12. The choice of aqueous solution has an influence on the long-term reversibility of filling/emptying cycles. We tested aqueous solutions with a pH between 1 and 10, with a variety of dissolved salts (Na, K, Cs, Sm, Cl, SO_4, NO_3, acetate etc.) and also with dyes added to the aqueous solution (e.g., black ink and Cresol Red). In every case, tests always exceeded 1000 filling/emptying cycles. Our longest test involved 200,000 filling/emptying cycles with a CsCl solution, showing a perfectly reversible behavior. Note that surface-active components in the solution can affect the hydrophobicity of the microchannel walls; this can be compensated for by a change of the hydrostatic pressure in the communication channels.
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Proximity-Induced Superconductivity in DNA

A. Yu. Kasumov,[1,2]* M. Kociak,[1] S. Guéron,[1] B. Reulet,[1] V. T. Volkov,[2] D. V. Klinov,[3] H. Bouchiat[1]

Conductivity measurements on double-stranded DNA molecules deposited by a combing process across a submicron slit between rhenium/carbon metallic contacts reveal conduction to be ohmic between room temperature and 1 kelvin. The resistance per molecule is less than 100 kilohm and varies weakly with temperature. Below the superconducting transition temperature (1 kelvin) of the contacts, proximity-induced superconductivity is observed. These results imply that DNA molecules can be conducting down to millikelvin temperature and that phase coherence is maintained over several hundred nanometers.

The desire to use molecules as the ultimate building blocks of electronic circuits motivates the quest to understand transport in molecular wires. However, most molecules with delocalized electronic orbitals undergo a structural Peierls transition to an insulating state at low temperature (*1*). Few systems are exceptions to this rule, with carbon nanotubes being one of them (*2*). The situation of DNA molecules is controversial. Optical experiments have indicated the possibility of charge transfer in DNA molecules (*3*). As for transport measurements, some indicate that DNA molecules could be conducting (*4*, *5*), and others indicate that they are insulating (*6*, *7*). Fink *et al.* (*5*) found that a small bundle of DNA molecules suspended across a hole in a metallic grid had an ohmic behavior (linear IV curve). They found a resistance on the order of 1 megohm for a 1-μm-long sample. In contrast, Porath *et al.* (*7*) measured a single 10-nm-long DNA molecule that had been electrostatically trapped between electrodes 8 nm apart and found a nonlinear current voltage characteristic, with an insulating gap of several hundred millivolts.

Motivated by this puzzle, we performed transport experiments on DNA molecules connected to superconducting electrodes 0.5 μm apart. We observed a conducting behavior, with signs of proximity-induced superconductivity below the superconducting transition temperature of the electrodes. The proximity effect (PE)—the penetration of superconducting correlations in a nonsuperconducting (normal) conductor connected to it—has been extensively measured in metallic multilayers, mesoscopic wires made of noble metals (*8*, *9*), and more recently in carbon nanotubes (*10*). Observing a PE in DNA molecules implies that these molecules are conducting, that their phase coherence length is on the order of the length of the molecules, and that they form a low-resistance contact with the superconducting electrodes.

The experimental system consisted of double-stranded 16-μm-long λ-DNA molecules connecting two superconducting rhenium/carbon (Re/C) electrodes, deposited by sputtering on a freshly cleaved mica substrate. The Re film was 2 nm thick. The same nominal thickness of C did not produce a smooth film but rather a "forest" of individual fibers up to 40 nm tall (Fig. 1). The resistance of the Re/C bilayer was 100 ohm per square and underwent a superconducting transition around 1 K. The chosen thickness of the Re film was intended to minimize kinks in the DNA molecules at the edges of the metallic pads, because such kinks could hinder electronic transport from the contacts through the molecule. The deposited Re/C film was cut by a focused laser beam (Fig. 1A) in order to prepare six structures for transport measurements. Each structure consisted of a double submicron slit that separated the Re/C film into two broad electrodes. The resistance of the structures was more than 1 gigohm and decreased to several kilohm after deposition of DNA molecules.

In order to obtain aligned DNA molecules across the submicron gaps, we first glow-discharged the Re/C-covered mica substrate in the presence of pentylamine vapor, in order to promote adhesion (*11*). We then combed the DNA molecules using a continuous flow of DNA solution (*12*–*14*). After deposition, the samples were imaged with an atomic force microscope (AFM). The density of deposited DNA molecules depended on the duration of deposition. We prepared two samples with different estimated linear densities of DNAs perpendicular to the flow: 3000 and 6000 cm^{-1}, corresponding, respectively, to 4 and 10 min of adsorption time. We estimate that about 100 and 200 DNA molecules bridged the two electrodes in these two respective samples, yielding a total resistance of 3 to 4 kilohm and 2 to 3 kilohm, respectively, and corresponding to an average resistance of about 300 kilohm per DNA molecule. However, this number is probably overestimated, because only a fraction of the combed molecules is likely to be in good contact with the electrodes. We also checked that the resistance of the structures remained greater than 1 gigohm after treatment in a buffer solution (without DNA) flow. After DNA deposition, we attempted to isolate a single DNA molecule by destroying the other molecules with a low-power focused laser beam. To this end, we scanned the focused laser beam at low power (the beam diameter was about 1 μm, with power about 10 times less than used for cutting of the Re/C film) along the slit, except for a window that was left unetched. Scanning along the gap destroyed DNA molecules connecting the two electrodes and increased the resistance of the structure.

