Metallic Conduction through Engineered DNA: DNA Nanoelectronic Building Blocks

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A novel way of engineering DNA molecules involves substituting the imino proton of each base pair with a metal ion to obtain *M*-DNA with altered electronic properties. We report the first direct evidence of metalliclike conduction through 15 μm long *M*-DNA. In contrast, measurements on *B*-DNA give evidence of semiconducting behavior with a few hundred meV band gap at room temperature. The drastic change of *M*-DNA conductivity points to a new degree of freedom in the development of future molecular electronics utilizing DNA, such as creating all-DNA junction devices for use as nanoelectronic building blocks.

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The use of DNA molecules in nanoelectronic circuits is very promising; their self-assembly and molecular recognition abilities may help alleviate the problems of interelement wiring and positioning at the nanometer scale [1]. While it has been proposed that the stacked aromatic bases of DNA may act as a "π-way" for the efficient transfer of electrons [2–4] and there have been reports that DNA may be a good linear conductor [5,6] others have found that DNA is only somewhat more effective than proteins as a conductor of electrons [7,8]. More recently, measurements of electrical transport through individual short (10 nm long) DNA molecules indicated wide-band-gap semiconductor behavior [9]. While the conductive properties of DNA may still be under debate, a reliable method for modifying the conductivity of DNA molecules would be much welcomed for DNA molecular electronics to become feasible. A novel way of "engineering" DNA molecules is being developed which involves substituting the imino proton of each base pair with a metal ion to alter the electronic properties of the DNA [10,11]. The resulting conformation is hereafter referred to as *M*-DNA. Initial fluorescence quenching and lifetime experiments of long *M*-DNA duplexes revealed features consistent with fast electron transfer [11]. Here we report the first direct evidence of metalliclike conduction through 15 μm long *M*(Zn)-DNA. For comparison, the same measurements were performed on *B*-DNA before conversion into *M*-DNA, and the results show semiconducting behavior with a band gap of a few hundred meV at room temperature. The drastic change of DNA conductivity enabled by engineering normal DNA into *M*-DNA allows all-DNA molecular devices to be realized.

The *M*-DNA used in the experiments has a Zn^{2+} metal ion replacing the imino proton of every base pair (Fig. 1) [10,11]. The estimated spacing between metal ions is about 4 Å regardless of sequence [11]. We used phage λ-DNA in our experiments which is about 15 μm long and has "sticky ends" which can be utilized to bind each end in turn to an individual electrode [12]. Conversion of the *B* form of λ-DNA into *M*-DNA is accomplished by the addition of 0.1 mM Zn^{2+} at *p*H 9.0 [13].

Preliminary conductivity experiments were performed with DNA strands placed between lithographically patterned gold electrodes on an insulating substrate, similar to what we used for conductivity measurements on carbon nanotubes and nanotube heterojunctions [14]. The results were difficult to quantify as the possible contribution of the DNA buffer solution on the measured electrical characteristics could not be assessed. We found that exposing the samples to "freeze-dry" methods could not rule out this contribution because of the existence of salt bridges formed on the substrate surface between electrodes. To address this problem we implemented a new design by placing DNA between two electrodes separated by a deep physical gap of width 1–30 μm and practically infinite depth [15] (Fig. 2). The interelectrode gap width was measured optically.

Four types of λ-DNA samples were prepared for conductivity measurements.

(1) *B*-DNA in standard buffer at *p*H 7.5 was dropped across the electrode gap and then dried *in vacuo*.

(2) *M*-DNA was prepared in 0.1 mM Zn^{2+} at *p*H 9.0 [10,11] and placed across the gap as above.

(3) *B*-DNA samples were prepared by making use of the DNA oligomer-based "gluing" technique [12] in which the

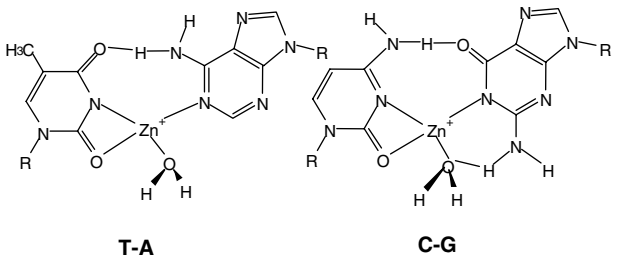

FIG. 1. Base-pairing schemes for *M*-DNA [10]. The imino protons with coordination to the N3 position of thymine and the N1 position of guanine are replaced by the Zn^{2+} ion.

