Lecture 5

Charge transport in DNA

Advantages of DNA for Molecular Electronics

DNA possesses several essential properties for molecular electronics

- Molecular recognition:
  - can drive fabrication of devices and integrated circuits from elementary building blocks
  - can rearrange upon interaction with specially designed molecules
- Self-assembling ability
  - capability of molecules to self-organize in supramolecular aggregates. DNA can assemble into pre-programmed complicated constructions
- High density of information (4-bit system)
- Accurate synthesis and precise structure
- Well developed enzymatic machinery

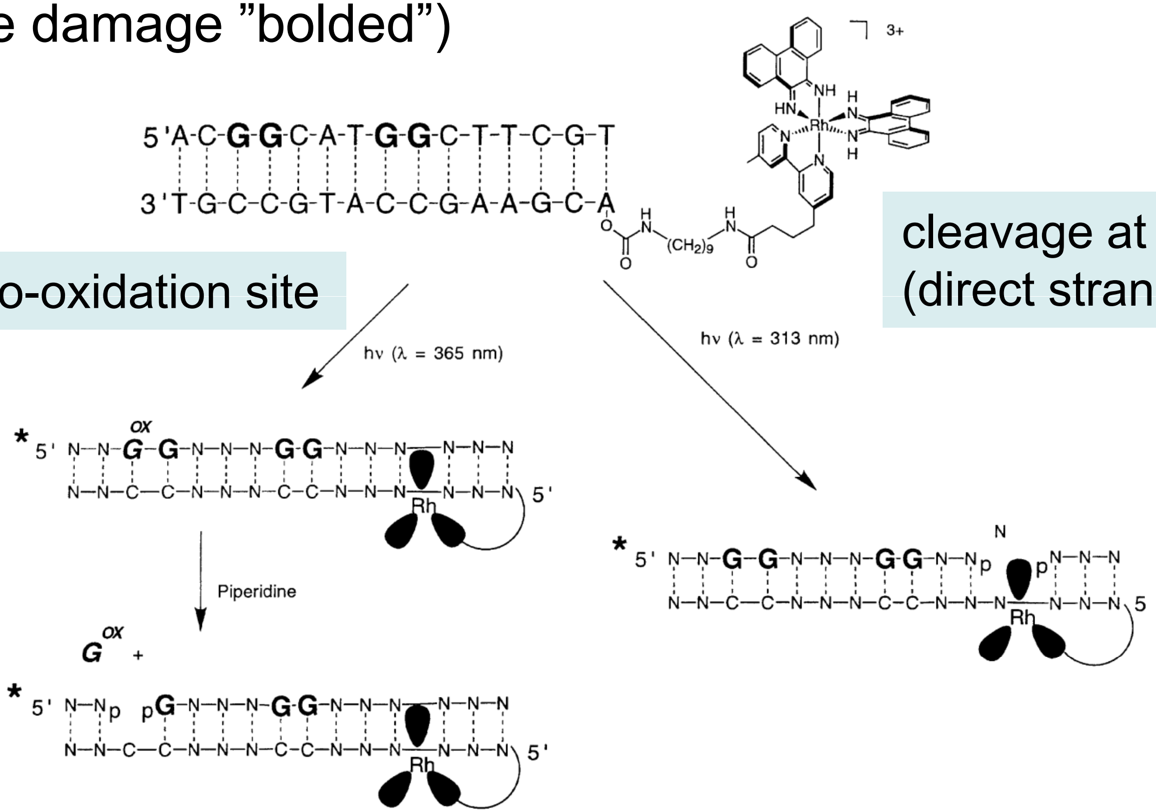
Brief History of DNA electronics

J.Barton et al, ”Oxidative damage through long-range electron transfer”, Nature 382, p.731 (1996)

- Short dsDNA oligomer with tethered $Rh(phi)_2DMB^{3+}$ intercalator were designed, where the place of intercalation and the place of possible oxidation damage were spatially separated.
- Electron donating ability goes like 5’-**G**A-3’, 5’-**G**G-3’, 5’-**G**GG-3’ (place of the oxidative damage ”bolded”)

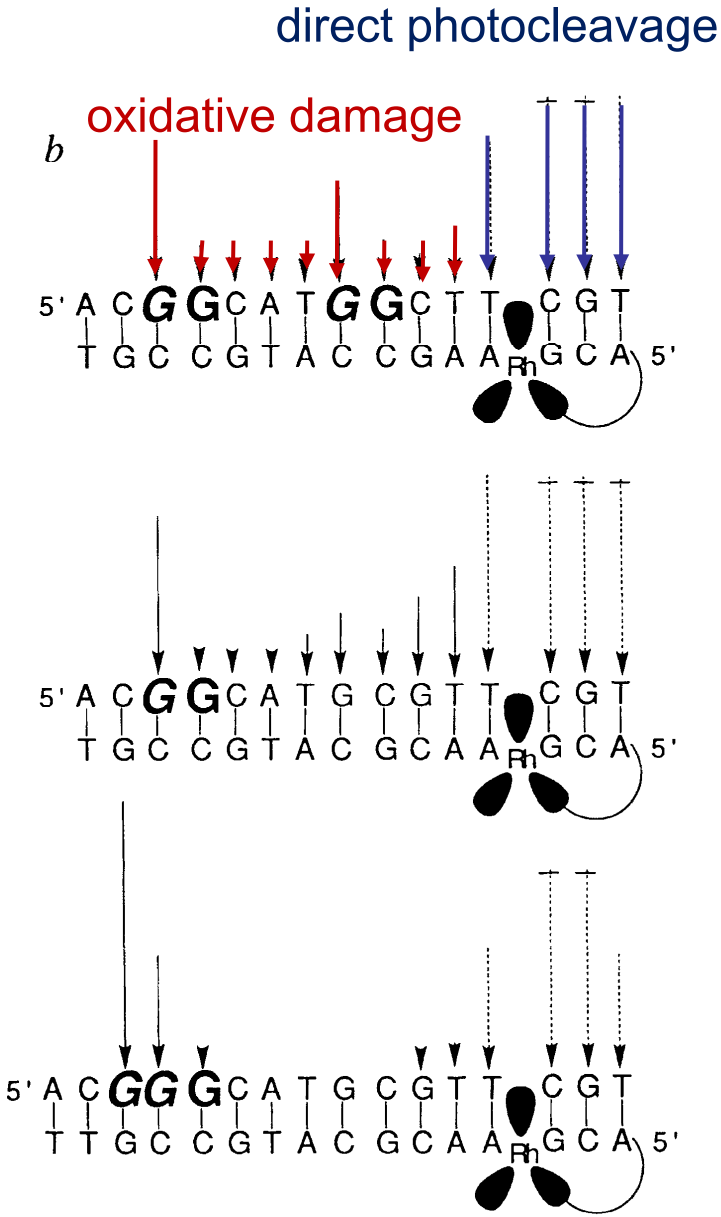
cleavage at photo-oxidation site

cleavage at intercalation side (direct strand cleavage)



