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Thermal and electrochemical gate effects on DNA conductance

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Abstract

In an attempt to understand the complexities of DNA charge transport we have used a scanning tunnelling microscope break junction to repeatedly form a large number of Au–DNA–Au junctions. The DNA is covalently bound to the Au electrodes via gold–thiol bonds, and all measurements are carried out in an aqueous buffer solution to maintain a biological conformation of the duplex. A statistical analysis is carried out to determine the conductance of a single DNA duplex. Previously, we have seen an algebraic dependence of the conductance on length, suggesting a hopping mechanism. To attempt to verify this as the conduction mechanism we have changed the solution temperature and applied an electrochemical gate to the molecular junction to help elucidate the charge transport properties. In an alternating GC sequence with a length of eight base pairs, neither the temperature nor the gate potential caused a significant change in the conductance within the available experimental window.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

DNA is emerging as an extremely promising material in the field of nanotechnology since its base recognition, self-assembly and structural properties are unparalleled in designed systems on this size scale [1–4]. However, despite these amazing mechanical and chemical properties, the charge transport properties of DNA have remained a contentious field in the last decade [5, 6]. Although DNA is a promising material mechanically, it is important to understand the charge transport properties for both studies of DNA in biological systems and the development of DNA based materials. It has been proposed that long-range electron transfer between distally bound proteins in a DNA-mediated reaction may play a role in damage detection by monitoring the integrity of DNA, and a fundamental understanding of how and

when DNA transfers charge along with the mechanism for doing so may help elucidate some previously unknown biological functions of DNA and its interactions in complex systems [7].

However, not only has the conduction mechanism in DNA been uncertain, but the type of conductor that DNA behaves as has also been hotly contested [8–11]. Despite these difficulties, in recent years photochemical measurements have began to demonstrate that the coupling of the donor and the acceptor units to the energy levels of the bases in the DNA stack play one of the key roles in the ability of DNA to transport charge [12]. These systems have shown that in some cases thermally activated hopping [13] is the most likely transport mechanism, while in other cases it is apparent that superexchange is the dominant mechanism [14, 15]. In some cases, it has been shown that there is a transition between hopping and superexchange [16]. It will be very important to understand this effect if DNA is to be used as a material at the nanoscale. And as such a material, it will be important to understand it as a system in which it is connected with the outside world via electrodes rather than through chemical reactions or photoexcitations.

Despite this desire, direct contact measurements have proven to be difficult to carry out experimentally [17]. Furthermore, the electrical properties of DNA from direct contact measurements vary over a wide range, from insulating [18, 19], semiconducting [20, 21] to conducting [10, 22]. Certainly the specific experimental details of the direct contact measurements seem to affect and even dominate the measured electrical properties and conductance [17]. In some cases bundles or networks are measured [8], often in a dry environment or even a vacuum [22]. Sometimes, covalent bonding is used [23], and other times, nonspecific binding is the only contact made to the DNA [24]. All of these details make it difficult to determine exactly what is dominating the measurement. Nevertheless, as one focuses more specifically on small scale measurements, less than or equal to 20 nm in length, a conductance is typically measured regardless of the specific types of contact, or the solution environment, allowing one to believe that at least at the mesoscopic scale there are some inherent conductance properties in DNA [21, 23, 25–27]. It is also important to note that in these cases the emphasis tends to relate to the conductance of a specific molecule or duplex rather than the conductivity, or the conductivity of base-pair additions. This terminology is used because, depending on the specific environment, the actual length and cross-sectional area vary with time. This lends itself to the point that it remains difficult to keep DNA in a biological conformation and access enough appropriate experimental variables not just to determine if DNA is a capable conductor, but also what type of conductor it is. Recently, conductance measurements for single molecules have advanced to the point where it is possible to change various parameters such as temperature and electrochemical potential, and see the resultant changes in the conductance of a single molecule through a statistical analysis [26, 28, 29].

In this paper we use the scanning tunnelling microscope (STM) break junction method to study the conductance of double-stranded DNA (dsDNA) in an aqueous solution with its two ends each covalently bound to a probing electrode. We perform a statistical analysis of ∼1000 individual curves per set of experimental variables to determine the conductance of a single dsDNA. To better understand the charge transport properties of this system we vary the temperature and the electrochemical potential of the solution while performing single-molecule measurements in the hope of elucidating the charge transport characteristics of DNA.