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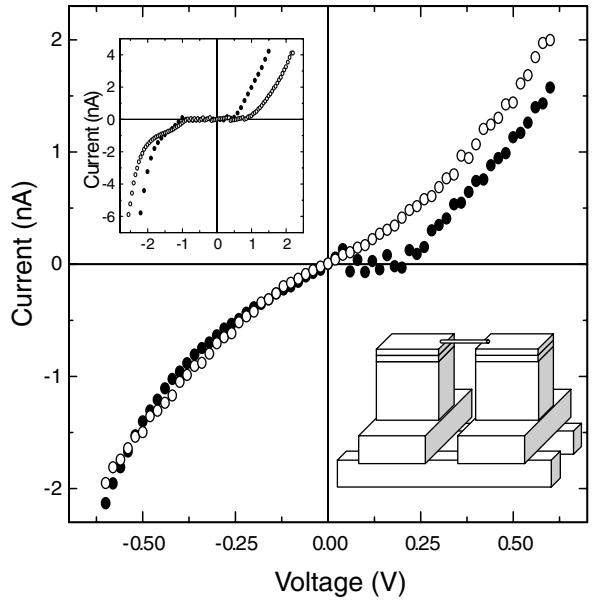

FIG. 2. Current-voltage curves measured in vacuum at room temperature on M-DNA (∘) and B-DNA (•) molecules. The DNA fibers are 15 μm long and the interelectrode spacing is 10 μm. In contrast to the B-DNA behavior, M-DNA exhibits no plateau in the I-V curve [16]. Lower inset shows a schematic experimental layout [15]. Upper inset shows two representative current-voltage curves measured in vacuum at room temperature on samples of type 3 (Au–oligomer–B-DNA–oligomer–Au in series) [17].

sticky ends of the DNA were attached to surface-bound oligomers.

(4) B-DNA at pH 7.5 with 0.1 mM of Zn^{2+}. At this pH M-DNA does not form but the contribution of DNA surface-bound Zn^{2+} ions on the measured electrical characteristics can be determined.

Conductivity measurements were performed on DNA bundles (ropes) of $\sim 10^2$ molecules each, as estimated from atomic force microscope (AFM) images (Fig. 3), both at ambient conditions and in vacuum. An example of current-voltage (I-V) curves measured in vacuum (10^{-3} Torr) at room temperature on samples of types 1 and 2 is shown together in Fig. 2 for comparison. A semiconductorlike plateau (conductance gap) of about 200 meV is observed for B-DNA (type 1), whereas this plateau disappears (or, at least, shrinks to a value which cannot be resolved at room temperature) in the case of M-DNA (type 2). The similar current flowing through type 1 and type 2 samples at high voltages (Fig. 2) strongly suggests a similar number of DNA strands crossing the gap between electrodes. Thus, the qualitative difference in I-V characteristics of M- and B-DNA samples we observed at low bias can only be attributed to a difference in their conduction mechanisms [16].

Typical I-V curves for samples of type 3 with "glue" oligomers are shown in the inset of Fig. 2. The recent finding [9] that short DNA oligomers behave like wide-band-gap semiconductors suggests that in type 3 samples the oligomer-associated contribution dominates the I-V plateau when measured in series with the B- (narrow-band gap) DNA molecules (Au–oligomer–B-DNA–oligomer–Au in series). This finding is in agreement with our data: The plateau observed is relatively large and varies between 1–2 V for different type 3 samples.