We present low-temperature transport measurements on three such structures: sample DNA1, with a 30-μm-wide unetched window, contained approximately 10 combed molecules as estimated from AFM observations; sample DNA2, with a 120-μm-wide window, had about 40 combed DNAs; and sample DNA3 had only a few molecules (probably two or three). The room tempera-

[1]Laboratoire de Physique des Solides, Associé au CNRS, Bât 510, Université Paris-Sud, 91405, Orsay, France. [2]Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences, Chernogolovka 142432 Moscow Region, Russia. [3]Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, Miklukho-Maklaya 16/10, Moscow 117871, Russia.

*Present address: Starlab, La tour de Freins, 555 rue Engeland 1180 Uclle, Brussels, Belgium.

ture (RT) resistance was 17, 11, and 40 kilohm, respectively. Measurements were made in a dilution refrigerator, at temperatures ranging from RT to 0.05 K, through filtered lines. Magnetic fields up to 5 T could be applied perpendicularly to the contacts and the molecules. The temperature dependence of the resistance of the three samples between RT and 0.05 K (Fig. 2) shows that down to 1 K, all three samples presented a moderate monotonous increase of resistance with decreasing temperature, which can be approximately fitted by a small negative exponent power law. The absolute value of this exponent increases with the resistance of the sample and can be determined within a 10% accuracy to be 0.03, 0.05, and 0.08, respectively, for DNA2, DNA1, and DNA3 (Fig. 2A). Over this temperature range, transport is ohmic.

The resistances R_m of DNA1 and DNA2 are on the order of the resistance quantum $h/2e^2 \sim 13$ kilohm, the maximum resistance of a phase-coherent conducting wire (above this value, strong localization is expected to take place) (*15*), indicating that the number of DNA molecules N_c participating in transport, with a typical resistance of N_cR_m, is on the order of one or two.

The temperature dependence changed dramatically below the superconducting transition of the Re/C contacts, around 1 K. The resistances of DNA1 and DNA2 decreased, by 75% at 0.05 K for DNA1 and by 15% for DNA2. The resistance of DNA2 increased slightly below 0.1 K (Fig. 2B). In contrast, the resistance of DNA3 (the most resistive sample) increased monotonically, with no change at the contact transition temperature. The transition observed on DNA1 and DNA2 was shifted to lower temperature in a magnetic field and disappeared at fields higher than 1 T, where the resistance increased with decreasing temperature, and all curves overlapped (Fig. 2B). We attribute these transitions to a lower resistance state to a proximity effect in the SNS (superconducting-normal-superconducting) systems constituted by DNA1 and DNA2 between the two superconducting electrodes. In contrast to DNA1 and DNA2, which had a positive magnetoresistance because of the PE (a magnetic field weakens the induced superconducting correlations and increases the resistance of the SNS system), DNA3 had a negative magnetoresistance up to 1 T (Fig. 2C). Further investigation with different field orientations with respect to the molecules may help discriminate between an orbital or spin origin of this singular magnetoresistance.

At low temperature, the transport on all samples was nonlinear (Fig. 3). In zero magnetic field, the differential resistance of DNA1 dipped at low voltage, with two sharp peaks at 300 μV (close to the gap of Re estimated around 200 μV at zero magnetic field), followed by bumps at higher voltage. The normal state resistance was recovered above 1 mV. This low-bias differential resistance dip became weaker and narrower at higher magnetic field and disappeared around 1 T. Above 1 T, the differential resistance peaked at zero current and was similar to that of DNA3. The behavior of DNA2 was intermediate, with a zero bias peak at all magnetic fields, within a larger dip that disappeared around 1 T. The differential resistance curve of DNA1 is reminiscent of what is observed in carbon nanotubes mounted on superconducting contacts, where the proximity-induced superconductivity is incomplete (*16*). The broad dip in DNA2 can also be interpreted as residual induced superconductivity. The most reasonable explanation for the different behaviors of the three samples is different transparencies of the contacts between the molecule and the superconducting film. It is also possible that the different base sequences in the different samples play a role.