Brief History of DNA electronics

- Photo-oxidative damage occurs at a distance of 17Å and 34Å from the intercalation site with the intensity of damage even higher at the distal GG doublet
- the transfer is intramolecular, the P^{32}-labelled molecules (w/o Rh-intercalator) added to the solution were not damaged

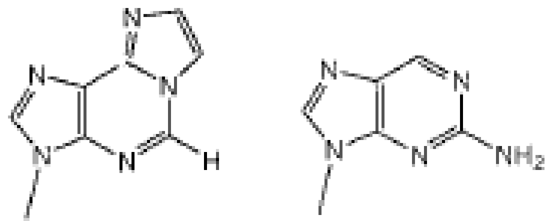


J.Barton et al, "Oxidative damage through long-range electron transfer", Nature 382, p.731 (1996)

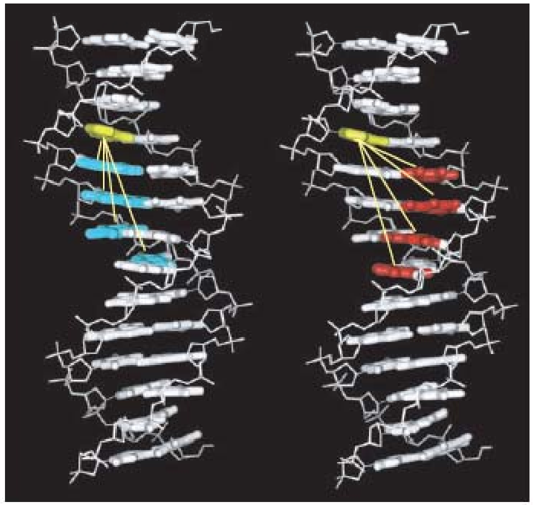
Brief History of DNA electronics

S.Kelley and J.Barton, "Electron transfer between bases in double helical DNA", Science 283, p.375 (1999)

- Fluorescent analogues of A (adenine) were used to investigate photoinduced charge transport through DNA π-stack
- donor (A2 or Aε) and quencher (G) were placed into the sequence of DNA
- investigated donor-acceptor distances 3.4, 6.8, 10.2 and 13.9Å.
- found for intrastrand β ~ 0.1 $Å^{-1}$, for interstrand β ~ 1.7 $Å^{-1}$.



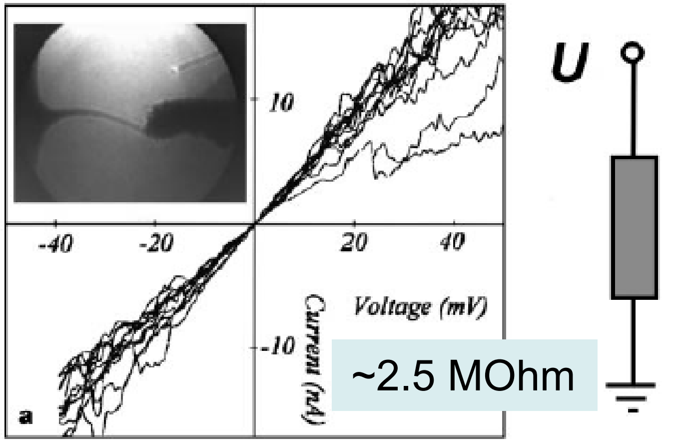
A_ε A_2



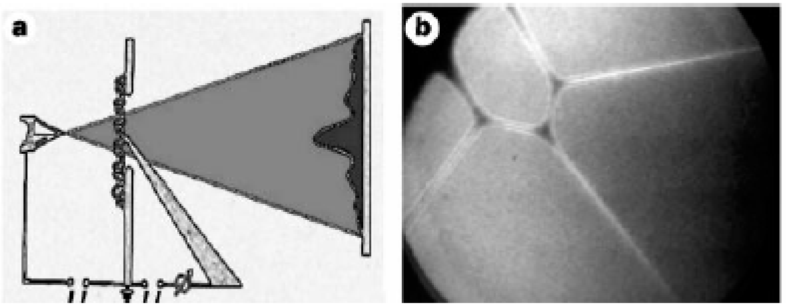
From the previous lectures:
for the case of non-resonant coherent transport $R \propto \exp(\beta \cdot d)$
typically, for phenyl monolayer β ~ 0.4 $Å^{-1}$, for alkane thiols monolayer β ~ 0.94 $Å^{-1}$
D.Frisbie et al, J.Phys.Chem. B. 106, p.2813 (2002)

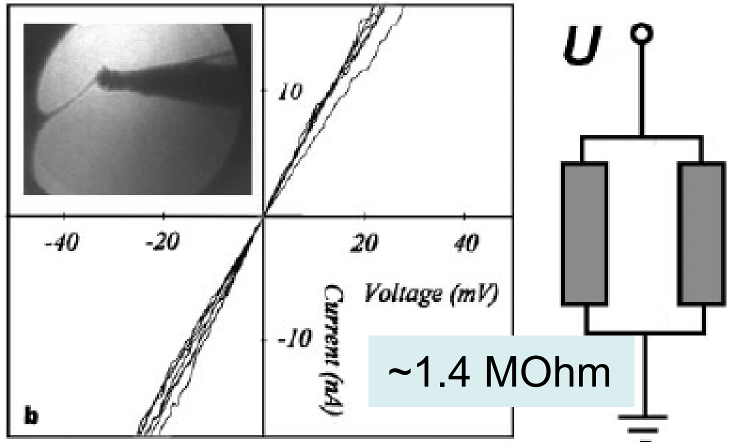
Brief History of DNA electronics

- *Hans-Werner Fink & Christian Schoenenberger, NATURE 398, p.407 (1999)*



- Low-energy electron source (LEEPS microscope, V=20-300V) used to image λ-DNA (deposited on a metal grid with 2µm holes) and observe the tungsten manipulation tip