2. Experimental details

Oligonucleotides were purchased from Integrated DNA Technologies, and purified by high-performance liquid chromatography (HPLC). Each of the oligos had a 3 methylene thiolated terminal group at the 3′ end of the oligomers. This group was protected with a

mercaptopropanol disulfide bond. Prior to use, the DNA was first suspended in 10 mM phosphate buffer (PBS) with 100 mM $NaClO_4$ at pH 7.4, and this solution was then diluted into another PBS solution that also contained 10 mM tris-(2-carboxyethyl)phosphine (TCEP) to create $\sim$10 μM single-stranded DNA solution. TCEP is a well-known reducing agent used to break the disulfide bond, thus effectively deprotecting the thiol on the DNA oligomers [30]. This solution was incubated for 3 h at room temperature and then run through a spin column (Roche Applied Science) to remove the TCEP and mercaptopropanol from solution. The resulting DNA solution was then heated to 80 °C in a 1 l bath of 18 MΩ water and allowed to cool back to room temperature over the course of $\sim$3 h to create dsDNA in solution. In this study all oligomers considered are self-complementary, thus allowing the creation of dsDNA simply by heating the solution above the melting temperature, and slowly cooling it back to room temperature. 70 μl of the above solution was then placed in a Teflon STM cell with an additional 70 μl of 100 mM $NaClO_4$ to maintain the counterion concentration in the cell so that the DNA maintained a B-form conformation. Perchlorate was used instead of chloride in this system because perchlorate binds less strongly to gold.

The substrate and tip used in the STM system were both of gold, which is capable of covalently binding to the thiol on the modified DNA. The substrate was prepared by thermally evaporating 130 nm of gold (99.9999% purity, Alfa Aesar) on a freshly cleaved mica surface (Ted Pella) in high vacuum ($\sim 5 \times 10^{-8}$ Torr). Just prior to measurements the substrate was annealed in a hydrogen flame to ensure a clean, atomically flat surface. The tips were prepared from 250 μm diameter Au wire (99.998% purity, Alfa Aesar). The tips were cut with scissors to prepare a sharp tip, and then coated with Apiezon wax to cover the surface and decrease the leakage current since the measurements were done in an aqueous solution. By properly coating the Au tip in this wax, leakage currents could be reduced to the order of $\sim$1 pA, which is near the resolution of our current amplifier, meaning that ionic current played no role in the measured values. Occasionally during the course of measurements a large surface area of the tip became exposed, causing an increase in leakage current; when this occurred the tip had to be replaced to continue measurements.

For the STM break junction measurements we used a Nanoscope IIIa controller from Digital Instruments, with Digital Instruments Nanoscope software version 4.23. This was attached to a molecular imaging STM head, and a homemade current preamplifier was placed inside the molecular imaging scanner. The current preamplifiers used in this study were 100, 10 and 1 nA V^{-1}. In each case, there was no difference in the results. This system was also attached to a second computer that has a LabView PCI-MIO-16E-4 DAQ card (National Instruments), LabView 6.1 (National Instruments), and a program written in-house to control the movement of the STM tip during the break junction measurements. The STM break junction measurements were carried out using the current as a feedback signal. Once the normal STM software had engaged the tip and imaged the surface, the feedback system in that controller was turned off and the LabView system was placed in control. This system moves the tip toward the surface until the current preamplifier is saturated, and then retracts the tip at a specific rate, generally between 20 and 40 nm s^{-1}. The current during the retraction process was recorded with a Yokogawa DL708 oscilloscope. Once the current reached the resolution of the preamplifier, the tip was moved back toward the surface, and the process repeated, as shown in figure 1(a). This process takes approximately 300 ms and can thus be repeated several times a second, allowing one to quickly obtain 1000–2000 current versus time curves under a specific set of experimental parameters.