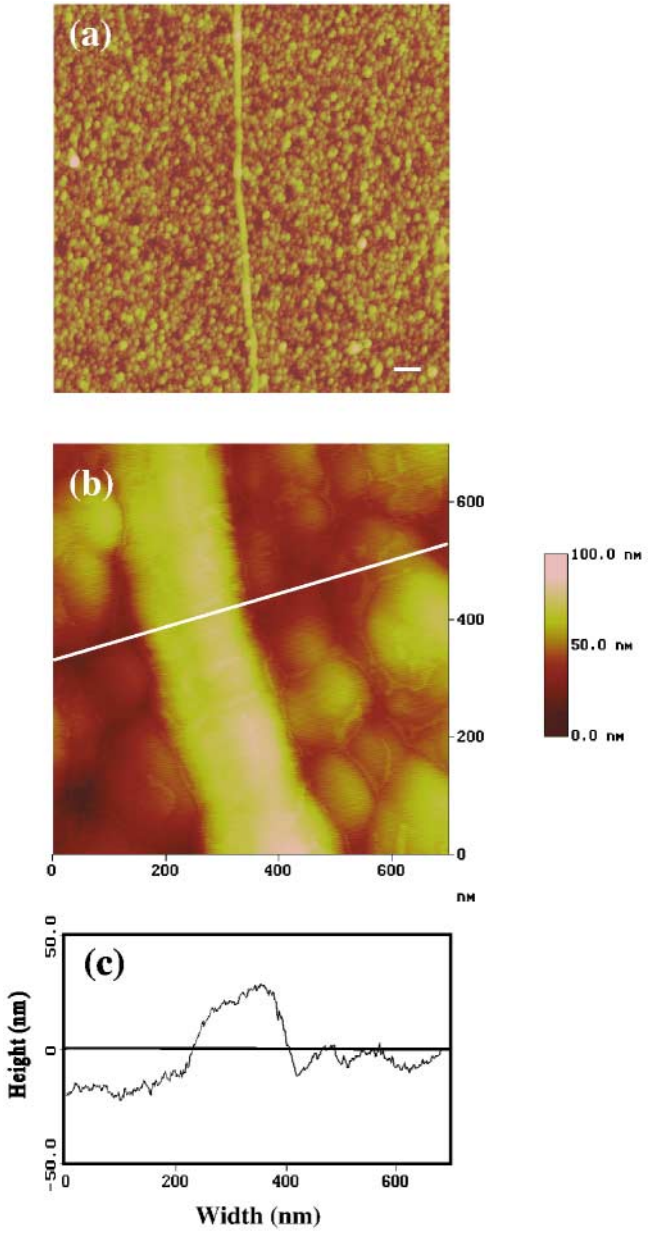

FIG. 3 (color). Images of a M-DNA bundle on the surface of gold electrode (type 2). (a) AFM image of the M-DNA bundle (scale bar: 1 μm). (b) AFM image of the M-DNA bundle at high resolution. (c) Cross section made along the white line in (b) using tapping mode AFM giving a bundle height of 20–30 nm and width of about 100 nm, which implies it consists of $\lesssim 3 \times 10^2$ DNA strands [18].

To verify that the DNA I-V characteristics are not due to buffer residuals or metallic ions adsorbed on the DNA surface we performed additional control experiments: For interelectrode spacing >1 μm we found that filling the gap with buffer and $ZnCl_2$ even at concentrations 10 times

exceeding those used in our experiments did not produce any appreciable signal (noise of <1 pA amplitude at 10^{-3} Torr vacuum). For further independent confirmation we measured type 4 samples (B-DNA at pH $= 7.5 +$ 0.1 mM of Zn^{2+}) and in contrast to unmodified B-DNA samples of type 1, there was no plateau in the I-V curve. However, the zero bias conductance was 3 orders of magnitude less than the characteristic M-DNA conductance.

It has been known that for surface states, phonon-assisted hopping provides the dominant contribution to the conductivity at room temperatures [19]. We can estimate the characteristic times of electronic transport through an M-DNA by calibrating against the result from type 4 samples. Given a residence time τ_r of a few picoseconds in the case of type 4, which is normal for a phonon-assisted charge transfer [19] [$\sigma \sim Ne^2d^2/T\tau_r$, σ being the conductivity, N being the effective concentration of electrons, d being the hopping length (base to base distance), and T being the thermodynamic temperature, $k_B = 1$], the measured M-DNA conductance implies that the electronic times τ_e for M-DNA are in the femtosecond range, characteristic of metalliclike behavior [20] ($\sigma \sim Ne^2d^2/T\tau_e$, $\tau_e^{-1} \sim 1/m_e d^2 \sim \varepsilon_F$, m_e being the electron mass, ε_F being the Fermi energy, $\hbar = 1$). Our findings can further be compared with fluorescence quenching experiments performed on long M-DNA molecules with fluorescein and rhodamine at opposite ends [21]. A charge transfer was observed over 500 base pairs in about 3 ns, which yields a diffusion transfer rate of over 10^{14} s^{-1} reasserting the metalliclike conduction through M-DNA molecules.

The nature of electronic transport through B- and M-DNA depends both on the properties of their internal structure and the DNA-electrode contact. Taking the common assumption of tunneling barriers at the DNA-gold contact [9], the difference between the Fermi level of the gold electrode and the edge of the molecular band of B-DNA suppresses tunneling through the electrode-DNA contact barrier. A large enough voltage bias applied to B-DNA can remove that difference to make electronic injection from the electrode to DNA feasible, which explains the plateau in the B-DNA I-V curves [22]. This picture modifies the Aviram and Ratner model [23] for charge transfer through organic molecules to accommodate transport through long DNA sequences [24,25], where an overlap of electron wave functions creates the "π-way" taken together with the periodicity of DNA structure, and molecular band formation can result. Inserting metal ions results in the formation of a d band aligned with the electrode Fermi level. As a result, injection of electrons (or holes) exhibits no voltage threshold and, consequently, no plateau appears in the I-V dependence.

