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Electrical Conductance

Direct Conductance Measurement of Individual Metallo-DNA Duplexes within Single-Molecule Break Junctions**

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DNA, as the product of million years of evolution, possesses the maximal density of functionalities embedded in its framework and superior sequence-specific self-assembly properties that make it a useful scaffold for the organization of molecules into higher-order nanostructures for the development of functional nanoscale devices and materials.[1] In this context, one major effort is to transform DNA into a conductive material that would make a significant contribution to the development of the vibrant field of DNA-based molecular electronics.[2] It turns out that unmodified DNA lacks sufficient electrical conductance, thus making it unsuitable for application in nanoelectronics.[2,3] To address this issue, a fascinating alternative solution of recent years is to exchange some or all of the Watson–Crick base pairs in DNA by metal complexes in a programmable fashion pioneered by Shionoya, Schultz, Carell, Müller, and others.[3b,c,4] The combination of DNA and functional metal complexes can introduce significant advantages for both the metals and the DNA structures, thus representing an important step for their potential application as nanomagnets,[4a,5] as self-assembling molecular wires, or as catalysts in chemical reactions. With a focus on DNA-based molecular electronics, it is currently urgent to unambiguously characterize the electrical conductance of these metal-containing DNA strands. Herein we demonstrate the first direct charge transport (CT) measurement of individual metallo-DNA duplexes using single-molecule break junctions (Figure 1). These findings provide a foundation for DNA-based hybrid materials as conductive biocompatible bridges that may interface electronic circuits with biological systems.

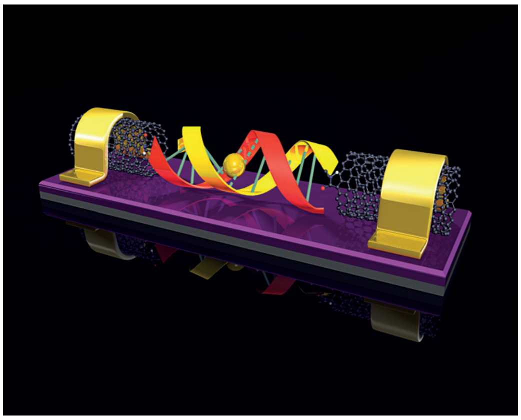

Figure 1. A schematic depiction of the single metallo-DNA device structure.

Numerous CT measurements on DNA strands that bridge two electrodes have been performed in an effort to explore the conductance of DNA (ref. [2f] and references therein). The reported resistance values in the literature spread over a great range from 1 to 1×10^{7} MΩ, a fact resulting from the differences in experimental techniques (connection to DNA, contact configuration, humidity, surface effects) and the plethora of sequences studied.[6] Recently we developed a system for measuring the conductance of a single molecule covalently immobilized within a nanotube gap.[7] In this system, gaps are formed in carboxylic-acid-functionalized single-walled carbon nanotubes (SWNTs) that can be reconnected by one or a few molecules attached to both sides of the gap through amide bond formation. Consequently, the devices are sufficiently robust so that a wide range of chemistries and conditions can be applied. By using this method we have made molecular devices that detect the binding between proteins and substrates at the single-event level,[8] and that probe charge transport dependence of a single intact DNA duplex on π-stacking integrity.[9]

The nanogapped SWNT point contacts were fabricated by the lithographical method described in detail elsewhere.[8,9]

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Three different DNA duplexes that are functionalized with amines at both ends were used in this study (Figure 2; see the Supporting Information for metallo-DNA synthesis). ODN–**H1** is a 15 nucleotide duplex with one pair of oppositely positioned hydroxypyridone nucleobases (**H**) as flat bidentate ligands in the middle, which form a stable metal-mediated base pair in the presence of a Cu^{2+} ion (**H**–Cu^{2+}–**H**), a motif geometrically similar to the hydrogen-bonded natural base pairs.[10] ODN–**H3** possesses three consecutive pairs of hydroxypyridone nucleobases in the middle of the 15-meric sequence, and ODN–**H0** is a natural 15-meric DNA duplex that contains a stretch of Watson–Crick pairs in this region as a control (Figure 2b).

