phosphate backbone is larger than through the bases of DNA polymer molecules, the double-stranded DNAs have less charge transfer than the sum of two single-stranded DNAs, as a consequence of the different charge transfer through the bases in single- and double-strand DNA polymer molecules, since the charge transfer through the DNA backbones is similar in both cases. We also found that charge transfer through the double-stranded nucleic acid base-stacking is lower than charge transfer through the sum of the corresponding two isolated single-stranded nucleic acid base-stacking, and their difference is similar to what was obtained for charge transfer through the DNA bases in single- and double-stranded polymer molecules.

The results described above suggest that the mechanisms of charge transfer through the bases of single- and double-stranded DNA polymer molecules and through the corresponding nucleic acid base-stacking, without the sugar-phosphate backbone included in the calculations, induced by an applied electric field should be similar. However, the distribution of the injected charge (electron or hole) throughout the direction of the applied electric field depicted in Figure 1 is completely different in both cases (see Figure 7). When one adds or removes one electron from a DNA polymer molecule, the excess charge distribution is found to be delocalised over several neighbouring bases in single and double-stranded DNA polymer molecules, in agreement with the theoretical results of Berlin et al. [19], the effect being more pronounced for the single-stranded molecules, and the distribution pattern varying with the type of base and the sign of the injected charge. These results suggest that band-like motion (coherent charge transport) or phonon-assisted polaron hopping (polaron drifting) should dominate

the injected charge transport through the bases in both single- and double-stranded DNA polymer molecules. In contrast, the excess of charge in nucleic acid base-stacking is found to be strongly confined to a single nucleobase, in agreement with *ab initio* calculations at Density Functional Theory level [20, 21]. The position of the injected charge depends on the type of stack (single-base stack or base-pair stack), the base sequence and the sign of the injected charge.

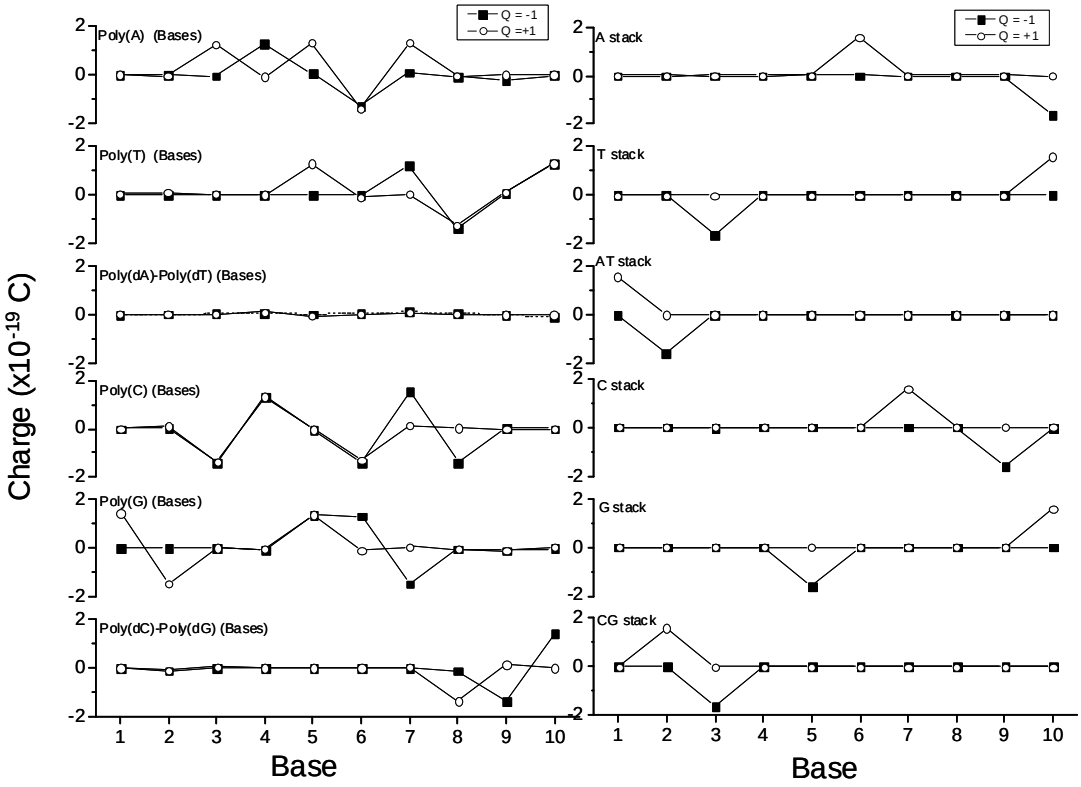

Figure 7. Change in the charge of the bases (or base-pairs) when one electron is added (Q = -1) or removed (Q = +1) from single- and double-stranded DNA molecules shown in Figure 1 (left-hand side) and from nucleic acid base (base-pair) stacking without the sugar-phosphate backbone (right-hand side). The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye.

