

Insulating behavior for DNA molecules between nanoelectrodes at the 100 nm length scale

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(Received 18 June 2001; accepted for publication 19 September 2001)

Electrical transport measurements are reported for double-stranded DNA molecules located between nanofabricated electrodes. We observe the absence of any electrical conduction through these DNA-based devices, both at the single-molecule level as well as for small bundles of DNA. We obtain a lower bound of 10 TΩ for the resistance of a DNA molecule at length scales larger than 40 nm. It is concluded that DNA is insulating. This conclusion is based on an extensive set of experiments in which we varied key parameters such as the base-pair sequence [mixed sequence and homogeneous poly(dG)·poly(dC)], length between contacts (40–500 nm), substrate (SiO₂ or mica), electrode material (gold or platinum), and electrostatic doping fields. Discrepancies with other reports in the literature are discussed. © 2001 American Institute of Physics.
[DOI: 10.1063/1.1421086]

Recently, a number of contradicting findings were reported regarding the charge transport properties of DNA.¹ The experiments appeared to indicate metallic,^{2–4} semiconducting,^{5–7} and insulating^{8,9} electronic properties. These transport experiments were inspired by electron-transfer experiments where one attaches donor and acceptor groups at both ends of DNA molecules and characterizes their electronic coupling through the DNA. Such experiments by Barton and co-worker¹⁰ and others showed that electron transfer is possible in DNA over distances of several nanometers. The results of some direct transport experiments have suggested that transport is also possible over much larger length scales, of the order of microns.^{2–4,7} In this letter, we report transport measurements on both individual DNA molecules as well as small DNA bundles (up to tens of molecules) that are connected on both sides to metallic electrodes. Our technique relies on well-defined electrodes with spacings in the range of 40–500 nm. Using state-of-the-art atomic force microscope (AFM) imaging we report images of individual DNA molecules positioned between electrodes. We find *no* evidence of any electronic conductivity for DNA molecules with various lengths and base pair sequences. Based on a set of experiments with a number of different sample layouts, we come to the conclusion that DNA at the single-molecule scale is insulating at length scales larger than 40 nm.

As an example of a typical result of our work, Fig. 1 shows a tapping-mode AFM height image of one of our devices with mixed-sequence double-strand DNA between gold electrodes spaced by 300 nm. On the SiO₂ in between the electrodes, individual DNA molecules are clearly discernable. Details of the assembly of this device are given below. The apparent height of the DNA is about 0.5 nm, and the width is about 10 nm, limited by the AFM tip radius. These values are typical of single DNA molecules.¹¹ From the height, width, and persistence length determined from the

images, we conclude that indeed individual DNA molecules are connected between our electrodes. No conductance was found for this device. The bias voltage was slowly increased to 10 V and the currents observed remained below a noise level of about 1 pA. From this experiment we thus obtain a lower bound of 10 TΩ for the resistance of this device, in which a total of about 10 DNA molecules were connected in parallel between the electrodes.

The outcome of this experiment is in clear disagreement with a number of previously reported experiments. To investigate whether our result is due to the intrinsic electronic properties of DNA or due to external conditions, a series of experiments was conducted in which a number of key parameters was varied, e.g., the base-pair sequence of the DNA, the type of substrate, the distance between the electrodes, and the contact material. An attempt was also made to dope the DNA electrostatically with an external gate electrode.

The basic sample layout for all experiments discussed in this letter is similar: DNA molecules are deposited from an aqueous buffer solution onto a substrate patterned with pairs of closely spaced thin metallic lines that are connected to larger pads which facilitate contact to the electrical equipment. The electrodes are fabricated using electron-beam lithography and subsequent liftoff. Noble metal (platinum and

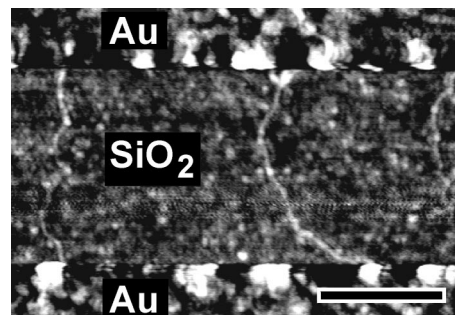


FIG. 1. Tapping-mode AFM height image of three DNA molecules connected between two gold electrodes that are separated by 300 nm. Scale bar: 200 nm. The measured resistance of this device was higher than 10 TΩ.