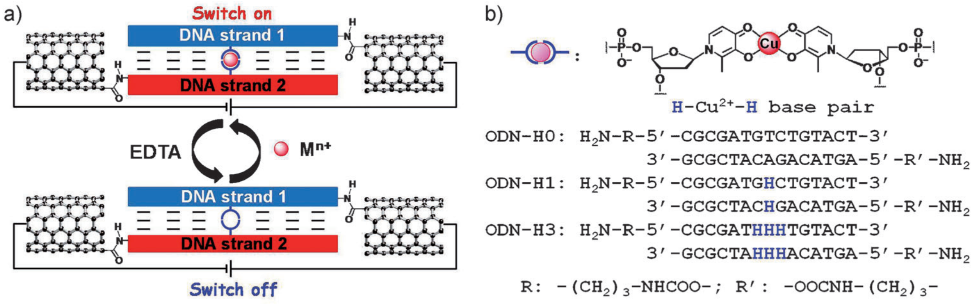

Figure 2. Components of metallo-DNA-bridged devices. a) Schematic representation of the sensing process. b) The molecular structure of the Cu^{2+}-mediated base pair based on hydroxypyridone nucleobases (**H**) and the DNA sequences used in this study. More details can be found in the Supporting Information.

The carbon nanotube ends were reconnected with individual amine-modified metallo-DNA duplexes in a two-step manner under mild conditions.[8b,9] Prior to the reconnection, metallo-DNA duplexes were prepared by the treatment of amine-modified DNA double strands, ODN–**H1** and ODN–**H3** (10 μm), with excess Cu^{2+} ions (2 equiv for ODN–**H1** and 6 equiv for ODN–**H3**). Under this condition, the hydroxypyridone nucleoside quantitatively forms a 2:1 metal complex (**H**–Cu^{2+}–**H**),[10] namely, almost all the DNAs were considered to contain one (ODN–**H1**) or three Cu^{2+} ions (ODN–**H3**) in the middle of the duplexes. Hereafter, these metallo-DNAs are denoted by ODN–**H1**–Cu^{2+} and ODN–**H3**–Cu^{2+}, respectively. Next, the freshly-cut carbon nanotubes were immersed in a 50 mm 2-morpholinoethanesulfonic acid (MES) buffer solution (pH 4.7) that contains standard amide coupling and activating agents (Sulfo-NHS, EDCI). Then, the activated carbon nanotube termini were reacted (phosphate-buffered saline (PBS) solutions, pH 7.2) with the amine-modified metallo-DNA duplexes (10 μm) to covalently bridge the gaps. The unreacted metallo-DNA and excess Cu^{2+} ions were washed off, and the devices were dried by a stream of nitrogen under ambient conditions. Note that conductance measurements for both metal-free ODN–**H1** and ODN–**H3** out of 1200 devices failed, most likely due to their high ohmic resistance resulting from hydroxypyridone nucleobases behaving like a mismatch in the absence of metal ions.[9,11] Considering that the cross-section area of DNA duplexes (ca. 3 square nm) is comparable to that of the SWNTs used here (< 3 square nm), it is unlikely that more than one DNA duplex can fit within the gap lengthwise. By applying the S/D bias voltage to metal contacts attached to the nanotubes and the gate bias voltage to the doped silicon as a global back-gate electrode, we can tune the carrier density in the devices. The measurements were carried out under ambient conditions with a constant moisture content (30%).

The current–voltage (I–V) curves for a representative device reconnected by ODN–**H1**–Cu^{2+} at different stages are shown in Figure 3. The black curve describes the source–drain current (I_D) as a function of the gate voltage (V_G) at a constant source–drain bias (V_D) of −50 mV for the pristine nanotube, representing that the SWNT before cutting shows a typical p-type semiconducting property. After cutting and initial treatment of the gap with coupling agents, the device shows no