In the case of nucleic acid base-stacking, it is easy to distinguish from the excess of injected charge distribution, the sign and localisation of the injected charge, and to follow

its transport along the stack as a function of the strength of the applied electric field. Therefore, in order to understand the charge transport mechanisms through the nucleobases of DNA polymer molecules, we will study the effect of an applied electric field of variable strength on the injected charge into single- and double-stranded nucleic acid base-stacking with B-DNA geometry.

When an electron or hole is injected into a deformable nucleic acid base-stacking, it induces distortions around the position where the excess of charge is localised, either inside the bases involving the change of chemical bonds and the positions of hydrogen and oxygen in agreement with the *ab initio* calculations of Alexander et al. [22] and the change in the inter-base distance in agreement with the SSH model calculations of Rakhmanova et al. [23] and Wei et al. [24], leading to the formation of a charged polaron.

If there is a uniform electric field applied parallel to the stack axis, and its strength is smaller than a threshold value, both positive and negative polaron-like transports can be realized along the stack. In this case, the motion of the polaron is a continuous translation along the stacking (polaron drifting) and small intrinsic fluctuations do not disturb the polaron motion in agreement with nonlinear lattice model calculations of Komineas et al. [25]. When the strength of applied electric field is just equal or above that threshold value, the coupling between the injected charge and the induced structural distortion is broken and the injected charge moves coherently towards the stack end favoured by the applied electric, before the nuclei is allowed to move, via delocalised orbitals along the base-stack units in agreement with the results from a lattice fermion model [26]. When the strength of applied electric field is strong enough, the injected charge localised at the stack end disappears and a gradient of the excess charge distribution is formed, as shown

in the Figure 6, leading to a delocalised polaron in agreement with the SSH model work of Johansson et al. [27].

In order to estimate and compare the charged polaron mobility of all nucleic acid base-stacking considered in this work, we use the definition of charge mobility as charge velocity per unit applied electric field and estimate the velocity of the single injected charge (electron or hole) for the same strength of the applied field, lower than the threshold value for coherent charge transport along all nucleic acid base-stacking, using the self-consistent quantum molecular dynamics approach based on the CNDO method. The results obtained for both the electric field threshold and the charged polaron mobility for an applied electric field of 0.1 MV/cm are shown in Table 1.

The analysis of our results presented in Table 1 shows several interesting features. First, there is clear dependence of the electric field threshold for coherent charge transport along the nucleic acid base-stacking on the base sequence, the interaction between the bases in hydrogen-bonded base-pairs stacking and the sign of the injected charge. Secondly, hole mobility is larger than electron mobility in double-stranded nucleic acid base-stacking. Thirdly, the polaron mobility in poly(dA)-Poly(dT) is higher than poly(dC)-Poy(dG), for the same applied electric field and injected charge, in agreement with the results from the extended tight-binding model of Cui et al. [28]. Another important aspect, it is that single-stranded nucleic acid base-stacking have higher polaron mobility than the double-stranded nucleic acid base-stacking for both electron and hole injection, which should be responsible for the charge transfer through a double-stranded DNA molecule to be slightly lower than through the corresponding two isolated single-stranded DNA molecules induced by a strong applied electric field and these results are

in agreement with conductive AFM measurements through a packed monolayer of single- and double-stranded DNA molecules with a complex base sequence [8]. One striking result, it is that the lowest electric field threshold for coherent charge transport and polaron mobility occurs for electron transport along the stack of cytosine-guanine base pairs, due to a strong interaction between these nucleobases, which leads to a delocalisation of the injected electron over both nucleobases of the hydrogen-bonded base pair during the electron transport between adjacent base-pairs, in contrast with the almost complete localization of the injected charge to an individual nucleobase in the DNA duplex for the other cases.