A shift of I-V curves towards positive voltages observed for B-DNA (Fig. 4) may be attributed to the buildup of internal electrical fields due to the presence of a characteristic double-well (DW) potential [26] associated with the

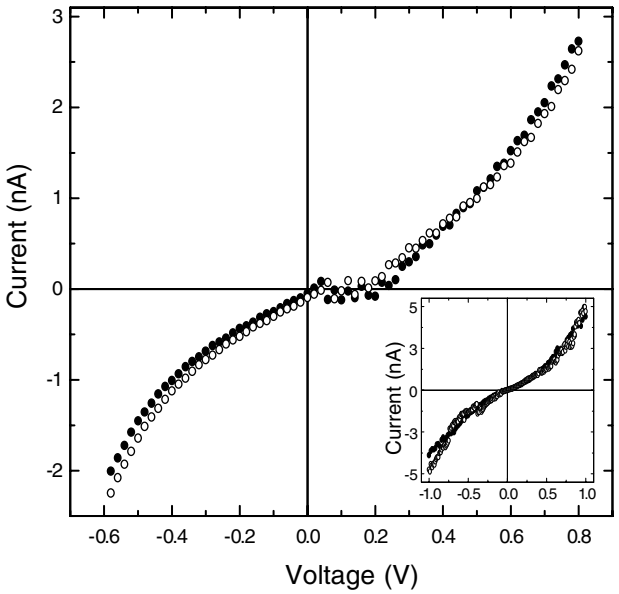

FIG. 4. Representative current-voltage characteristics measured at room temperature on samples of type 1 (B-DNA). The shift in I-V characteristics towards positive voltages is observed which disappears when B-DNA is converted into M-DNA form (inset shows similar symmetric I-V curves obtained for two representative M-DNA samples).

imino protons in the center of the helix with coordination to the N3 of thymine and N1 of guanine in every base pair (Fig. 1). In M-DNA, the imino protons are replaced with Zn^{2+} substantially deepening the local potential relief due to the strong hybridization of p-nitrogen and d-zinc electron states [27]. This, in turn, means sufficient chemical bond contraction with a DW collapse [26] at room temperature.

In summary, direct conductivity measurements on M- and native B-DNA 15 μm long macromolecules indicate the difference in their conduction mechanisms. The evidence of metalliclike conduction through M-DNA is found, while B-DNA exhibits the narrow-band-gap semiconductor behavior. The ability to convert normal DNA into M-DNA and the resultant drastic change of DNA conductivity opens up a whole new range of opportunities for molecular electronic engineering, and provide us a new degree of freedom in molecular electronics and sensor designs.

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[15] The formation of the microgap is accomplished as follows. Initially, thin metallic layers (Cr-Au or W-Pt-Au) of less than 1 μm in thickness were sputtered onto a thick dielectric substrate. The multilayer film ensured good adhesion to the substrate and enhanced chemical stability. The samples were then cracked by force mechanically, brought back together again, and later glued to a rigid support frame while applying external pressure. We are able to control the interelectrode spacing down to about 1 μm. The presence of such a gap between the electrodes ensures that no traces of solution but those adsorbed on the DNA surface remain within the interelectrode space.
[16] Quantitative information about the DNA-associated electronic density of states could be extracted from dI/dV data related to zero bias conditions if we knew the contact barrier transmission coefficients. In contrast, the I-V behavior at higher voltages is mainly due to the barrier characteristics themselves. From this standpoint, the similarity of the I-V curves between the highly biased B- and M-DNA strands appears to be due to the similarity in the characteristics of the tunneling barriers of the DNA-electrode contact. Once the applied bias has aligned the electrode Fermi level with the edge of the B-DNA molecular band, electronic transport becomes similar to that through the M-DNA, where no appreciable conductive band offset exists.
[17] Wide-band-gap semiconducting behavior is observed. I-V curves show a variation of the width of the voltage gap between 1–2 V similar to [9].
[18] The apparent discrepancy in the width of the DNA bundle in Fig. 3 is likely caused by the "convolution effect" due to the lateral interaction of the sample and the progressively tapered AFM tip. Such interaction can result in the bundle appearing wider than it really is (DI 3100 User's Manual). We estimate the true bundle width as $\sim$100 nm by using the points at which the cross section begins to taper downwards on either end of the bundle plateau.
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