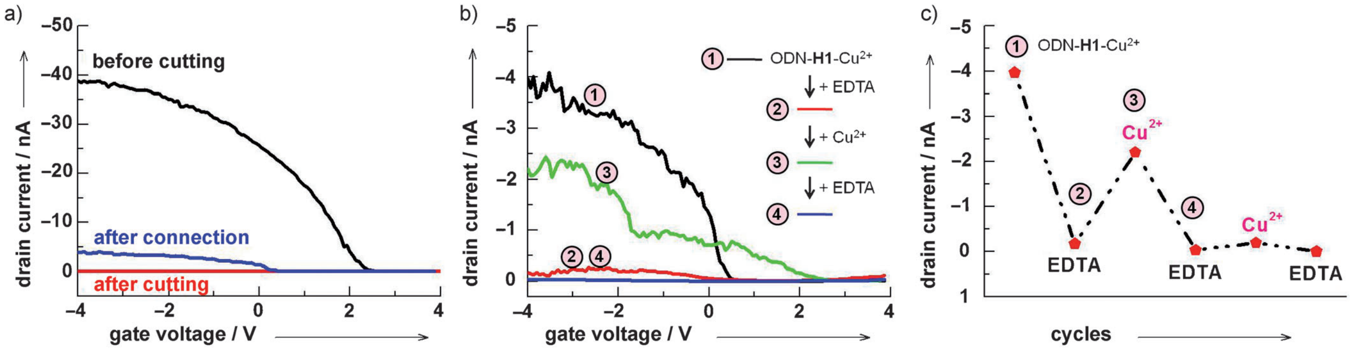

Figure 3. Electrical characteristics of metallo-DNA-bridged devices. a) Device characteristics of a typical device reconnected by ODN–**H1**–Cu^{2+} before cutting (black curve), after cutting (red), and after DNA reconnection (blue). b) The I–V curves of the same device at different stages; after DNA reconnection (black: 1), after the first EDTA treatment (red: 2), after further Cu^{2+} ion treatment (green: 3), after the second EDTA treatment (blue: 4). c) The switching cycles for the same device upon alternate treatments with EDTA and Cu^{2+} ions (all current values were taken at $V_G = -4$ V). All the measurements were carried out at $V_D = -50$ mV.

measurable current at the noise level of the measurement (<100 fA) as indicated by the red curve. The blue curve illustrates the conductance of the ODN–**H1**–Cu^{2+}-rejoined device measured within the optimized gate voltage range from 4 V to −4 V.[8b,9] By using this method, we obtained 12 working devices rejoined by ODN–**H1**–Cu^{2+} out of approximately 450 that were tested (ca. 3% yield).[12] All the working devices recovered their original (semiconducting or metallic) electrical properties, while the others showed no conductance. Table S1 in the Supporting Information summarizes the device characteristics measured in the course of this study for the devices at each step of the procedure. The resistance of DNA duplexes containing only one **H**–Cu^{2+}–**H** base pair is within the range of 0.1–5 MΩ, which is very similar to those of natural DNA duplexes with similar length.[9] This result suggests that the positively charged Cu^{2+} ion of the flat metallo-base pair behaves like a "big proton" normally found in hydrogen-bonded base pairs and does not significantly alter the charge transport properties of natural DNA.[13] Thus, to increase DNA conductance, the incorporation of additional adjacent metallo-base pairs is required as demonstrated in the case of ODN–**H3**–Cu^{2+}.

The contacts made by covalent amide bond formation are quite robust and tolerate a broad range of chemical treatments, thus offering the chance to study the chemistry of coordination reactions (Figure 2a). Temperature-dependent UV absorption investigations (see Figure S1 in the Supporting Information) clearly showed that the thermal stability of ODN–**H1** duplexes increases in the presence of Cu^{2+} ions, while it decreases after ethylenediaminetetraacetic acid (EDTA) treatment in a PBS buffer solution (pH 7.2). This observation verifies the existence of two distinct states of the ODN–**H1** double helix (metal-containing and metal-free) in solution. Figure 3b shows the *I–V* curves of the same device shown in Figure 3a under sequential operations. Interestingly, the conductance of the device significantly decreased upon reannealing the duplex on the device in an EDTA buffer solution after heating it above its melting temperature (70°C). This observation should arise from the removal of the Cu^{2+} ion from the metallo-base pair and the consequent formation of a metal-free ODN–**H1** duplex still bridging the nanotube gap with a mismatch-like base pair that prevents charge transport through π stacking in DNA.[9,10] This result is consistent with the fact that we failed to find any working devices initially reconnected by the metal-free ODN–**H1** as mentioned above. On the contrary, no obvious changes in conductance were observed when the rejoined devices were incubated in an EDTA buffer solution below their DNA melting temperature or reannealed in a buffer solution without EDTA (see Figures S2 and S3 in the Supporting Information). It should be noted that these control experiments also confirm that the metallo-DNA on the carbon nanotube device is stable enough throughout the measurement unless treated with EDTA.

