CMLS, Cell. Mol. Life Sci. 58 (2001) 1–3
1420-682X/01/010001-03 $ 1.50 + 0.20/0

CMLS Cellular and Molecular Life Sciences

Visions & Reflections

DNA and conducting electrons

H.-W. Fink

Physik Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich (Switzerland),
Fax +41 1 635 57 04, e-mail: hwfink@physik.unizh.ch

Received 29 June 2000; received after revision 27 October 2000; accepted 27 October 2000

The DNA molecule: a conducting nanowire

How do electrons behave in a DNA molecule? Are they all involved in more or less localized bonds, be it covalent or hydrogen-bridge bonds, or are there also free electrons present in the molecule? If so, can one take advantage of these mobile charge carriers confined to the elongated shape of the DNA molecule, which would then define a one-dimensional electrical conductor? These are the questions that this article will try to reflect on. Despite the fact that the chemistry of the DNA molecule happens to be extremely well understood, it has only recently been considered as a possible candidate for molecular wires. This might mainly be due to the fact that individual DNA molecules are much more difficult to observe than microscopic metal structures or carbon nanotubes: those can readily be visualized in conventional electron microscopes. Whereas chemists have developed a variety of tools and methods to precisely characterize and control an ensemble of DNA molecules, experiments on individual species require new approaches for visualization and manipulation on a molecular scale.

However, once the technology to image and manipulate individual molecules is readily available, the prospects of employing DNA as molecular wires are truly exciting. A great number of catalytic reactions, carried out by enzymes, are well known. They allow for multiplying, cutting and joining the DNA molecules. Length determinations on a large ensemble of molecules can be done by electrophoresis techniques. Filtering techniques are at hand to achieve monodisperse molecules at almost any desired length from a few nucleotides to macroscopic length scales. It is even feasible to design and construct two- as well as three-dimensional geometrical objects made up of DNA molecules [1]. Last, but not least, the DNA is soluble in water, and methods have been developed to stretch out long DNA molecules on various surfaces, including those of silicon wafers [2]. All this would, at least in principle, allow interfacing these biomolecules in a highly parallel fashion to structures produced by silicon technology. Provided the DNA is capable of carrying out electronic functions, this could be the beginning of a development that might lead to integrated DNA-based electronic devices.

Electron transfer versus electron transport

An electrically conducting wire is an elongated object capable of transporting charges from one place to another. Since molecular biologists, biochemists and physicists often use different languages, it is worth coming to grips with the definition of the term ‘charge transfer’ as opposed to ‘charge transport’.

Charge transfer processes and the distance and time scales involved are important events that relate to the functions of biological systems. The question is how effectively an electric charge, an electron or a missing electron can be transferred from one part of the system to another, a certain distance away. The charge might be injected into the biological system by a particular designed molecule attached to a specific site in the system. At a later point the absorption of the charge can subsequently be detected by another molecule located at a distant position from the emitting site, as illustrated at the top of figure 1. The pioneering work of Barton et al. [3] has provided detailed information about electron transfer in the DNA double helix. Electron donor respectively acceptor molecules are intercalated into DNA, and short laser pulses are used to monitor the electron emission and

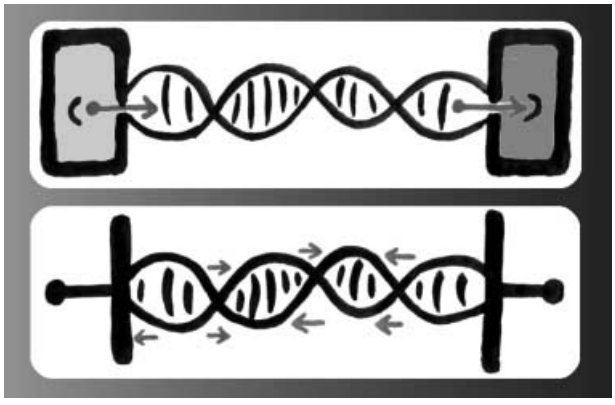

Figure 1. Schematic representation of electron transfer (top) and electron transport (bottom) processes through a DNA molecule.

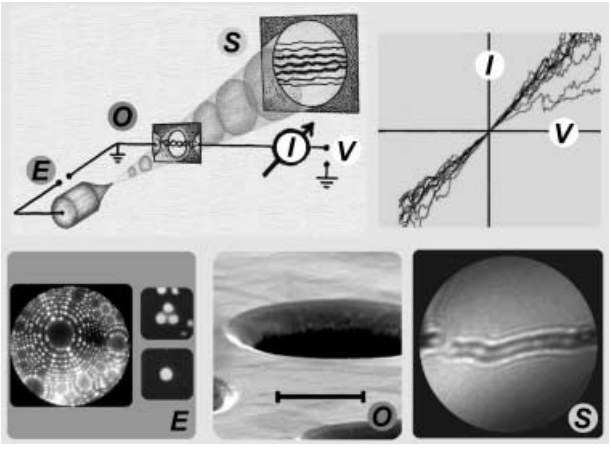

Figure 2. Imaging and in situ measurement of electron transport in DNA molecules is done using the LEEPS microscope. Electron Source (E), shaped by field ion techniques to the size of three or just one single atom, from which low-energy electrons are emitted. Object plane (O), an array of 2-µm-diameter holes in a thin film, provided by Quantifoil, over which λ-DNA molecules are stretched. The bar in the scanning electron microscope image of the sample holder corresponds to 1 µm. Screen (S) for the observation of the projection images of the DNA molecules. With a voltage (V) applied between the ends of a DNA rope, a current (I) signal is detected.

subsequent absorption processes. These charge-transfer processes are relevant for the biological function of the DNA and possibly link to such important processes as radiation damage repair. However, the study of charge transfer does not directly address the question of electrical conductivity. A prerequisite for electrical conductivity is charge transport. It requires the presence of charge carriers within the object at any time. Electrons must be able to move freely under ordinary thermal conditions, even in the absence of an external force, as sketched at the bottom of figure 1. If the system is not subject to an applied potential difference, the net current merely fluctuates around the zero value due to the statistical motion of the charges. The conventional way of probing the presence of mobile charges in macroscopic wires is to arrange for a small disturbance by applying a voltage. In a conducting material, the response of the system is an electrical current that follows the direction of the potential gradient.