After the samples were warmed to RT, microdrops of a saline buffer (1 mM $CaCl_2$

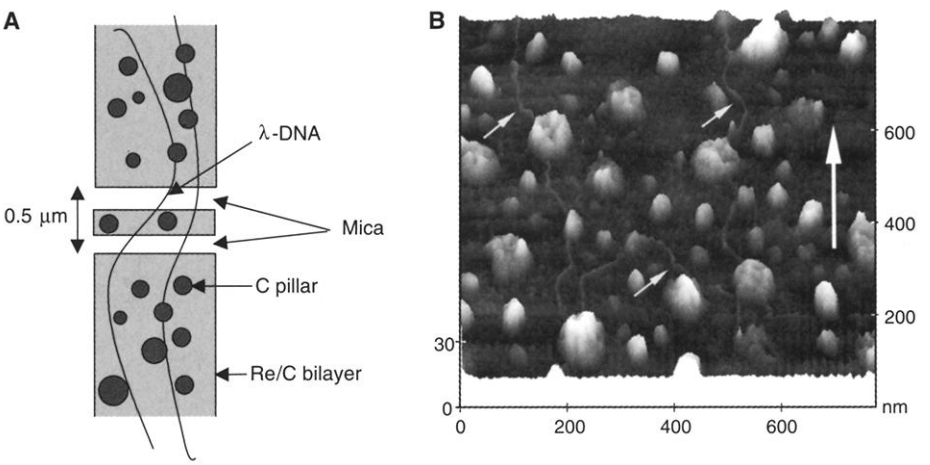

Fig. 1. Sample layout. (**A**) Schematic drawing of the measured sample, with DNA molecules combed between Re/C electrodes on a mica substrate. (**B**) Atomic force microscopy image showing DNA molecules combed on the Re/C bilayer. The large vertical arrow indicates the direction of the solution flow. The small arrows point toward the combed molecules. Note the forest structure of the carbon film.

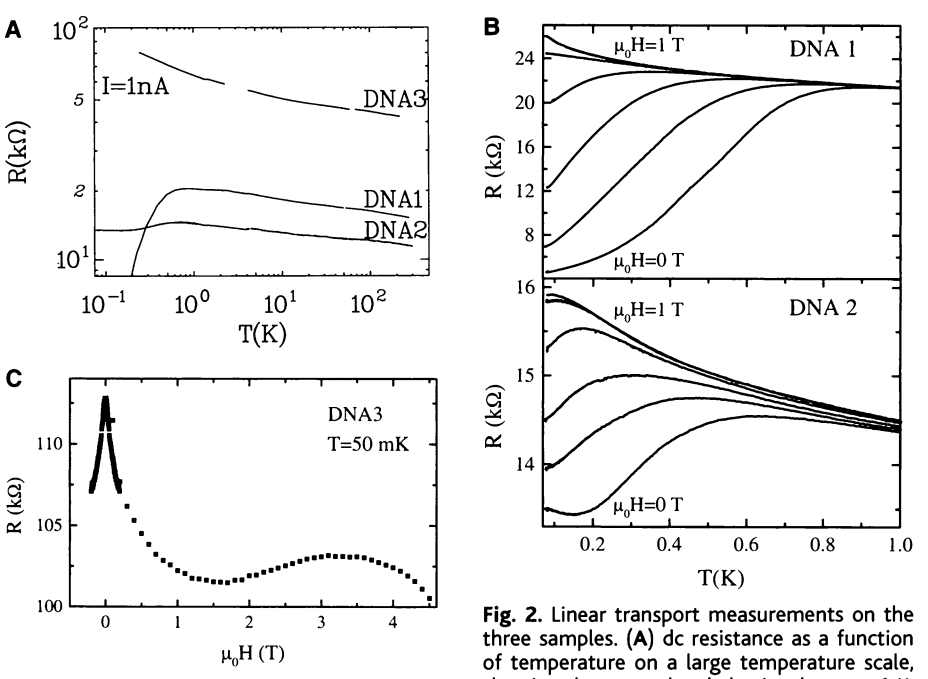

Fig. 2. Linear transport measurements on the three samples. (**A**) dc resistance as a function of temperature on a large temperature scale, showing the power law behavior down to 1 K. (**B**) dc resistance of DNA1 and DNA2 as a function of temperature, below 1 K, for different values of the magnetic field. μ_0H = 0, 0.2, 0.4, 0.6, 0.8, and 1 T for DNA1 and 0, 0.2, 0.4, 0.8, and 1 T for DNA2. (**C**) Magnetoresistance of DNA3 at 50 mK. All these measurements were done with an ac excitation current of 1 nA at 30 Hz.

and 10 mM tris) were continuously deposited on DNA1. The sample resistance remained identical to its initial value for more than half an hour of continuous buffer deposition. But when a deoxyribonuclease (DNAse) enzyme was added to this buffer, the resistance rapidly increased to about 1 gigohm after 30 s, providing additionnal proof that the transport was taking place through DNA molecules. Similar verifications were performed on the other samples. This test also shows that the conduction of DNA is the same in a dry and a biological environment. A systematic investigation as a function of the buffer's ionic concentration still remains to be conducted.