To further rule out potential artifacts, two additional sets of control experiments were carried out under the same treatment conditions. In the first experiment, devices reconnected by ODN–**H0** with the same sequence as ODN–**H1** but lacking hydroxypyridone ligands (**H**) presented no obvious current changes after the same sequential treatments (see Figure S4 in the Supporting Information), and thus the influence of the nonspecific binding of Cu^{2+} ions outside the DNA duplex or onto the carbon nanotube was negligible. Secondly, we performed the same operations on partially cut SWNT devices that were not completely cut during the oxygen plasma etching. There is only a negligible change in conductance, probably due to chemical doping during the treatments (see Figure S5 in the Supporting Information). Therefore, the conductance changes shown in Figure 3 should arise from the metallo-DNA itself. The finding that the effective removal of Cu^{2+} ions by EDTA causes a decrease in the conductance of the metallo-DNA led us to come up with the idea that reversible coordination reactions can enable on–off switching of the conductance (Figure 2a). This hypothesis was confirmed by successive treatments of the same devices with EDTA and Cu^{2+} ion solutions. After incubating the EDTA-treated devices in a 1 mM copper sulfate solution, the device conductance was dramatically enhanced as shown in Figure 3b (green curve: 3). That is, a significant decrease in conductance was observed after removal of Cu^{2+} ions through EDTA incubation; on the contrary, the devices displayed a dramatic increase in conductance upon further addition of Cu^{2+} ions. As shown in Figure 3c, the conductance switching cycle was repeated three times, before the change became indistinct. The gradual decrease in the conductance of ODN–**H1**–Cu^{2+} could be ascribed to device degradation during multiple treatments and/or unexpected interactions of the metal ions with the nanotube or the substrate. Control experiments using devices reconnected by ODN–**H0** and partially cut SWNT devices did show only negligible changes in conductance under the same operation conditions (see Figures S4 and S5 in the Supporting Information). These results consistently prove that, in comparison with the case of mismatch-like metal-free DNAs, the introduction of metal ions inside the DNA base core rigidifies the π stacking between base pairs, thus facilitating DNA charge transport. The most interesting result here is that the electrical properties of these devices can be efficiently switched on-and-off by sequentially alternating treatments with EDTA and Cu^{2+} ions.

To our surprise, similar conductance switching profiles were obtained when other metal ions, such as Ni^{2+} and Fe^{3+} instead of Cu^{2+}, were used for the same experiments (Figurse S7a,b and S7c,d, respectively) while these metals have not yet been proven to quantitatively form stable metal-mediated base pairs (**H**–Ni^{2+}–**H**, **H**–Fe^{3+}–**H**) of a 2:1 ligand to metal stoichiometry under similar conditions in solution-based experiments.[14] Because the control experiments using devices reconnected by the natural strand, ODN–**H0**, showed that the influence of the nonspecific metal binding to the natural bases and the DNA backbone on the conductance was negligible (see Figure S4 in the Supporting Information), these phenomena should be attributed to the binding of the metal ions to the hydroxypyridone moieties in the case of ODN–**H1**. Although further investigation on their coordination structures is needed, it is noteworthy that the proven switching reproducibility and reversibility of these single-molecule devices bridged by metallo-DNAs form the basis for new types of molecular switches and chemical sensors.

After having understood the electrical properties of metallo-DNA duplexes with only one metal inside, we turned our attention to examine the effect of multiple metal ions on DNA conductance using ODN–**H3** with three neighboring **H** artificial base pairs in the same sequence. With the same reconnection strategy as used above, we achieved 22 working devices reconnected by ODN–**H3**–Cu^{2+} out of approximately 280 that were tested as summarized in Table S2 (ca. 8% yield).[12] Figure 4a presents the electrical characteristics of a typical rejoined device under different treatment conditions. Similar to those of ODN–**H1**–Cu^{2+}-rejoined devices, the source-drain current (I_D) of this device showed an apparent decrease after heating in an EDTA buffer solution at 70°C and recovered to a different extent after further Cu^{2+} ion incubation. The limited reversibility might result from device degradation as observed for the ODN–**H1**–Cu^{2+} devices.