We should note that, the calculated electronic structure and the molecular orbitals are strongly dependent on the CNDO parameters used and the basis set of atomic orbitals used to construct the wave function. Therefore, the absolute value of the calculated electric field threshold for coherent charge transport and polaron mobility may not be correct, but we expect the predicted trends to be reliable and these show important features, which are a useful approximation of probable behaviour at the temperature of zero Kelvin or at closely packed structures within a monolayer because thermal fluctuations are constrained by intermolecular interactions.

Since the structure of single- and double-stranded DNA polymer molecules, the distortion within their nucleobases and the distance between their stacked bases are expect to change drastically with the increase of the temperature and in aqueous solutions [9, 29], the predicted results for the electric field threshold for coherent charge transport and charged polaron mobility should be significantly different in those cases than the ones reported in Table 1, but their estimates is out of the scope of this work. Previous results

showed that the disorder, due to the increasing of temperature and environment, might decrease (increase) charge transfer in DNA molecules with homogeneous base sequence (random base sequence) [12, 19, 30-43].

Table 1. The strength of the electric field threshold needed for coherent transport of the injected electron (Q = -1) and hole (Q = +1) and the charged polaron mobility induced by an uniform applied electric field of 0.1 MV/cm, for various nucleic acid base-stacking with 10 nucleobases (or nucleobase-pairs) per stack in B-DNA conformations.

Base stack	Injected Charge	Threshold for coherent charge transport (MV/cm)	Charge mobility for the applied electric field of 0.1 MV/cm ($cm^2 V^{-1} s^{-1}$)
Adenine (A)	-1	2.7	3.97E-02
	+1	9.6	4.64E-02
Thymine (T)	-1	2.9	5.79E-02
	+1	7.4	5.33E-02
Cytosine (C)	-1	6.5	5.77E-02
	+1	5.2	4.25E-02
Guanine (G)	-1	8.3	4.58E-02
	+1	4.5	4.53E-02
Adenine-Thymine (AT)	-1	3	2.79E-02
	+1	7.8	3.63E-02
Cytosine-Guanine (CG)	-1	0.2	1.98E-02
	+1	5.4	3.19E-02

If we assume that there is an uniform electric field applied along the tilted 26 bases long DNA molecules (8.5 nm length), contributing to the current flow in the conductive AFM measurements through a packed monolayer of single- and double-stranded DNA molecules with complex sequence [8], with a strength of approximately 2MV/cm

(estimated from the experimental conditions reported) and only a single charge is allowed to be injected into each molecule and to move along it by polaron drifting before the injection of the next one, as a result of Coulomb blockade, we can estimate the current flow through each one of them ($I=|e|/\Delta t$, where e is the electron charge Δt is the time for the injected charge moves along the entire molecule).

Considering that the polaron velocities, calculated from Table 1, are field-independent and the lowest polaron velocity is the determinant step in the transport of the injected charge through the nucleic acid base-stacking, we can roughly estimate the current flow through single- and double-stranded base-stacking for both electron and hole injection. The results obtained by this rough estimation for electron (hole) transport are 0.5 nA (0.6 nA) for the double-stranded base stacking, 1.5 nA (1.6 nA) for two single-stranded base-stacking and 2.3 nA (2.4 nA) for three single-stranded base-stacking, and they are in very good agreement with the experimental findings [8] if we consider that one double-stranded and three single-stranded DNA molecules contribute to the current obtained in the experiments. Our results suggest that the maximum number of molecules contributing to the current flow in the experimental system used should be three, in agreement with the conclusion drawn from further experiments using the same experimental setup [44].

CONCLUSIONS

We studied the distribution of the injected charge (one electron or one hole) into isolated single- and double-stranded DNA polymer molecules, with the same length and different molecular structures and base sequences, and the effect of an applied electric field on the injected charge.

Our results show that when a strong electric field is applied along the molecular axis there is charge transfer along all the molecular strands that compose the DNA polymer molecule giving rise to a gradient of charge distribution as a result of coherent charge transport, regardless of the sign of the injected charge, the molecular structure and the base sequence. Moreover, the amount of charge transfer through each strand of a double-stranded DNA molecule is slightly lower than through the corresponding isolated single-stranded DNA molecules. These results correlate well with polaron mobility induced by a low applied electric field through single-stranded base-stacking being higher than through double-stranded base-stacking for both electron and hole injection. Therefore, the mechanisms for charge transport through single- and double-stranded DNA polymer molecules should be similar and charge mobility should be dependent on the strength of the applied electric field. The difference in the amount of charge transfer/transport observed in the experiments seems to depend on DNA molecular structure and the number of the strands involved in the electrical conduction process.

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