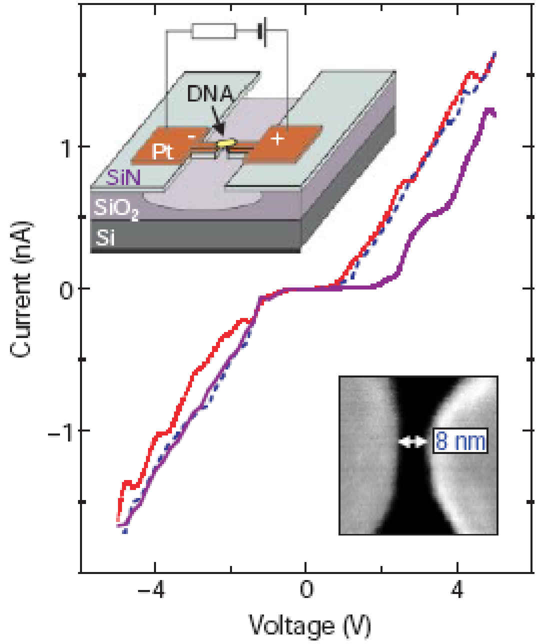




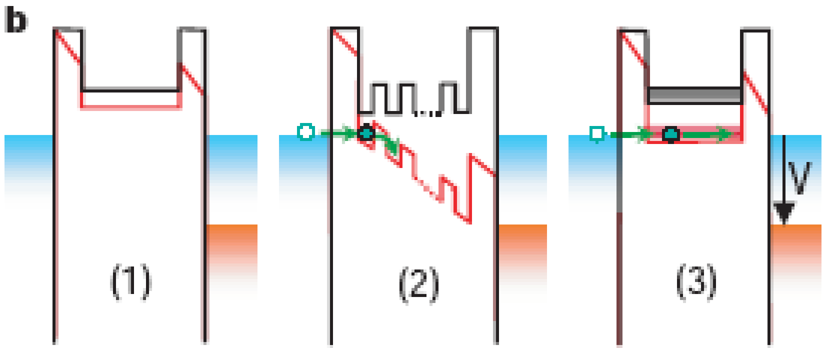
- Conduction measurements through bundles (approx 600nm long) of DNA:
  - DNA exhibit linear IV-curves (metallic)
  - should not be related to ionic transport in water (measurements in vacuum)
  - probably a ballistic wire?

Brief History of DNA electronics

- *Danny Porath, Alexey Bezryadin, Simon de Vries & Cees Dekker, "Direct measurement of electrical transport through DNA molecules", Nature 403, 635 (2000)*

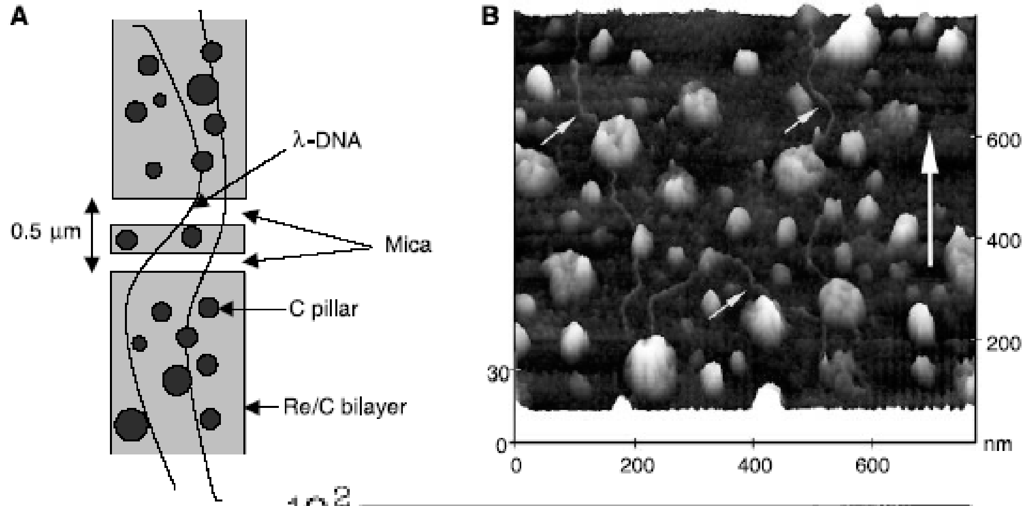


- 30bp (10.4nm long) DNA polyC-polyG electrostatically trapped between Pt-electrodes
- Measurements from RT down to 4K
- Molecules can reproducibly (no electrical damage (discharge) like would be in the case of an insulator)
- Overall semiconductor behaviour with a gap and switching between several possible configurations was observed
- Dnase assay proved no conductance after Dnase cutting of the trapped molecules



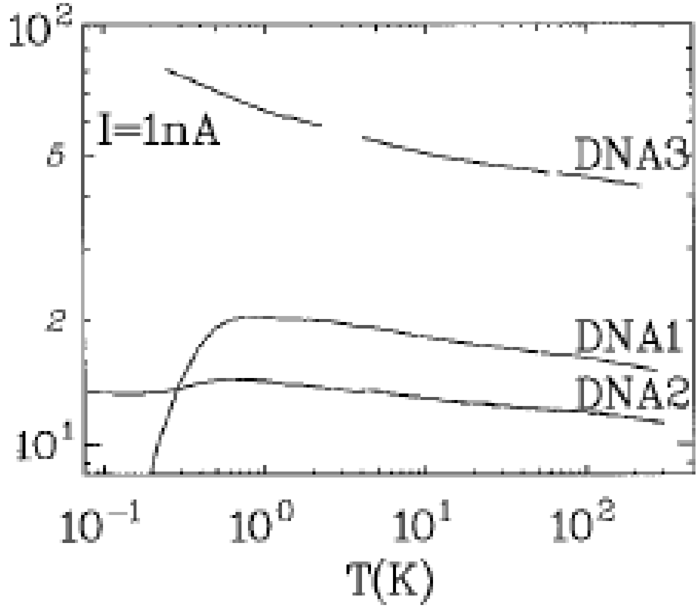
Brief History of DNA electronics

- *A. Yu. Kasumov, M. Kociak, S. Gueron, B. Reulet, V. T. Volkov, D. V. Klinov, H. Bouchiat, “Proximity-Induced Superconductivity in DNA”, Science 291, 280 (2001)*



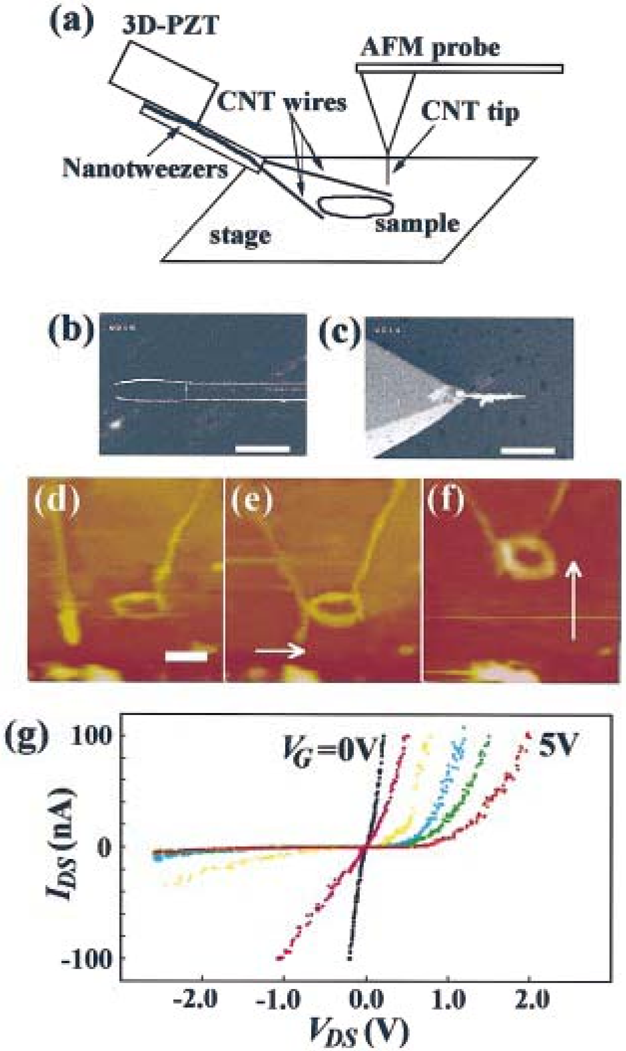
Experimental:

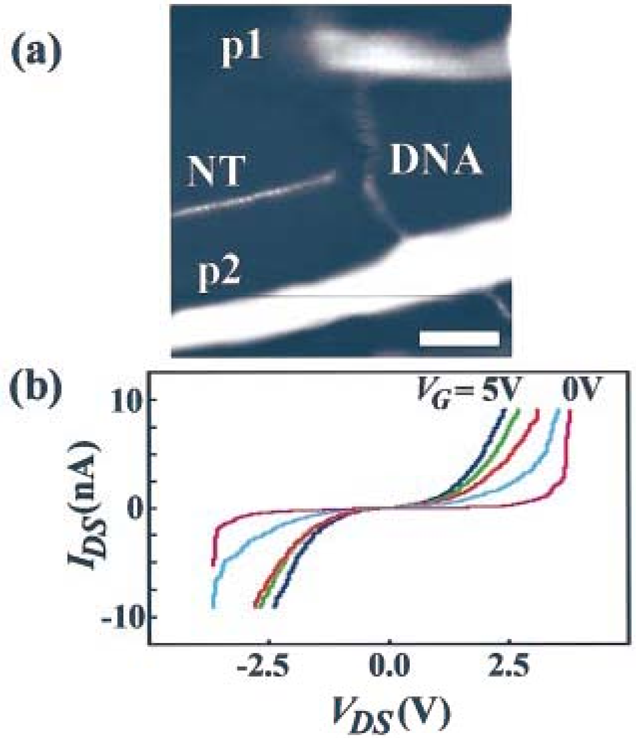
- λ-DNA deposited (flow combed) on superconducting Re/C electrodes
- Low temperature measurements RT down to 0.05K



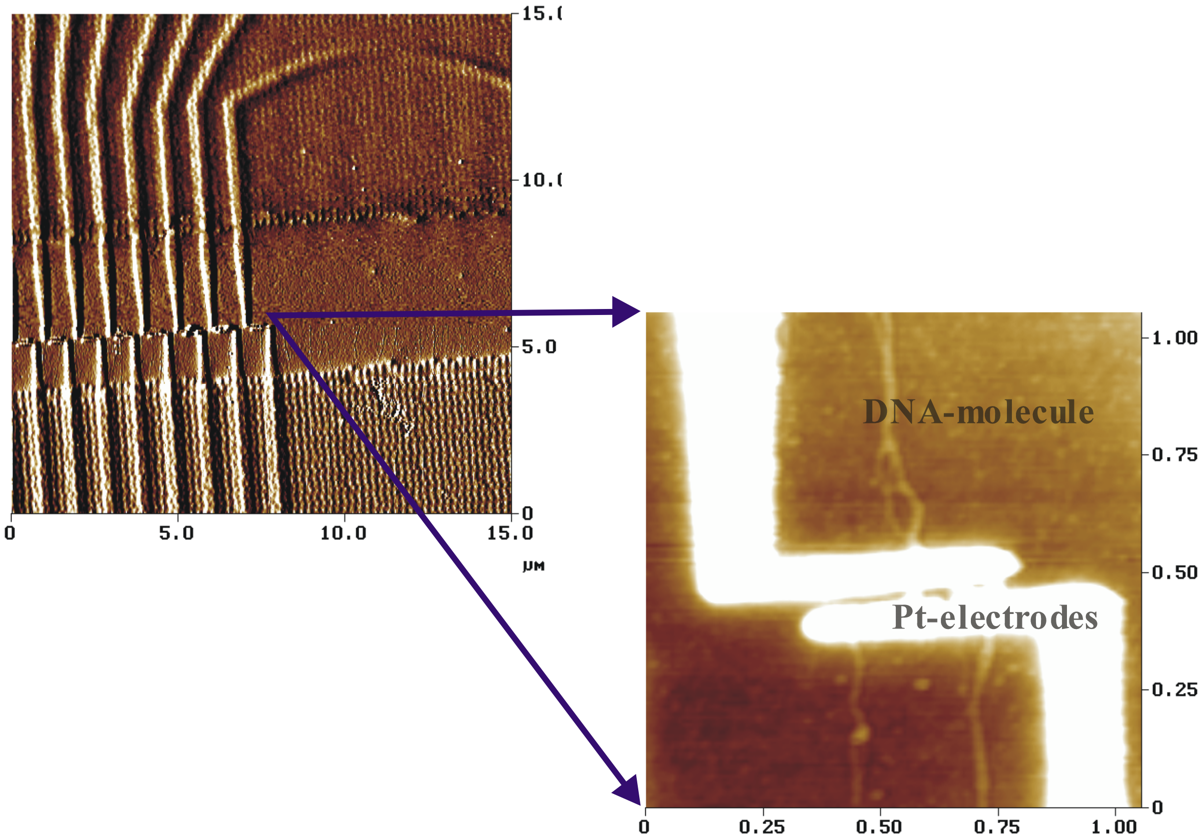
Brief History of DNA electronics

- *H.Watanabe et al, Single molecule DNA device measured with triple-probe atomic force microscope, Appl.Phys. Lett. 79, p.2462 (2001)*



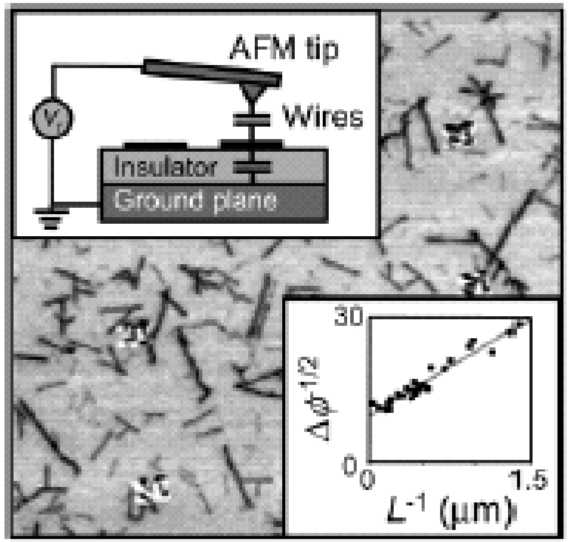


Stretching between the contacts

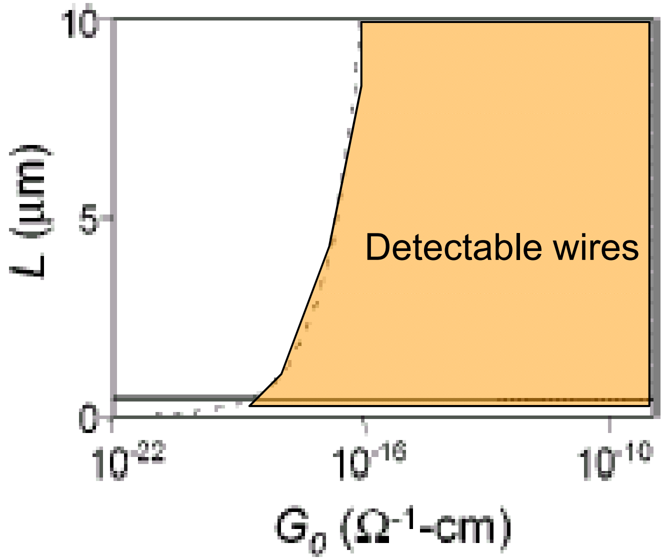


No conductance… Contact resistance?