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gold) films were used as electrode materials. The metal thickness was about 15 nm, and was evaporated on top of a 3 nm titanium sticking layer. After liftoff, residues of the organic poly(methyl methacrylate) double-layer resist were removed by immersion in fuming nitric acid. DNA molecules were deposited from a 20 mM HEPES buffer solution (pH 6.5). The DNA concentrations were in the range of 1–250 ng/ μ l, and 5 mM of MgCl₂ was added to promote DNA adhesion to the surface. A droplet of about 3 μ l is deposited on the substrate for about 20 s, after which the sample is rinsed with de-ionized water and dried in a flow of nitrogen gas. The presence of DNA molecules was confirmed by AFM imaging. Electrical transport measurements were performed at room temperature under ambient conditions.

The first set of experiments discussed here was performed on DNA with a mixed sequence immobilized on a silicon oxide substrate. Because DNA binds only weakly to the SiO₂ and is easily rinsed off, we used DNA modified with thiol (–SH) groups at both ends of the molecule. The sulfur atom of the thiol group will bind strongly to the platinum or gold of the electrodes, which chemically anchors the molecule to the metal at its terminal ends. Double-strand DNA with a (CH₂)₆SH group at each 5' terminal phosphate was obtained by performing a polymerase chain reaction (PCR) with λ DNA as a template using thiolated primers, following the procedure of Hegner *et al.*¹² Dithiothreitol (DTT) was added to prevent oxidation of the thiols during the PCR. Using this technique, DNA fragments of 900 and 4500 base pairs were obtained and purified that were 300 nm and 1.5 μ m long, respectively. These fragments contain a mixed sequence of bases, and are representative of natural DNA. Figure 1 shows an AFM image of the 1.5 μ m fragments positioned on Au electrodes spaced by 300 nm. Because the DNA is much longer than the distance between the electrodes, a considerable length of DNA overlaps both electrodes and this facilitates good electrical contact. As mentioned above, no electron transport was observed for this sample. The same absence of conductance was observed for a number of similar samples with electrode spacings in the range of 200–500 nm.

Considerable effort was put into the fabrication of smaller spaced electrodes, without losing the possibility of imaging in between the electrodes using AFM.¹³ Figure 2(a) shows DNA located across a gap of about 40 nm. In this experiment we deposited DNA from a 1 ng/ μ l solution of thiolated PCR fragments of 900 base pair lengths. AFM inspection showed a small amount of DNA material between the electrodes. From the width and height of the DNA it is estimated that at most five DNA molecules are present in parallel between the electrodes. No charge transport was observed for bias voltages up to 10 V. From this experiment we again find a lower bound for the device resistance of 10 T Ω .

Experimental¹⁴ and theoretical⁹ studies of DNA charge transport suggest higher transport rates poly(dG)·poly(dC) DNA compared to for mixed-sequence DNA. To investigate this experimentally, we assembled devices with poly(dG)·poly(dC) DNA molecules with an average length of several microns.¹⁵ No thiol groups were present on this molecule. It was found that DNA is immobilized on the SiO₂ surface after rinsing and drying for relatively high DNA con-

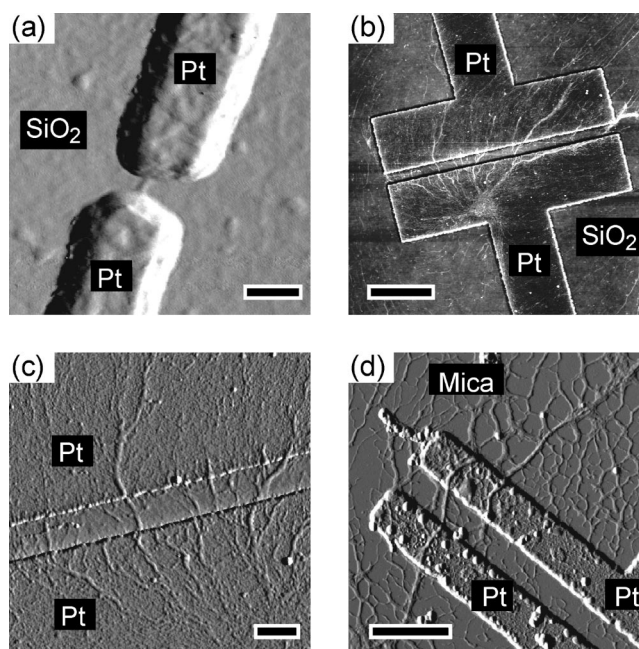


FIG. 2. AFM images of DNA assembled in various devices. (a) Mixed-sequence DNA between platinum electrodes spaced by 40 nm. Scale bar: 50 nm. (b) Height image of poly(dG)·poly(dC) DNA bundles on platinum electrodes. The distance between electrodes is 200 nm, and the scale bar is 1 μ m. (c) High magnification image of the device shown in (b). Several DNA bundles clearly extend over the two electrodes. Scale bar: 200 nm. (d) Poly(dG)·poly(dC) DNA bundles on platinum electrodes fabricated on a mica substrate. Scale bar: 500 nm. For all these devices, we observe an absence of conduction.