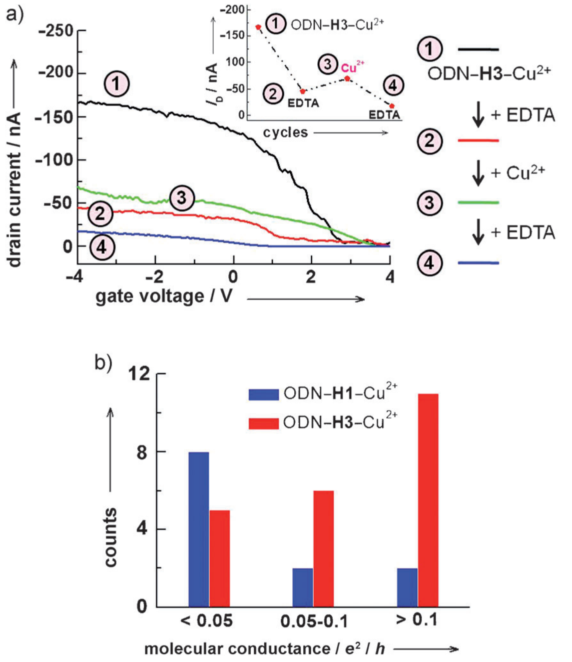

Figure 4. Electrical properties of ODN–**H3**–Cu^{2+} duplexes. a) The *I*–*V* curves of an ODN–**H3**–Cu^{2+}-reconnected device at different stages; after DNA reconnection (black: 1), after the first EDTA treatment (red: 2), after further Cu^{2+} ion treatment (green: 3), after the second EDTA treatment (blue: 4). Inset shows the reversibility for the same device upon alternate treatments with EDTA and Cu^{2+} ions (all current values were taken at $V_G = -4$ V). All measurements were carried out at $V_D = -50$ mV. More details about the device used here can be found in the Supporting Information (Figure S8). b) Statistical conductance comparison between ODN–**H1**–Cu^{2+} and ODN–**H3**–Cu^{2+} duplexes listed in Tables S1 and S2.

To compare the conductance between ODN–**H1**–Cu^{2+} and ODN–**H3**–Cu^{2+}, the resistance and thus the molecular conductance were calculated from the drop in current of all the working devices as listed in Tables S1 and S2. Although a device-to-device conductance variance exists because of some inevitable factors (SWNT diversity, DNA conformation, contact configuration, and lack of precise cutting procedure),[9] we could statistically analyze the results. To clearly compare the distribution in each case, we tentatively divide them into three groups ($< 0.05\,e^2h^{-1}$, 0.05–0.1 e^2h^{-1}, and $> 0.1\,e^2h^{-1}$, Figure 4b). It showed that ODN-**H3**-Cu^{2+} devices tend to exhibit higher conductance than ODN–**H1**–Cu^{2+}. This result may be attributed to the synergistic effect of increased rigidity of the π stacking and the electronic coupling for hole transfer induced by metal ions.[13] The summarized results are the first direct experimental support for the hypothesis that the precise arrangement of metal-mediated base pairs into DNA scaffolds may improve insufficient electrical conductance of DNA duplexes.[3b,c]

In conclusion, we described a method to make robust devices for directly measuring charge transport of metallo-DNA duplexes using single-molecule break junctions with SWNTs as point contacts. **H**–Cu^{2+}–**H** base pairs incorporated parallel to the neighboring natural base pairs in DNA could modulate its structural stability, rigidify π stacking between DNA base pairs, and mediate the electronic coupling for hole transfer, thus favoring DNA charge transport, as compared to the ligand-containing metal-free DNAs. Because the devices made in a well-defined covalent fashion in this study are sufficiently stable so that a wide range of chemistries and conditions could be applied, it is remarkable that the electrical properties of metallo-DNA-bridged devices can be efficiently switched on-and-off by sequentially alternating the treatments with EDTA and metal ions. Another important result we achieved here for the first time is to experimentally support the idea that it is possible to enhance the electrical conductance of DNA by rational arrangement of multiple metal ions inside the core of the DNA base-pair stack. These results demonstrate that metallo-DNA molecules bridging nanodevices can surely serve as an effective mediator for charge transport and single-molecule devices such as molecular switches and reversible sensors, thereby opening up a new promising and exciting scientific research field that interfaces molecular nanodevices with biomacromolecules for a wide variety of potential applications, such as molecular electronic circuits,[2a,f,3a] nanomagnets and molecular spintronics,[4b,5b] asymmetric catalysis,[4j] and information processing.[15]