During the stretching process there are typically three types of curves that appear, some are simply an exponential decay ($\sim$70%), some have a large amount of noise imposed upon them, or a few large spikes ($\sim$15%), and the others have one or two steps that occur below the

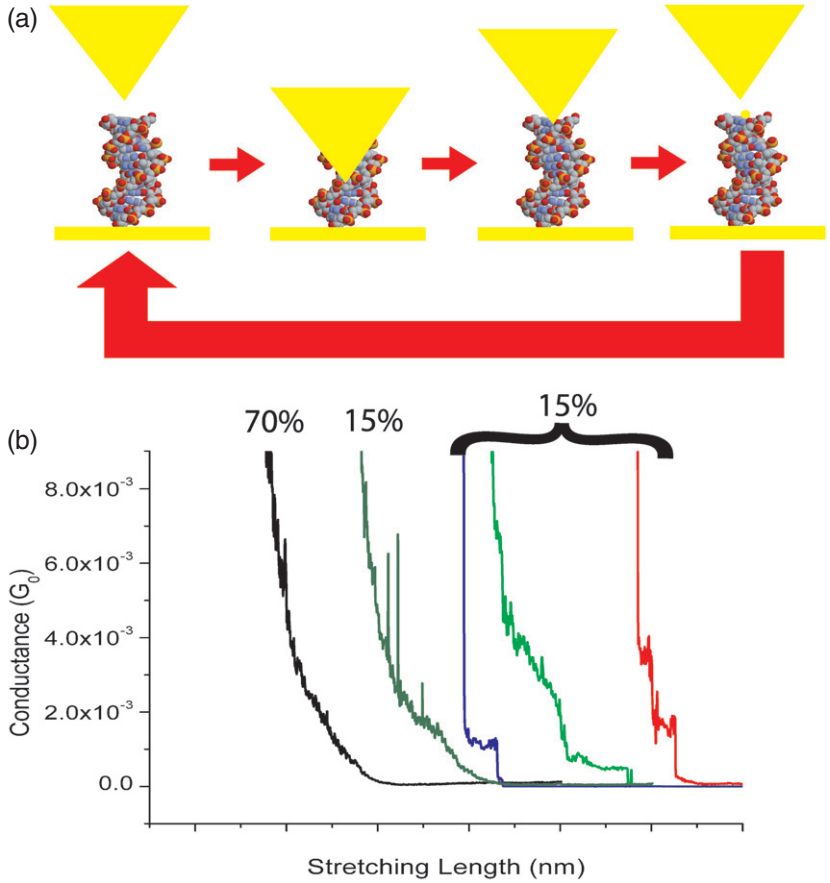

Figure 1. STM break junction measurements. (a) Idealized illustration of the STM break junction process. An Au tip is brought near an Au substrate in the presence of DNA. Occasionally, a dsDNA molecule will bridge the junction, and steps will occur in the current transient. The process is repeated several times a second. (b) Examples of the current transients recorded during measurements. Some curves are simple exponential decay, some have noise and approximately 15% of the curves show steps.

fundamental conductance quantum, G_0 ($2e^2/h$ or 77.5 μS) (15%). This value is the maximum conductance of a one-channel, one-dimensional conductor connected to bulk electrodes. The conductance values presented in this paper will be given in terms of this unit to demonstrate the difference between the measured molecule and the gold quantum point contact. Furthermore, it is worth noting that the percentage of curves with steps (10–15%) is significantly lower than that seen in other systems like the alkanedithiols [31]. This difference must be attributed to the specific details of the experiment such as the solvent, and the size and flexibility of the molecules involved. These 15% of curves were then used to construct a histogram by sampling the data and counting the number of times a specific conductance occurred. By adding together the individual counts from each of the traces, a conductance histogram was constructed that appears similar to the one shown in figure 2(a). Our previous studies [23, 32], as well as the work done by others [33], have demonstrated that the first peak in the conductance histogram corresponds to the conductance of a single dsDNA molecule, and each of the other peaks corresponds to the conductance of an integer number of dsDNA molecules between the tip