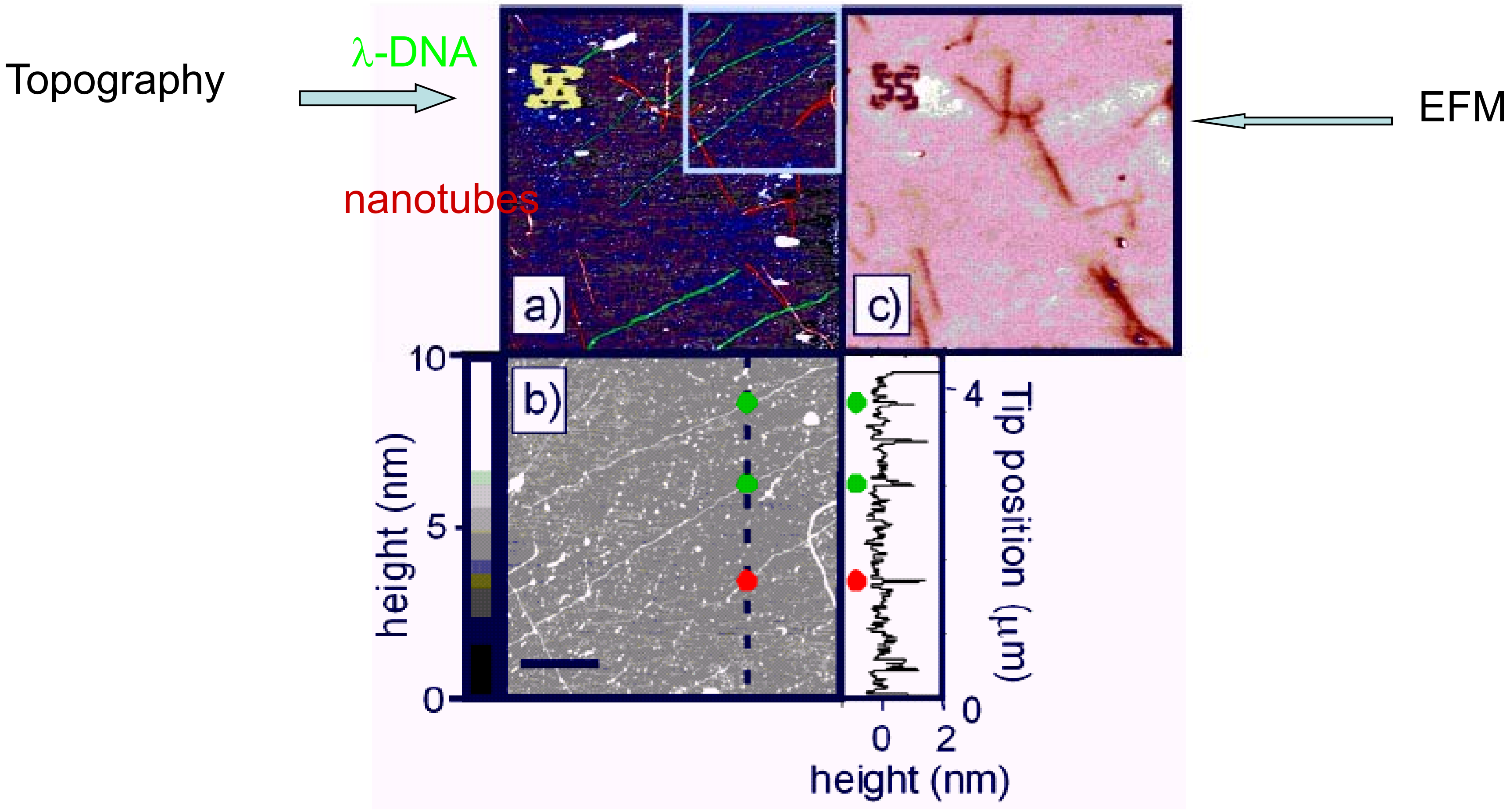
EFM on Nanotubes and λ- DNA



EFM phase image of carbon nanotubes deposited on the Si/SiO_2



EFM on Nanotubes and λ- DNA II

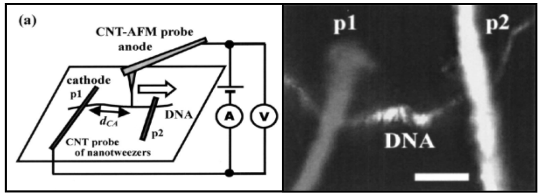


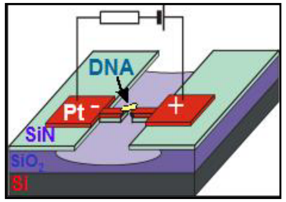
While having similar topography, DNA molecules are not detectable by EFM. $R>10^{16}$ Ohm/cm

Brief History of DNA electronics

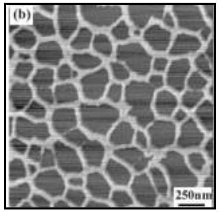
Review of experiments: Porath et. al. in Topics in Current Chemistry, Ed. G. Shuster, Vol. 273, (2004)

- Charge can be transported along **short** and **single** DNA polymers

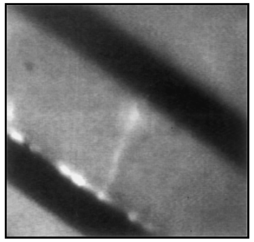


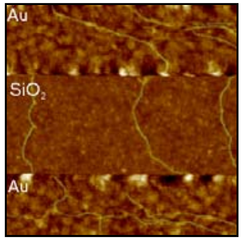


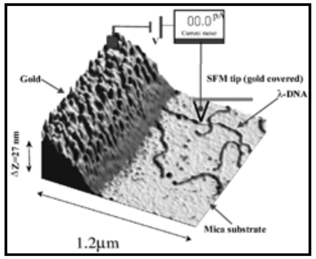
- Charge can possibly be transported in **bundles** and **networks**



- Charge transport is blocked for **long single** DNA polymers attached to surfaces