There are two major problems in doing these sorts of experiments with DNA molecules: first, one has to be able to identify the 2-nm-wide biopolymer and, second, one has to attach leads to the molecules to probe their conductivity.

Contacting individual DNA molecules

In a macroscopic sample containing millions of DNA molecules the interconnections between the individual biopolymers limit the current that can flow between two macroscopic electrodes when a potential difference is applied to them. Since neither the details of the molecular arrangements nor the connections between the polymers are known, it is almost impossible to draw conclusions about the intrinsic properties of molecular conduction. Thus, it seems desirable to carry out such experiments on individual species.

The low energy electron point source (LEEPS) microscope [4] offers the unique possibility to image individual free-standing DNA molecules [5]. For the purpose of this short account, it appears appropriate to view this tool simply as an electron optical projection scheme, as illustrated in the top left part of figure 2. The key to the LEEPS technology is an electron source of atomic dimension. The emitted electrons exhibit a wavelength of the order of an Ångstrom and are thus capable of depicting individual DNA molecules. The image is generated by projecting the DNA molecule, stretched over a hole in a micromachined sample holder, onto a distant screen. The low energy of the electrons, between 20 and 300 eV, provides a high contrast in imaging unstained molecules and avoids radiation damage. In order not just to visualize the molecules but also to be able to manipulate them during observation, a manipulating tip, not shown in figure 2, is placed between sample and detector. Once the molecules are in contact with the manipulating tip, it is just a matter of applying an electrical potential difference between the manipulating tip and the grounded sample holder to probe the conductivity of the DNA. The I–V curves, also shown in figure 2, indicate ohmic-like behavior and exhibit a resistance value of 2.5 MΩ for a 600-nm-long DNA rope. This corresponds to a resistivity on the order of 1mΩcm [6]. Since we have no a priori knowledge about the potential drops at the contacts, the quoted resistivity value needs to be viewed as an upper limit for the DNA molecule alone. This was the first experiment

in which individual DNA molecules were imaged and contacted in situ to probe their conductivity.

More recently, a group from Delft University [7] reported further evidence for electron transport through individual DNA molecules. The researchers use an electric field to trap short synthetic DNA molecules between two electrodes of just 10 nm separation. Apart from the fact that the Delft experiment also detected a current, agreement with the previously discussed experiment is poor. The I–V curves are not linear but show a pronounced gap at low bias. The main difference between the two experiments is in the lengths of the molecules and in the way they were contacted. The contact resistances appear to be a major cause of uncertainty in all areas of molecular electronics. In the first experiment [6] the contact to both ends of the 600-nm-long DNA rope is made over an extended area to a gold layer, whereas in the trapping experiment [7] the DNA just fits the 10-nm separation between the two electrodes. The electric fields employed in the trapping experiments reported by the Delft group are about six orders of magnitude larger than typical fields for electrophoresis experiments, and it is not yet clear how the molecule is arranged between the two electrodes.

There have also been reports on using DNA as a template for metalization in order to arrive at a conducting metal wire [8]. In these findings, unless silver atoms are attached to the DNA molecule, it is interpreted as an insulator. It seems that the controversy surrounding the biochemical electron transfer experiments pioneered by Barton et al., persists among the community of physicists who have only recently started to study electron transport through individual DNA molecules.

But there is hope of resolving the major discrepancies apparent in the limited amount of conductivity data on individual molecules available today. The details of experimental arrangements – like the amount of control over contact resistances – could well account for quantitative disagreements in the resistivity values, although unless one uses insulating linkers to attach to the molecules, they would hardly explain the qualitative disagreements. There must be more intrinsic differences in the experimental setups. For example, they might be associated with the environment of the DNA molecules, in the way the molecules are able to exercise their internal degrees of freedom. It is known that the DNA is a rather flexible molecule able to undergo rapid internal fluctuations at finite temperatures. Whereas the π-electron overlap of the base stacking might not be significant in a model of static DNA, the internal vibrations could lead to temporarily close separations between the bases that would create freely moving electrons. A model of phonon-assisted charge migration was recently put forth and is described in detail by Handerson et al. [9]. If one accepts this model at least qualitatively, the three experiments mentioned above appear in a different light. In the first experiment [6] the DNA molecules are supported only at the contacts which are separated by at least 600 nm. A rich phonon spectrum is likely to be present under these conditions, and a current is consequently observed even at low bias. In the second experiment [7] the fixed contacts are only 10 nm apart. It is conceivable that such a short DNA molecule would not be able to build up large amplitude vibrational modes. In the third experiment [8] the DNA is adsorbed on a surface. Whatever the details of the binding to the substrate, it is most likely that the vibrational modes are significantly damped if not completely suppressed. Phonon-assisted charge migration should thus not be possible.

I would like to conclude this brief account on DNA conductivity with a speculative, possibly even provocative answer to the question: is DNA an insulator, semiconductor or metal-like conductor? A possible answer might be, all three: it just depends on the way one arranges the molecules on the structure on which one wants them to function in a certain way. If this should actually turn out to be true, it would make the DNA molecule an even more exciting candidate for possible future molecular electronic devices.

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