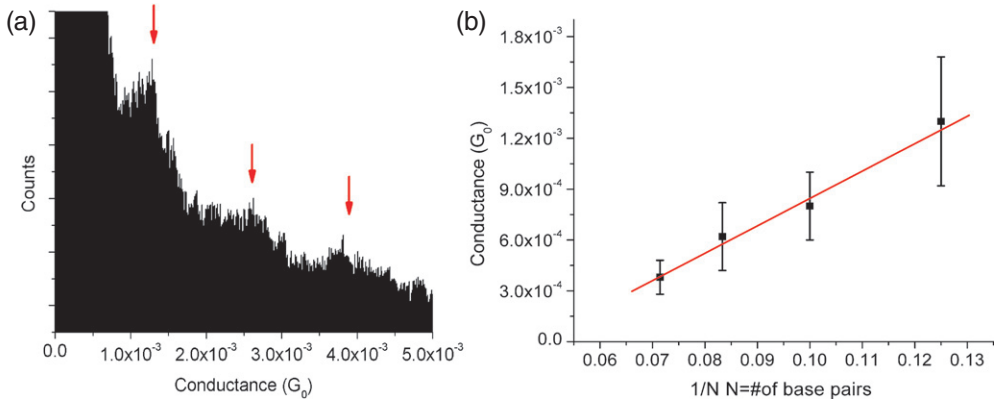

Figure 2. Length dependence of DNA conductance. (a) Typical conductance histogram of dsDNA conductance at room temperature, without electrochemical potential control. (b) Dependence of the conductance on the length of the DNA. Alternating GC sequences were used.

and the surface. Occasionally, a second set of peaks was visible in the DNA conductance data four to five times higher than that of the peaks discussed, but this was not consistent enough for thorough analysis.

Temperature studies were carried out by using either a Peltier or resistive heating STM stage from Molecular Electronics, and the temperature was controlled using a PID controller on a Lakeshore 331 temperature controller. Using the Peltier stage allowed measurements to be carried out from 5 to 40 °C, and higher temperatures had to be accessed using the resistive heating stage. Electrochemical control was applied to the system using a PicoStat Controller from Molecular Imaging in conjunction with the Digital Instruments control software. A silver quasi-reference electrode was used as a reference electrode, and an Au counter electrode was used. The electrochemical potentials discussed in this paper have been converted to the Ag/AgCl standard reference potential. Also, since both the potentials of the tip and substrate are controlled with the PicoStat, all potentials quoted here are the substrate potential with respect to the reference electrode. The tip bias quoted here is the potential of the tip versus the substrate potential.

3. Results and discussion

The sequence studied in this paper is an alternating guanine (G), cystosine (C) sequence with thiol linkers at the 3′ end, SH–$(CH_2)_3$–GCGCGCGC, plus the complement, and as such one thiol linker is on each strand of the DNA duplex. These sequences have been studied by a variety of methods including NMR, x-ray crystallography, circular dichroism (CD) spectroscopy and thermodynamics [34–36]. It forms stable B-form dsDNA helices in aqueous solution. Furthermore, this conformation is stable in moderate salt concentrations, meaning that the DNA can maintain the biological B-form duplex during our experiments.

Previously, Xu *et al* [23] reported a series of measurements done on such an alternating sequence and found the conductance to be $1.3 \times 10^{-3} G_0$. Along with this sequence that is 8 base pairs in length, this alternating GC sequence was measured at a length of 10, 12 and 14 base pairs in length [23]. As is shown in figure 2(b), the conductance varies linearly with the inverse of the length of the molecule. This observation is consistent with a sequential hopping mechanism [37, 38]. As is often discussed in photochemical measurements of DNA

