

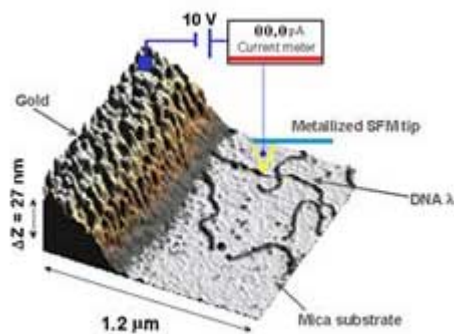
DNA: the miracle molecule.

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Abstract

DNA is a long molecule with a central role in biology. DNA molecules can be tailored to have almost any length between a few nanometers and several microns, its base sequence can be known with a high degree of accuracy, it is easy and cheap to synthesize and well characterized from a biological point of view. For these reasons and many others, the potential applications of DNA as a molecular wire are very appealing. A fundamental requirement for a molecule to be considered a molecular wire is the ability to transport electrical charge with a reasonably low resistance. Whether or not DNA is an electrical conductor is a question that seems to be very difficult to answer. Depending on the study DNA is a good conductor with linear I/V characteristics, a conductor with a gap that gets wider with temperature, a fairly good insulator, or even a superconductor with very low resistance at room temperature. In what follows we will briefly review the situation of DNA conductivity.



. Fig.1.a) Three-dimensional SFM image of the experimental set-up used for our measurements¹¹, showing three DNA molecules in contact with the left gold electrode. We also present a scheme of the electrical circuit used to measure the DNA resistivity.

Science is based on original ideas like using DNA as a molecular wire. Daniel Eley and D. I Spivey were the first to suggest DNA as an electrical conductor.

More recently, J. Barton and co-workers measured the charge transfer along a DNA chain by intercalating fluorescent molecules in the DNA base sequence. The results indicated that DNA might support electrical transport¹.

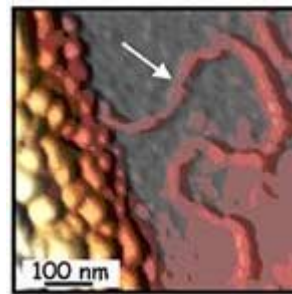


Fig.1.b) DNA image partially covered with gold

These studies have a significant importance in biology since electronic transport through DNA is essential in life processes, such as radiation damage and repair². However, the physical character of the problem of electronic transport through nanowires, and its importance for nanotechnology, has also motivated the study of DNA conductivity from a more physical point of view^{3, 4}. A clear breakthrough in these studies is the work by Fink and Schoenenberger⁵; using a low electron energy shadow microscope they were able to image and contact DNA molecules.

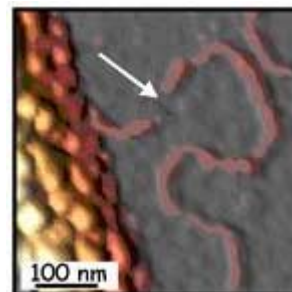


Fig.1.c) Same molecule after several contact experiments with increasing force. Observe the gap produced by the SFM tip.

In the experiments the authors observed low electrical resistance ($\sim 1 \text{ M}\Omega$) for $1 \mu\text{m}$ length λ -DNA chains⁶. Moreover,

following this work, DNA might behave as a ballistic conductor; in other words, charge can be transported through the DNA molecules with minimum (if any) energy dissipation. This result was confirmed two years later by another work by Kasumov et al.⁷. In this work, two metal electrodes were micro-fabricated on a freshly cleaved mica substrate, and then, double-stranded 16- μm -long λ -DNA molecules were absorbed connecting both electrodes. The authors reported superconductivity on DNA for temperatures below 1 K and even more important, the electrical resistance per molecule at room temperature was less than 100 k Ω . In fact, some of the molecules presented resistance about 12 k Ω suggesting again ballistic transport. Between those two results, different contributions indicate all kind of electrical behavior for DNA. Porath et al.⁸ obtained experimental evidences of electrical transport through Poly(G)-Poly(C) DNA⁹ chains suspended between two platinum electrodes only 8 nm apart. The non-linear current vs. voltage characteristics showed in this work presented a clear gap near 0 V. This gap gets wider as the temperature was reduced suggesting some kind of polaronic electrical transport. The resistivity of the molecules in this work was several orders of magnitude larger than the one obtained in^{5, 7}. Moreover, if the electrical transport were ballistic as suggested by^{5, 7} the well defined base sequence of Poly (G)-Poly(C) should increase the coherent electrical transport length reducing the resistance. Astonishing enough, the result reported in⁸ was the opposite of the expected.

Different groups have used Scanning Probe Microscopy to measure DNA conductivity. The experiments are performed on an insulating substrate: mica, glass, silicon oxide... partially covered with a metal: gold, platinum, cobalt... that is used as a first electrode. The molecules have one end contacting this electrode while the other end is on the insulating substrate (see figure 1). By contacting the free end of the molecule with a metal-coated Scanning Force Microscope tip (second electrode) the molecule is biased. Using this method, Cai et al¹⁰ were able to measure electrical transport in Poly(G)-

Poly(C) DNA molecules adsorbed on mica with resistance ranging between 10⁹ Ω and 10¹² Ω . Our group used a similar experimental set-up¹¹ to measure electrical current through λ -DNA chains (see figure 1) but no current was detected above our sensitivity limit (10⁻¹² A) obtaining a lower bound for 100 nm DNA molecules of 10¹² Ω . This absence of electrical current through DNA molecules was in good agreement with the first principle calculation also presented in reference¹¹. The computer simulations were performed on a Poly(G)-Poly(C) DNA chain with a unit cell of eleven base pairs (3.058 nm) showing two continuous energy bands separated by a gap of 2 eV¹². If disorder is introduced by swapping a (G) and a (C) the band structure is dramatically modified. The HOMO of the swapped guanine sinks 0.6 eV (15 times the HOMO bandwidth) into lower valence band levels. Thus, the band structure of λ -DNA is typical of an insulator. A. J. Storm has confirmed the conclusions obtained in¹¹ in a recent work¹³. The authors found a lower bound of 10 T Ω for the resistance of a DNA molecule at length scales larger than 40 nm. It is concluded that DNA is an insulator in clear disagreement with^{6,7}.