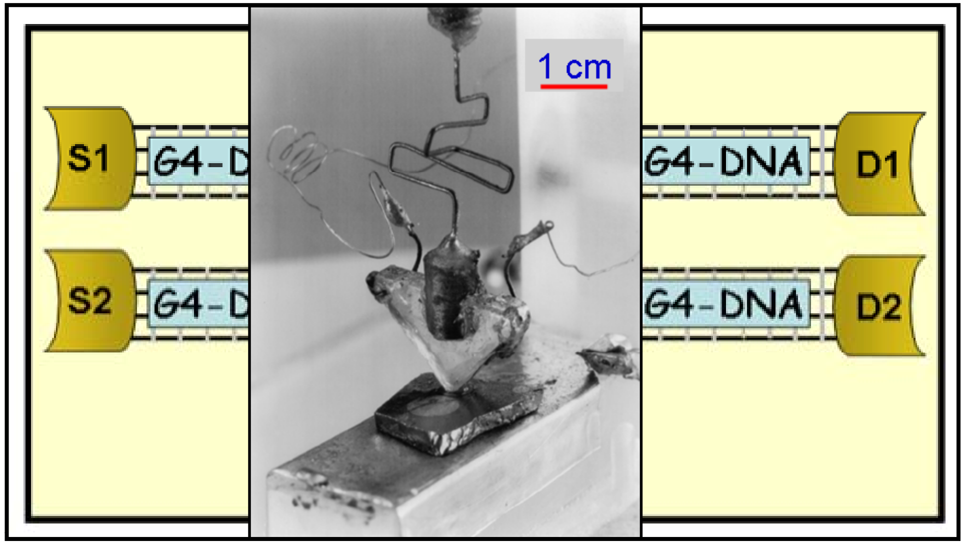
Brief History of DNA electronics

Problems

- The molecules are sensitive to the enviromental conditions (humidity, buffer composition etc.)
- Exact configuration of a soft polymer is difficult to control and predict.
- Contact are irreproducible and difficult to control

Current research

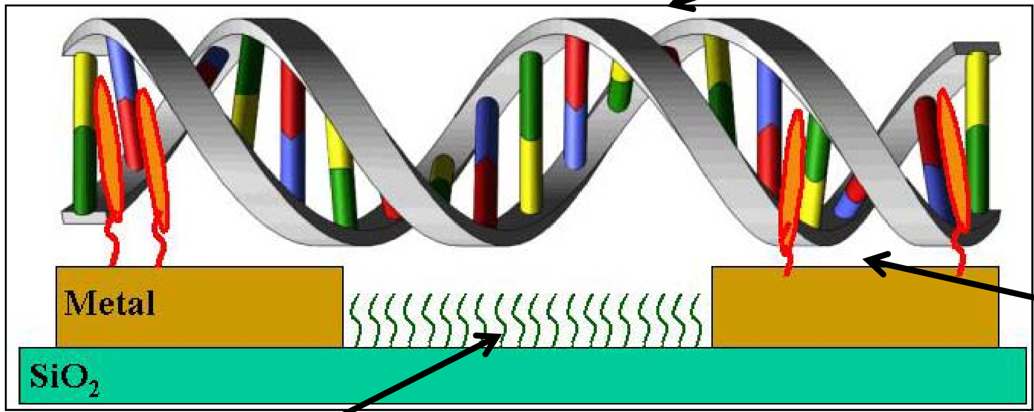
- Our group is a part of EU consortium on DNA nanodevices



Current research

- Our group is a part of EU consortium on DNA nanodevices

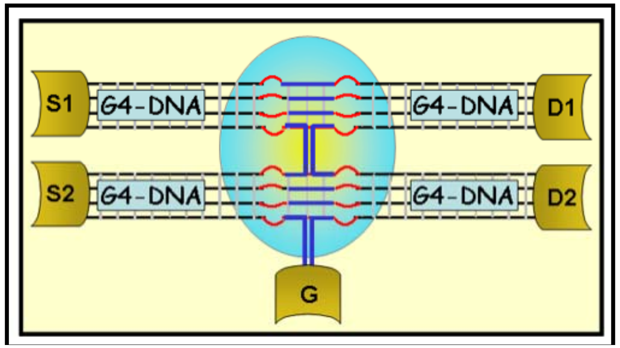
Find optimal DNA-based structure (G4 is currently in favour)



Optimize charge injection at the contacts

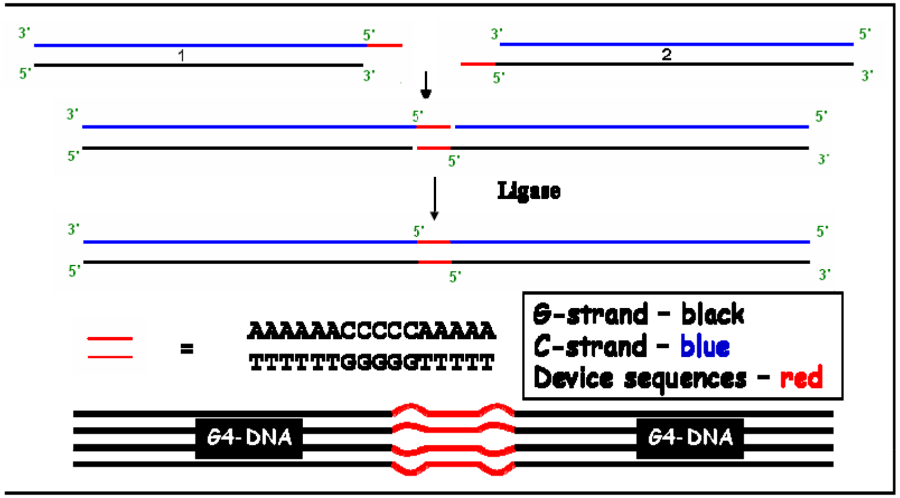
Optimize surface or DNA coating to reduce the DNA deformation

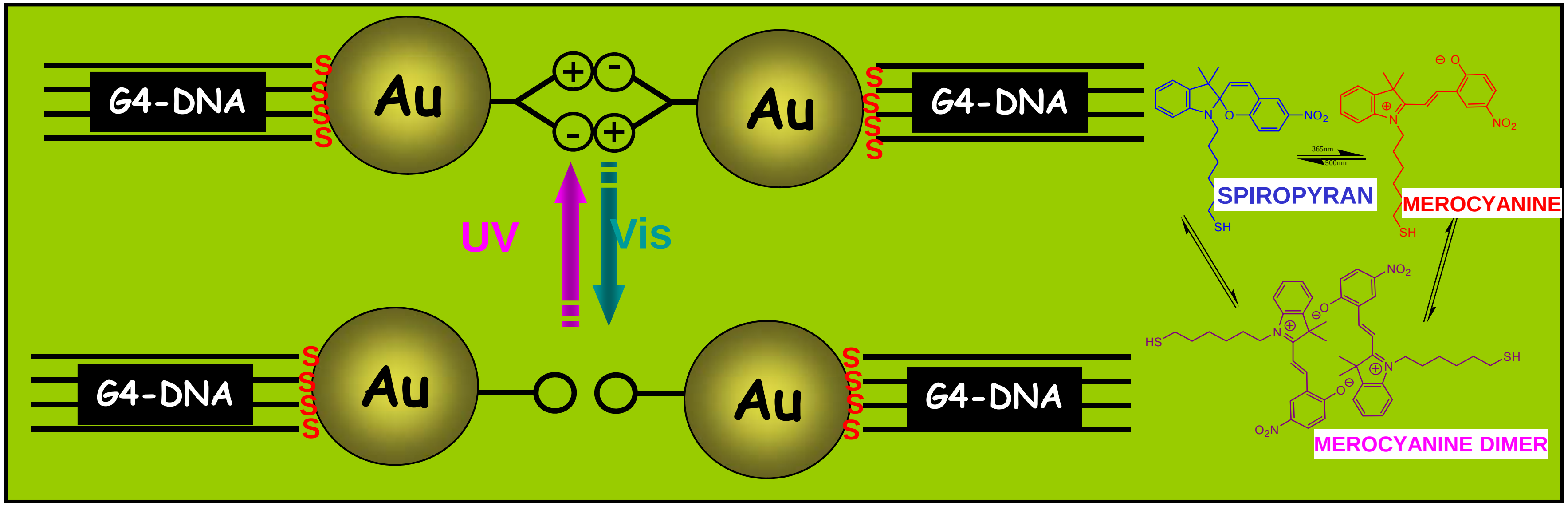
Eventually create complicated functional devices