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[1] a) F. A. Aldaye, A. L. Palmer, H. F. Sleiman, *Science* **2008**, *321*, 1795–1799; b) A. Heckel, M. Famulok, *Biochimie* **2008**, *90*, 1096–1107; c) N. C. Seeman, *Mol. Biotechnol.* **2007**, *37*, 246–257; d) M. Endo, H. Sugiyama, *ChemBioChem* **2009**, *10*, 2420–2443; e) C. Lin, Y. Liu, H. Yan, *Biochemistry* **2009**, *48*, 1663–1674.

[2] a) T. Carell, C. Behrens, J. Gierlich, *Org. Biomol. Chem.* **2003**, *1*, 2221–2228; b) E. Braun, Y. Eichen, U. Sivan, G. Ben-Yoseph, *Nature* **1998**, *391*, 775–778; c) F. D. Lewis, T. Wu, Y. Zhang,

R. L. Letsinger, S. R. Greenfield, M. R. Wasielewski, *Science* **1997**, *277*, 673–676; d) G. Taubes, *Science* **1997**, *275*, 1420–1421; e) P. Aich, S. L. Labiuk, L. W. Tari, L. J. Delbaere, W. J. Roesler, K. J. Falk, R. P. Steer, J. S. Lee, *J. Mol. Biol.* **1999**, *294*, 477–485; f) J. C. Genereux, J. K. Barton, *Chem. Rev.* **2010**, *110*, 1642–1662.

[3] a) J. Richter, *Phys. E* **2003**, *16*, 157–173; b) J. Müller, *Nature* **2006**, *444*, 698; c) G. H. Clever, M. Shionoya, *Coord. Chem. Rev.* **2010**, *254*, 2391–2402.

[4] a) K. Tanaka, M. Shionoya, *J. Org. Chem.* **1999**, *64*, 5002–5003; b) K. Tanaka, A. Tengeiji, T. Kato, N. Toyama, M. Shionoya, *Science* **2003**, *299*, 1212–1213; c) K. Tanaka, G. H. Clever, Y. Takezawa, Y. Yamada, C. Kaul, M. Shionoya, T. Carell, *Nat. Nanotechnol.* **2006**, *1*, 190–194; d) E. Meggers, P. L. Holland, W. B. Tolman, F. E. Romesberg, P. G. Schultz, *J. Am. Chem. Soc.* **2000**, *122*, 10714–10715; e) S. Atwell, E. Meggers, G. Spraggon, P. G. Schultz, *J. Am. Chem. Soc.* **2001**, *123*, 12364–12367; f) G. H. Clever, C. Kaul, T. Carell, *Angew. Chem.* **2007**, *119*, 6340–6350; *Angew. Chem. Int. Ed.* **2007**, *46*, 6226–6236; g) G. H. Clever, K. Polborn, T. Carell, *Angew. Chem.* **2005**, *117*, 7370–7374; *Angew. Chem. Int. Ed.* **2005**, *44*, 7204–7208; h) G. H. Clever, Y. Soltl, H. Burks, W. Spahl, T. Carell, *Chem. Eur. J.* **2006**, *12*, 8708–8718; i) J. Müller, *Eur. J. Inorg. Chem.* **2008**, 3749–3763; j) J. Müller, *Metallomics* **2010**, *2*, 318–327; k) K. Tanaka, M. Shionoya, *Coord. Chem. Rev.* **2007**, *251*, 2732–2742; l) H. Yang, K. L. Metera, H. F. Sleiman, *Coord. Chem. Rev.* **2010**, *254*, 2403–2415.

[5] a) S. S. Mallajosyula, S. K. Pati, *Angew. Chem.* **2009**, *121*, 5077–5081; *Angew. Chem. Int. Ed.* **2009**, *48*, 4977–4981; b) G. H. Clever, S. J. Reitmeier, T. Carell, O. Schiemann, *Angew. Chem.* **2010**, *122*, 5047–5049; *Angew. Chem. Int. Ed.* **2010**, *49*, 4927–4929.