centrations of about 100 ng/ μ l in buffer solutions of 20 mM HEPES and 5 mM MgCl₂. Reactive-ion etching before metal deposition was used to make the surface of the platinum electrodes the same height as the SiO₂ substrate in order to prevent kinks in the DNA and to minimize tip convolution effects. Figure 2(b) shows poly(dG)·poly(dC) molecules on electrodes spaced by 200 nm. Figure 2(c) shows a magnification of the image displayed in Fig. 2(b). Due to the high concentration, not only single molecules are observed, but also thicker bundles of molecules, which are estimated to have at least 10 parallel strands of DNA. No conduction was found for these samples either. We estimate that in this experiment there are roughly 50 DNA molecules connected in parallel. Similar results were obtained on devices with a spacing of 100 nm.

Additionally we attempted to electrostatically dope the DNA with additional charge carriers in order to increase the conductance. This was done by applying a gate voltage to the silicon substrate with respect to one of the electrodes. No increase in conductance was found for gate voltages in the range of –50 V to +50 V. The thickness of the silicon oxide was 200 nm.

Finally, we discuss the possible influence of the substrate. Both Kasumov *et al.*⁴ and Cai *et al.*⁶ reported finite DNA conductance in devices in which the DNA was immobilized on mica substrates. Using a slightly modified fabrication recipe, we were able to fabricate patterned electrodes on mica substrates, with an electrode spacing of 200 nm. Figure 2(d) shows poly(dG)·poly(dC) molecules between platinum contacts on mica. DNA was deposited from a high-concentration buffer solution with approximately 250 ng/ μ l

DNA. Under these conditions, DNA self-assembles into networks similar to those observed in the work of Cai *et al.*⁶ Subsequent electrical transport experiments showed a high resistance of about $1\text{ T}\Omega$, a typical value that we also found for mica devices before DNA deposition. In a flow of dry nitrogen gas, this value was found to increase. We therefore attribute this background conduction to the thin water layer present on the hydrophilic mica.¹⁶

We conclude that DNA is insulating at length scales longer than 40 nm, with a $10\text{ T}\Omega$ lower bound for the resistance of a DNA molecule. Our experiments were performed using straightforward lithography, standard DNA buffer conditions, and high-resolution sample characterization using AFM imaging. The suggested formation of an electronic π band¹⁷ appears not to occur over length scales of 40 nm or more, even for homogeneous poly(dG)·poly(dC) sequences. In most theoretical models it is assumed that the charge transport rate through DNA decays exponentially with distance.¹⁸ Experimental evidence of exponential decay was reported by Cai *et al.*⁶ Our findings are therefore not necessarily in disagreement with DNA charge transport experiments performed on the scale of a few nanometers, where relatively high transport rates have been reported.^{5,10}

Our results are in agreement with the results of De Pablo *et al.*⁹ and with Braun *et al.*,⁸ who also found the absence of electronic transport through DNA. Clear disagreement is found with the work of Kasumov *et al.*⁴ and of Fink and Schönenberger³ who reported high conductivity of λ DNA on the scale of $0.5\ \mu\text{m}$. For a single DNA molecule about 500 nm in length, they observed typical resistances of about 300 k Ω and 3 M Ω , respectively, which is at least six orders of magnitude lower than that observed in our experiments. In the experiments by Fink and Schönenberger, a small DNA bundle was freely suspended in vacuum, but Kasumov *et al.* used a layout similar to ours. Kasumov *et al.* used electrodes consisting of thin rhenium film covered with sputtered carbon on a mica substrate. We use platinum and gold contacts instead, but we do not see how this difference can lead to the dramatically different experimental results. Cai *et al.*⁶ found resistance of about 200 G Ω for bundles of poly(dG)·poly(dC) at a length scale of 200 nm. If we com-

pare this value to our lower boundary of $1\text{ T}\Omega$ for similar bundles of 200 nm length, there is only a slight discrepancy.

Our results clearly limit the use of bare DNA as a conducting molecular wire. The self-assembling properties of DNA, however, may be very useful for nanotechnology, for example, as a scaffold to construct self-assembled electronics based on the technique of DNA metallization discussed by Braun *et al.*⁸

The authors thank E. Yildirim, H. W. Ch. Postma, K. A. Williams, B. Rousseeuw, A. K. Langen-Suurling, and R. N. Schouten for experimental assistance and discussions. This research was financially supported by the Dutch Foundation for Fundamental Research on Matter (FOM) and the European Community IST-FET project “DNA-based Electronics.”

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