"Scanning tunneling spectroscopy and polarizability measurements of DNA and G4-DNA molecules"

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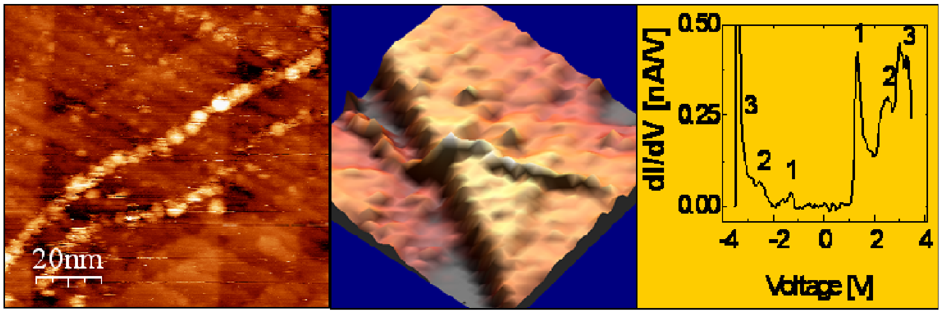
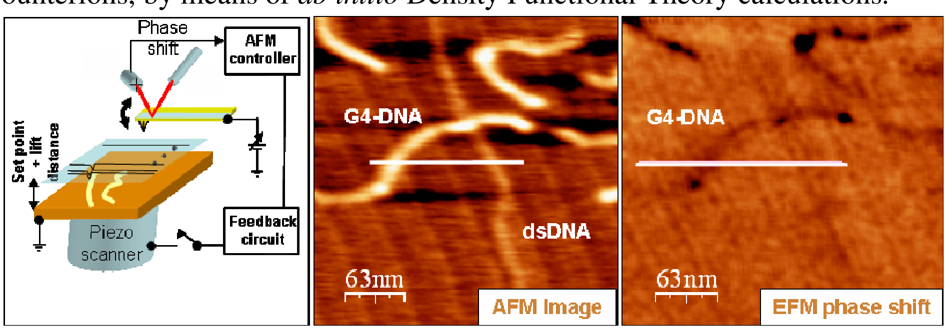


STM and STS of poly(G)-poly(C) DNA. (a) Topography image of the DNA on Gold (b). 3D presentation of the same image (c) STS on the molecule.

DNA, the most important bio-molecule, has been in the center of the scientific research for decades. In particular, DNA was considered as one of the attractive candidates for molecular electronics. DNA was, therefore, naturally chosen as one of the first investigation targets[1,2] following the invention in 1982 of the scanning tunneling microscope (STM) — the first tool for direct space morphological and electrical investigation of single objects on surfaces. Attempts to resolve the energy level structure of single DNA molecules span over the last two decades,[3,4,5,6] thanks to the unique ability of scanning tunneling spectroscopy (STS) to probe the local density of states of deposited objects.[7,8,9] Nevertheless, success was hindered by extreme technical difficulties in stable deposition and reproducibility.[10] By measuring STS on DNA at cryogenic temperature,[11] for the first time we disclosed the energy spectrum of poly(G)-poly(C) DNA[12] and G4-DNA[13] molecules deposited on gold.[14] The tunneling current-voltage (*I-V*) characteristics and their derivatives (*dI/dV-V*) exhibit a clear gap and a peak structure around the gap. Limited fluctuations in the I-V curves are observed and statistically characterized. The character of the observed *dI/dV-V* peaks is assigned to orbitals originating from the different molecular components, namely the nucleobases, the backbone and the counterions, by means of *ab initio* Density Functional Theory calculations.



EFM of G4-DNA crossing dsDNA. (a) Scheme of the measurement method. (b). Topography image of the G4-DNA (bright) and the dsDNA. (c) EFM of the molecules in (b), showing that the G4-DNA is polarizable.

Double-stranded DNA (dsDNA) was marked as one of the leading candidates for molecular wires in nano-electronics. Conductivity measurements in DNA provided, however, diverse results, mainly due to the variability in the measured systems: single molecules, bundles, networks, various length and compositions, and due to the different measurements conditions: on surfaces, free standing, chemically or physically connected etc. In most of the measurements the contacts played a major influencing role and indeed some of the measurements were done by contactless methods.[15,16] It became clear that dsDNA is very sensitive to the environmental conditions and to the measurement technique and that long dsDNA adsorbed on hard surfaces is electrically insulating and non-polarizable. As a remedy to these two issues we have developed a new type of DNA-based molecule: G4-DNA,[16] a DNA derivative with a quadruple helical motif of stacked guanine tetrads,[17] which is stiffer, more rigid and more resistant to surface forces. It has a high "surface area" in each tetrad (the molecule cross-section) for π-stacking and rich guanine content. We report measurements of this novel molecule using sensitive contactless electrostatic force microscopy (EFM) methods[18] that enable to detect polarizability – a strong indication for possible conductivity. In these measurements we find that the long G4-DNA molecules adsorbed on mica surface are polarizable whereas co-adsorbed long dsDNA are electrically silent, as was previously reported. This evidence may be interpreted as an indication that the conductivity of G4-DNA is potentially better than that of dsDNA, making G4-DNA a valid alternative to dsDNA to develop DNA-based nano-electronics.

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