[6] a) H. W. Fink, C. Schonenberger, *Nature* **1999**, *398*, 407–410; b) D. Porath, A. Bezryadin, S. de Vries, C. Dekker, *Nature* **2000**, *403*, 635–638; c) A. J. Storm, J. van Noort, S. de Vries, C. Dekker, *Appl. Phys. Lett.* **2001**, *79*, 3881–3883; d) A. Y. Kasumov, M. Kociak, S. Guéron, B. Reulet, V. T. Volkov, D. V. Klinov, H. Bouchiat, *Science* **2001**, *291*, 280–282; e) H. Gohen, C. Nogues, R. Naaman, D. Porath, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 11589–11593; f) H. van Zalinge, D. J. Schiffrin, A. D. Bates, E. B. Starikov, W. Wenzel, R. J. Nichols, *Angew. Chem.* **2006**, *118*, 5625–5628; *Angew. Chem. Int. Ed.* **2006**, *45*, 5499–5502; g) J. Hihath, B. Xu, P. Zhang, N. Tao, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 16979–16983; h) S.-P. Liu, S. H. Weisbrod, Z. Tang, A. Marx, E. Scheer, A. Erbe, *Angew. Chem.* **2010**, *122*, 3385–3388; *Angew. Chem. Int. Ed.* **2010**, *49*, 3313–3316.

[7] a) X. Guo, J. P. Small, J. E. Klare, Y. Wang, M. S. Purewal, I. W. Tam, B. H. Hong, R. Caldwell, L. Huang, S. O'brien, J. Yan, R. Breslow, S. J. Wind, J. Hone, P. Kim, C. Nuckolls, *Science* **2006**, *311*, 356–359; b) A. K. Feldman, M. L. Steigerwald, X. Guo, C. Nuckolls, *Acc. Chem. Res.* **2008**, *41*, 1731–1741.

[8] a) X. Guo, A. Whalley, J. E. Klare, L. Huang, S. O'brien, M. Steigerwald, C. Nuckolls, *Nano Lett.* **2007**, *7*, 1119–1122; b) S. Liu, X. Zhang, W. Luo, Z. Wang, X. Guo, M. L. Steigerwald, X. Fang, *Angew. Chem.* **2011**, *123*, 2544–2550; *Angew. Chem. Int. Ed.* **2011**, *50*, 2496–2502.

[9] X. Guo, A. A. Gorodetsky, J. Hone, J. K. Barton, C. Nuckolls, *Nat. Nanotechnol.* **2008**, *3*, 163–167.

[10] K. Tanaka, A. Tengeiji, T. Kato, N. Toyama, M. Shiro, M. Shionoya, *J. Am. Chem. Soc.* **2002**, *124*, 12494–12498.

[11] Some of the devices tested here should have failed at the reconnection of the DNA strands. However, high ohmic resistance of the "mismatched" DNA makes it difficult to distinguish between the devices that succeeded at the reconnection and those that failed at the DNA reconnenction.

[12] These yields are consistent with our previous experiments with natural DNA strands (see Refs. [8b] and [9]).

[13] a) J. Joseph, G. B. Schuster, *Org. Lett.* **2007**, *9*, 1843–1846; b) A. A. Voityuk, *J. Phys. Chem. B* **2006**, *110*, 21010–21013.

[14] It is important to note, however, that both discussed metal ions Ni^{2+} and Fe^{3+} have been shown to interact with hydroxypyridone-containing oligonucleotides in solution-based experiments under circumstances different from the conditions used here. Fe^{3+} is able to assemble homooligomeric sequences $\mathbf{H}_n$ ($n = 2$–4) into triple-stranded helices: Y. Takezawa, W. Maeda, K. Tanaka, M. Shionoya, *Angew. Chem.* **2009**, *121*, 1101–1104; *Angew. Chem. Int. Ed.* **2009**, *48*, 1081–1084. Ni^{2+} was shown to be incorporated into hydroxypyridone-containing double strands above pH 8 (unpublished results).

[15] R. Freeman, T. Finder, I. Willner, *Angew. Chem.* **2009**, *121*, 7958–7961; *Angew. Chem. Int. Ed.* **2009**, *48*, 7818–7821.