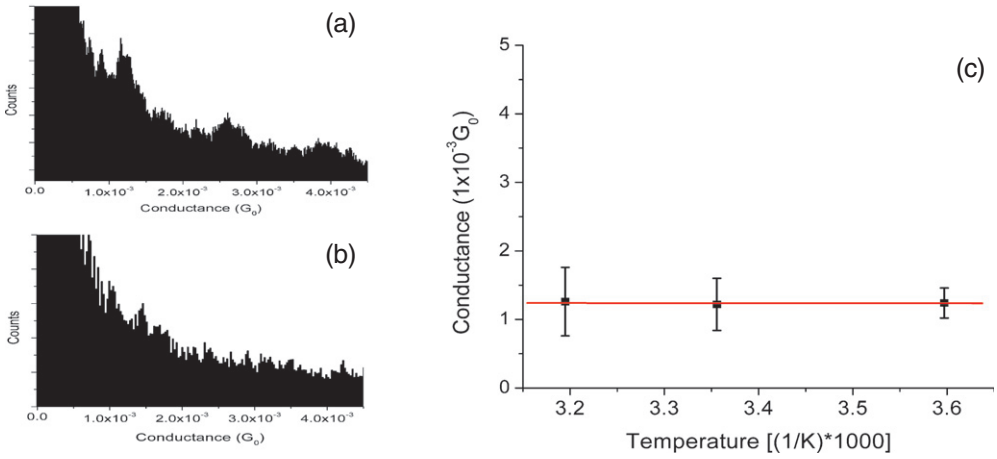

Figure 3. Temperature dependence of the conductance of DNA. (a) A conductance histogram of CG8 DNA at 5 °C. (b) Conductance histogram of CG8 DNA at 55 °C, no obvious peaks in the histogram. (c) Conductance of dsDNA versus 1/Temperature; no difference in the conductance was visible within the experimental temperature range.

charge transfer rates, and has been discussed at length by Jortner *et al* [13, 39, 40], appropriate coupling of the donor and acceptor to the bridge sites should allow a weak algebraic N dependence on the number of sites. However, it is also important to point out that charge transfer rate measurements and direct conductance measurements, while related, deal with some fundamental differences in the coupling to the macroscale systems involved. Nitzan has worked out a relation between these two, but the application of this relation requires one to use certain parameters that are not known in this system such as the coupling strength of the electrodes to the molecule itself [41].

3.1. Temperature studies

Since the preliminary studies have indicated that a thermally induced hopping mechanism may be involved in charge transport in DNA, one of the most important experimental variables one can access is a change in temperature. To this end, we have chosen one of the molecules in the above sequence to look for a temperature dependence of the conductance. However, as is shown in figure 3, no dependence was observed within the experimental temperature range. This sequence was measured from 5 to 40 °C using the Peltier stage as described above. A resistive stage was used to measure the DNA at 55 °C, and at this point fewer steps were observed (only 7% of curves are in the histogram), and no obvious peaks are seen. Attempting to push the temperature above 55 °C resulted in no valuable data. At these elevated temperatures, the leakage current quickly increased to the point where it was not possible to make any useful measurements. This effect is most likely due to the softening of the wax near the apex of the tip at higher temperatures. Furthermore, since the measurements are done in aqueous solution, the lower limit of the temperature range is near 0 °C. Also of note is the calculated melting temperature, T_m, of this sequence at this concentration and the salt concentration is 57 °C (calculated with Integrated DNA Technologies OligoAnalyzer 3.0). As such, the data at 55 °C seem reasonable, as 50% of the DNA is no longer hybridized, and measurements above this temperature should continue this trend. Therefore, the experimental temperature window where DNA exists in the duplex and the solution is not frozen is rather limited. However, is it still reasonable that no temperature dependence should be seen in this temperature range?

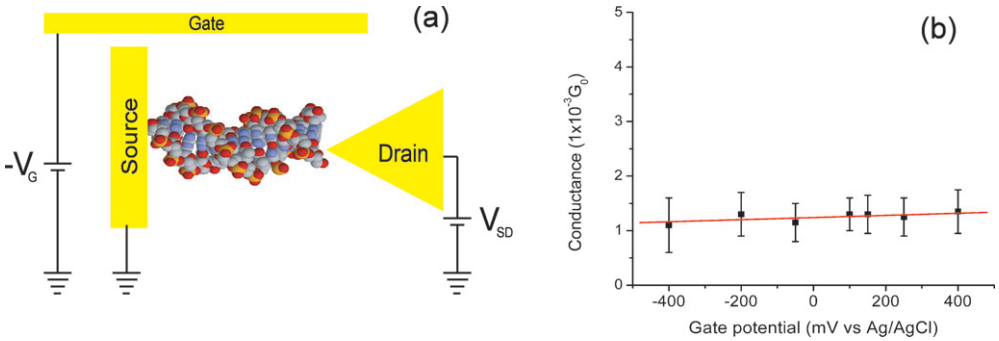

Figure 4. (a) Schematic illustration of the electrochemical gate applied to a dsDNA bound to the source and drain electrodes. (b) Conductance of CG8 DNA measured with varying gate potentials.

