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, SO₄, NO₃, 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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13. Supplementary material is available at www.sciencemag.org/cgi/content/full/291/5502/277/DC1.


Proximity-Induced Superconductivity in DNA

A. Yu. Kasumov,1,2* M. Kociak,1 S. Guérón,1 B. Reulet,1 V. T. Volkov,2 D. V. Klinov,3 H. Bouchiat1

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. (3) 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 buffer solution (without DNA) flow. 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 TEM 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-
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 $\hbar/2e^2 \sim 13$ 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 $N_{p}$ participating in transport, with a typical resistance of $N_{p}R_m$, 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 CaCl₂, www.sciencemag.org SCIENCE VOL 291 12 JANUARY 2001
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 coming. 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).

References and Notes
14. Two leveled plastic tubes connected to the outlets of a peristatic pump (in order to control the flow rate) were fixed on the sample holder touching the mica surface. The DNA solution [DNA (0.1 ngliter), 20 mM NH4Cl, 7 to 9 mM MgCl2] flowed from one tube into the other with a velocity of roughly 1 to 2 cm/s.
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.
26. It is, however, quite probable that the technique we have used to comb DNA molecules across the metallized contacts will not work for single-strand DNA because of a much lower rigidity of the molecule. This difference could also be used as an alternative hybridization test.
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