These experiments show that ohmic electric conduction can occur through DNA molecules over distances on the order of a few hundred nanometers, even at very low temperature. This result corroborates previous observations by Fink *et al.* (*5*), but we found resistance values one order of magnitude lower, for samples with comparable numbers of molecules. This is probably due to better contacts in our case. The power law temperature dependence is in agreement with the Luttinger liquid behavior expected in one-dimensional electronic systems (*17*). The measured value of the exponent is known to depend on the transparency of the contacts when their transmission is on the order or smaller than the resistance quantum, with no temperature dependence in the case of perfectly transmitting contacts (*18*). Our results

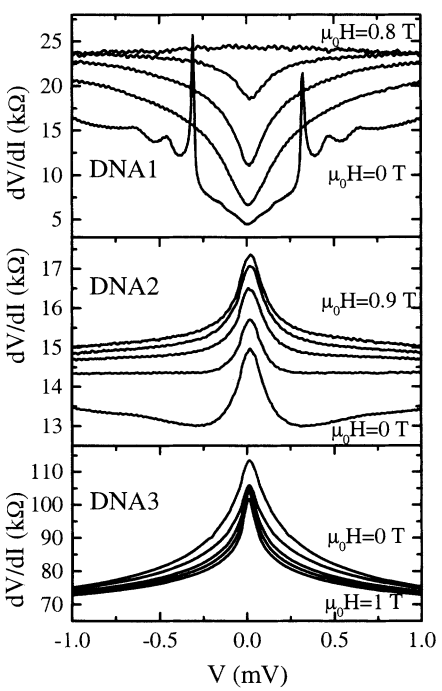

Fig. 3. Voltage dependence of the differential resistance measured at 50 mK in magnetic fields of 0, 0.2, 0.4, 0.6, 0.8, and 1 T for all samples. These measurements were done with an ac excitation current of 1 nA at 30 Hz.

show an increase of the power law exponent with the sample resistance value, in qualitative agreement with this prediction. Finally, observation of proximity-induced superconductivity indicates that electronic quantum phase coherence is achieved (*8–10*) in DNA molecules at low temperature on a length on the order of a few hundred nanometers. The physical mechanism involved in the conduction process remains unclear. The electronic structure of the molecules is not a priori favorable to the existence of chains of delocalized π orbitals along the molecule that would form a half-filled conduction band, as is the case in carbon nanotubes. On the other hand, several authors have suggested (*19*, *20*) that the structure of DNA with a π electron system of four bases stacked on each other can provide a mechanism of electron transfer along the DNA, involving hole hopping from one guanine base to the next. This conduction process is strongly dependent on the base sequence and is thermally activated; it should therefore lead to an exponential increase of resistance at low temperature, which is in strong disagreement with our experimental findings. It could, however, explain the temperature dependence observed in ac absorption experiments on unconnected DNA molecules (*21*). We should emphasize that the role of the contacts could be crucial in acting as strong electron or hole dopants. They could provide a sufficient number of carriers delocalized along the molecular wire because of the quasi-absence of electrostatic screening in one dimension (*22*). A systematic investigation of the transport properties of DNA molecules connected to metal contacts with different electronic work functions should be a way to shed light on this issue. The influence of the substrate may also be important. The surface of mica is known to be electrostatically charged because of the existence of uncompensated charges of OH^- ions, which also could affect transport through deposited DNA molecules. Finally, it has been shown that DNA molecules present self-assembling properties: They can be cut at precise points with specific enzymes and subsequently hybridized to complementary template (*23*). In this context, the present demonstration of conducting behavior of DNA molecules, when properly connected to electrodes, could yield interesting applications. For example, the presence of a particular sequence in a connected DNA molecule could be detected by a quick and simple conduction test using restriction enzymes cutting the DNA molecule at this particular sequence. One can also detect the presence of a very small number of molecules having a specific length in a solution (*24*). The accuracy of these tests requires straight combed molecules, which can be obtained using the method described in (*25*), where molecules are attached by one end on the substrate before combing. Also, previous experiments on a plastic DNA film (*4*) have indicated that the conduction of single-strand DNA could be considerably less than the conduction of double-strand DNA. If this property is confirmed at the single molecular level, it could be used as an efficient and cheap hybridization test on DNA chips (*26*).

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24. This can be done using a chip containing various pairs of electrodes characterized by a given spacing between them and subsequently combing DNA molecules across these electrodes. The presence of DNA molecules of length *L* will be characterized by electric conduction between electrodes separated by a distance smaller than *L* and the absence of conduction between electrodes separated by a larger distance.
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