Recently, van Zalinge *et al* [42] also carried out a series of measurements on a SH–$(CH_2)_3$–$(G)_{15}$ sequence (plus complement), and also observed no dependence of the conductance on temperature. Although these measurements were carried out in air, and therefore the exact conformation is somewhat uncertain as it is known that the conformation of DNA depends on the humidity when it is not in solution phase [43, 44], those measurements were conducted over a similar temperature range to ours, and show similar results with a guanine rich sequence. However, if hopping is a thermally activated process one would expect a temperature dependence. Therefore, these results are a little perplexing. Nonetheless, if one considers a phenomenological activation process, such as $G \sim \exp(-E_A/kT)$, then as long as the activation energy is small, as would be expected when adjacent sites are nearly isoenergetic as in this case, then the effect of temperature may be small. Even so, with the associated error bars in our experiments, the maximum activation energy in our experiments could be as large as 116 meV and not be resolved in these measurements. It is also important to note that although some photochemical measurements were able to demonstrate large differences in charge transfer rates with temperature, sequences similar to the ones used in the present work, and with similar temperature ranges, were in some cases on the order of 10–20% [45]. Therefore, it seems that because the available temperature window is small that perhaps no temperature dependence should be seen for this specific sequence.

3.2. Electrochemical gate effect

Since the thermal measurements did little to elucidate the conduction mechanism in DNA, another variable that can be used to help determine the mechanism is the electrochemical potential of molecular junctions. Again, the alternating GC sequence of length 8 was used to probe the electrochemical gating properties of DNA conductance. The experimental setup is shown in figure 4(a). Two working electrodes (substrate and tip) serve as the source and drain electrodes, respectively, and the reference electrode acts as a gate; the counter electrode is omitted for clarity. Such a system can be used to help determine whether a two-step hopping mechanism or resonant tunnelling occurs, but as is seen in figure 4(b), little change in the conductance was observed when the gate potential varied between −400 and +400 mV versus Ag/AgCl. It was not possible to extend the range of the potential window due to the evolution of hydrogen and the oxidation of gold. In both cases, the number of curves with obvious steps decreased dramatically outside of this range.

It is well known that the bases in DNA are electroactive, guanine being the easiest to oxidize at 1.1 V versus Ag/AgCl, followed by adenine at 1.2 V versus Ag/AgCl. Alternatively,

cytosine is the easiest to reduce at −1.3 V versus Ag/AgCl [46]. Therefore, it may be possible that in this system the potential window is simply too small to effectively move the energy levels of the molecule into or out of resonance with the electrodes. It is known that the gating efficiency in an EC STM system depends significantly upon the specific details of the ionic screening and molecular size and position between the electrodes. Furthermore, the charge of the backbone and the counterions around the dsDNA may effectively screen the bases from some of the applied EC potential. As such, although there is no gate effect seen in this GC sequence in the potential window available, it is not possible to rule out either a thermally induced hopping mechanism or a resonant tunnelling mechanism, as the available potential window on an Au surface is too small to align with the energy levels of the bases.

4. Conclusions

Although DNA has been shown to be a promising material in nanotechnology, much still needs to be understood about its electrical properties. A wide range of experiments have shown that DNA is capable of charge transport at some level. However, using the STM break junction approach we studied the dependence of the conductance of single dsDNA molecules on temperature and electrochemical gate. In both cases, the conductance did not change noticeably until the junction properties were destroyed (at high temperature or large potential). Thus, although an alternating GC DNA sequence shows an algebraic decrease in conductance with increased length, other experimental handles cannot support any specific thermally activated process as the conduction mechanism because the system itself remains stable in only a small thermal or electrochemical potential window. However, these experiments do not provide insight into the possibility of a sequential tunnelling system, and this remains a likely mechanism for transport in these sequences. As such, much work is still needed to understand DNA charge transport in a solid-state system.

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