A final consideration that has to be done with respect to the different measurements on DNA conductivity is the role played by the contact electrodes. For example, in the case of carbon nanotubes, depending on the metal used as electrode, the contact resistance may vary from several M Ω , using platinum, to a few k Ω using gold. It could be that the situation for DNA is even more dramatic than in the case of carbon nanotube, and hence the electrical resistance is critical with the metal/s used to make the contact. In order to address this issue, we have carried out several contactless experiments^{14, 15} based on the electrostatic interaction between a metal covered SFM tip and a molecule. The experiment basis is shown in figure 2. Figure 2c shows an SFM topographic image of one DNA molecule parallel to a single walled carbon nanotube (SWNT), a well known molecular wire (upper molecule). None of these molecules are

connected to any metal electrode. After this topographic image, the tip is lifted 100 nm above the mica substrate while oscillating at the free cantilever resonance frequency (fig. 2a).

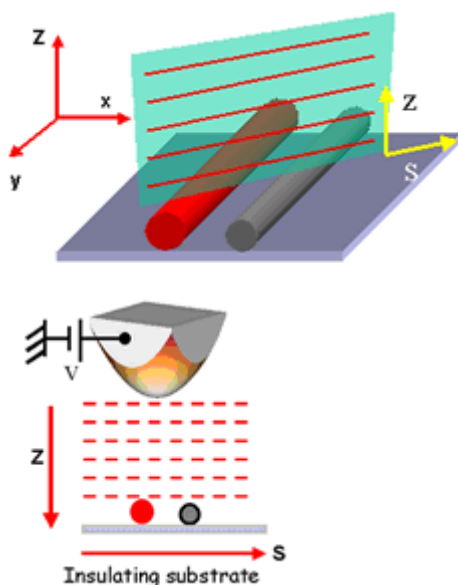
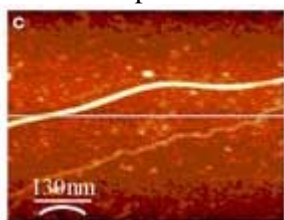


Fig.2(a) and (b) show a scheme of the contactless experiment performed on two different molecules co-adsorbed on an insulating substrate. Frequency shift measurements are taken at different tip-sample distances. In the experiment, the SFM tip never contacts the adsorbed molecules.

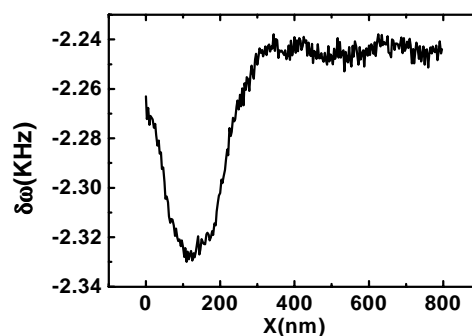
A bias voltage of +6 V is then applied to the metal-coated tip before scanning over the SWNT and the DNA molecule (fig 2b). As the tip approaches the surface a monotonic decrease of the resonance frequency $\delta\omega$ is observed due to the electrostatic force produced by the polarization of the mica. Figure 2d is a frequency shift plot taken along the blue line drawn in (fig. 2c), with the tip situated 10 nm above the surface.



(c) SFM topographic image showing a SWNT and a DNA molecule adsorbed on mica.

While a remarkable decrement of the resonance frequency appears at the nanotube position, no signal, above our noise level, is detected when the tip is over

the DNA molecule. Since the electrostatic force between tip and sample is basically produced by the effect of the polarization induced by the applied bias, the absence of a signal over the DNA molecule implies that the dielectric constant of the DNA and substrate are similar. No significant contrast was detected over the DNA molecule at any bias voltage between ± 10 V. On the contrary, the SWNT is a good conductor and hence its dielectric constant is very high. Thus, it presents a marked electrostatic signal with respect to the insulating substrate. If the experiment is repeated on a glass substrate a similar behaviour is observed. This result suggests that DNA molecules are insulators, and no matter the metal/s used to produce the contact no electrical current will pass through the molecule.



(d) Shows a frequency shift plot along the blue line drawn in figure 3c. A clear frequency shift is observed above the SWNT, whereas no measurable change appears above the DNA molecule. This profile was taken with the tip placed at 10 nm above the surface.

In our opinion electrical transport in conventional DNA was a mirage. Nevertheless, the final word has not been pronounced yet. New investigations on modified DNA may still provide interesting results. In addition, DNA can still be used as scaffold to construct self-assembled electronics devices as suggested by Braun et al¹⁶

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⁶ λ -DNA is a natural type of DNA. What matters for electrical conductivity is that the base sequence in this kind of DNA can be considered random.

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¹² The calculated band gap is 2.0 eV, but this number is to be taken with caution since DFT tends to underestimate band gaps in insulators. The experimental band gaps for DNA in solution are close to 7 eV, but most of this gap is due to solvent effects.

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¹⁵ A. Gil, P. J. de Pablo, J. Colchero, J. Gomez-Herrero and A.M. Baro. Submitted to Nanotechnology.

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