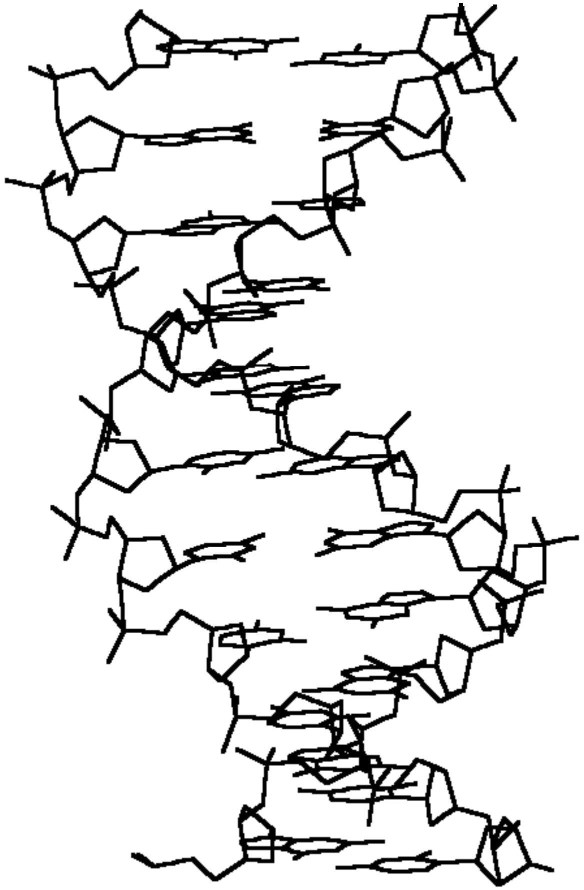
Current research

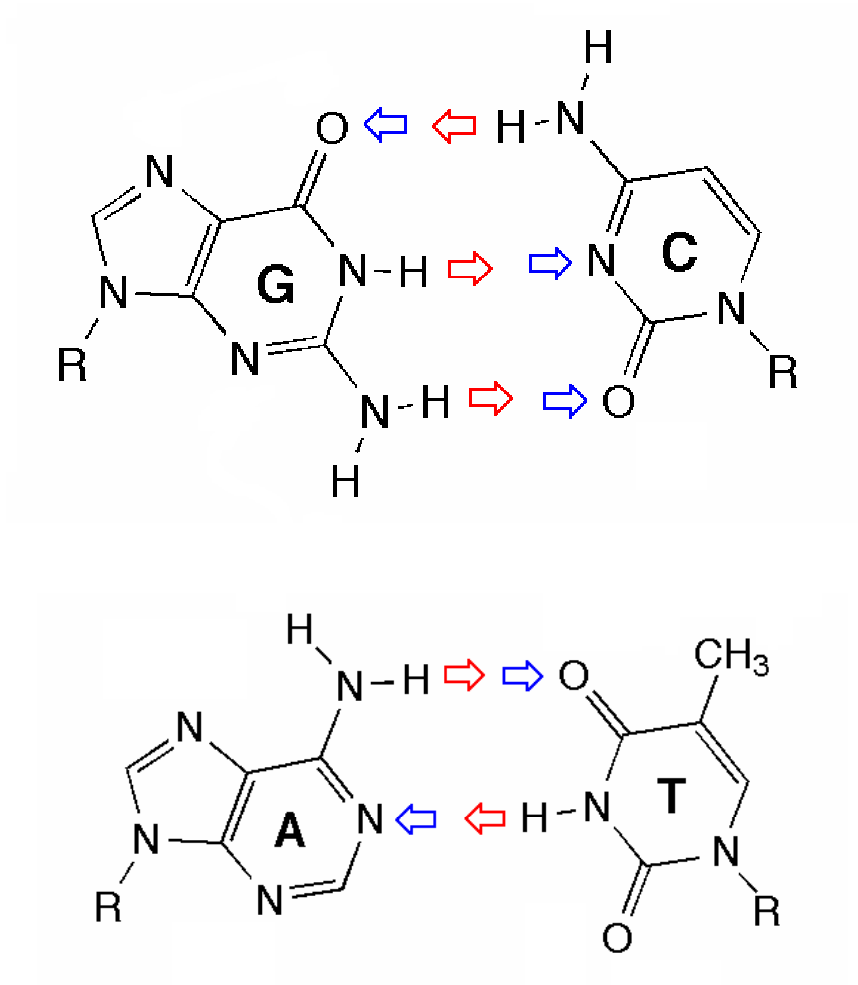
- Possible DNA devices:





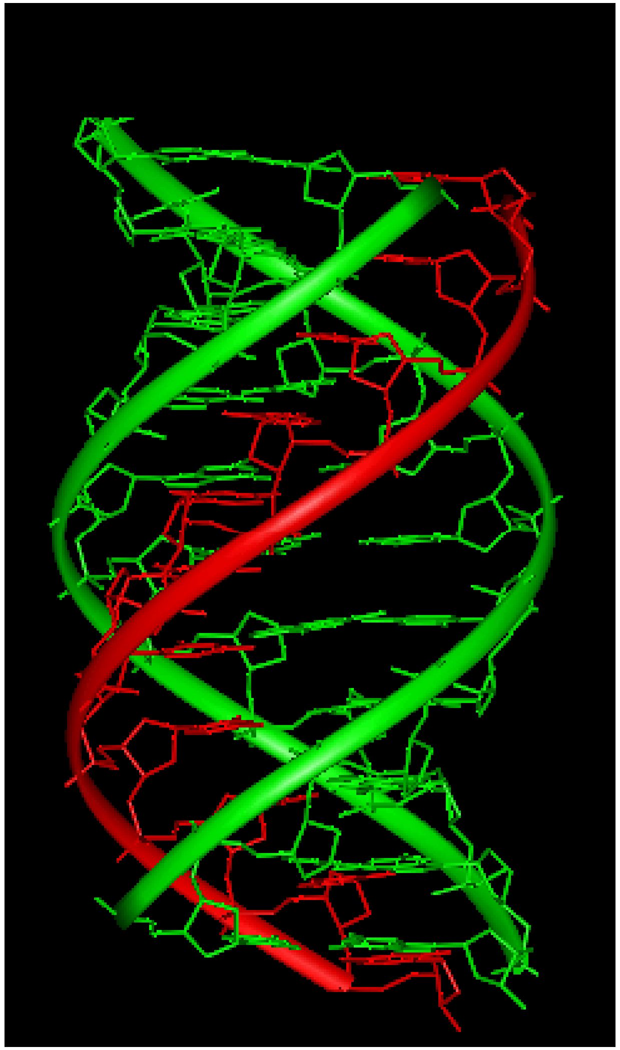
The Structure of duplex DNA

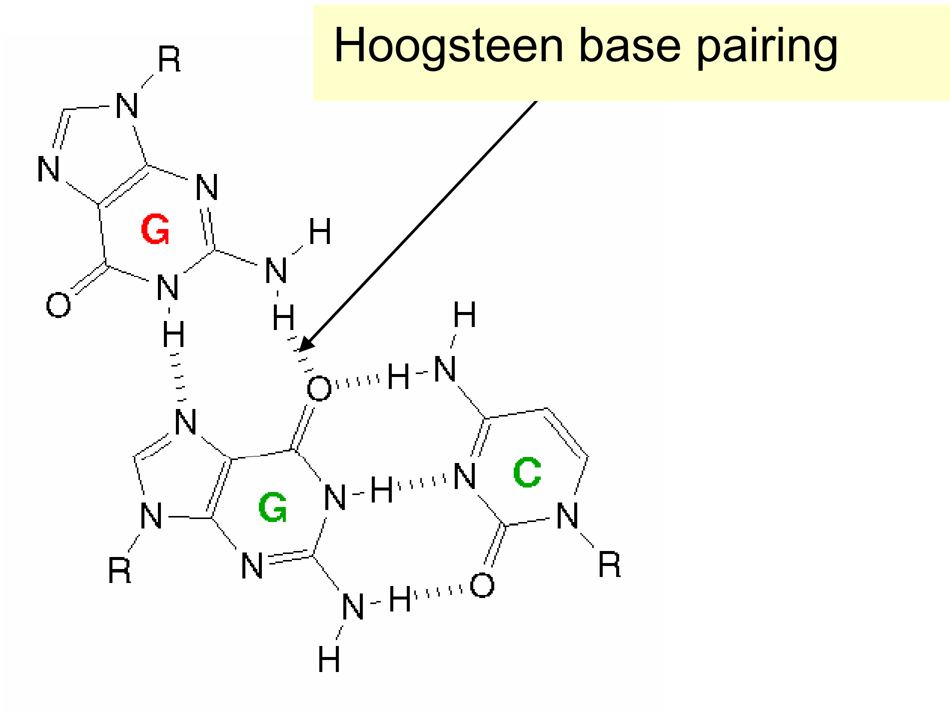




Base-Pairing

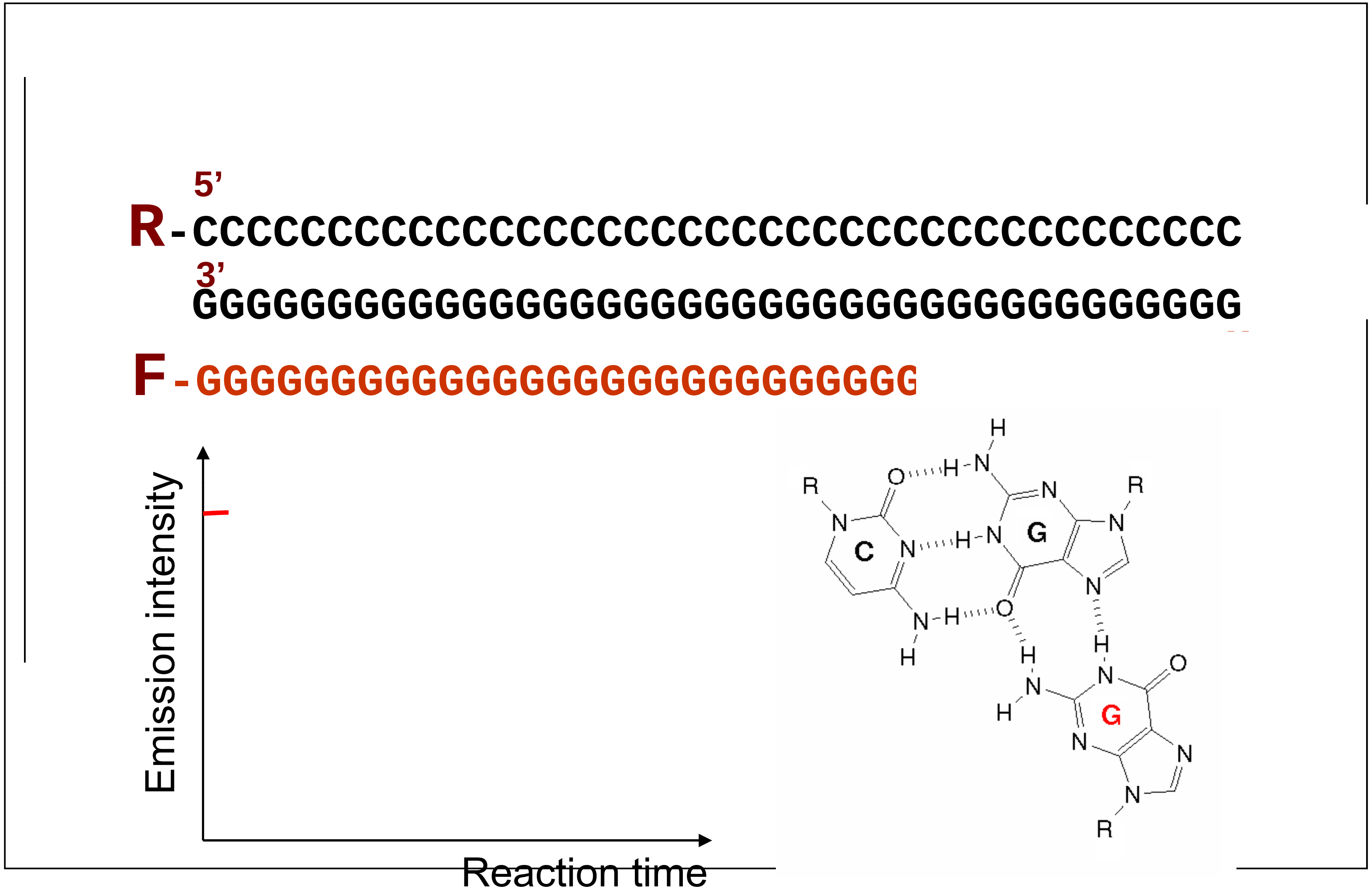
The Structure of triplex DNA





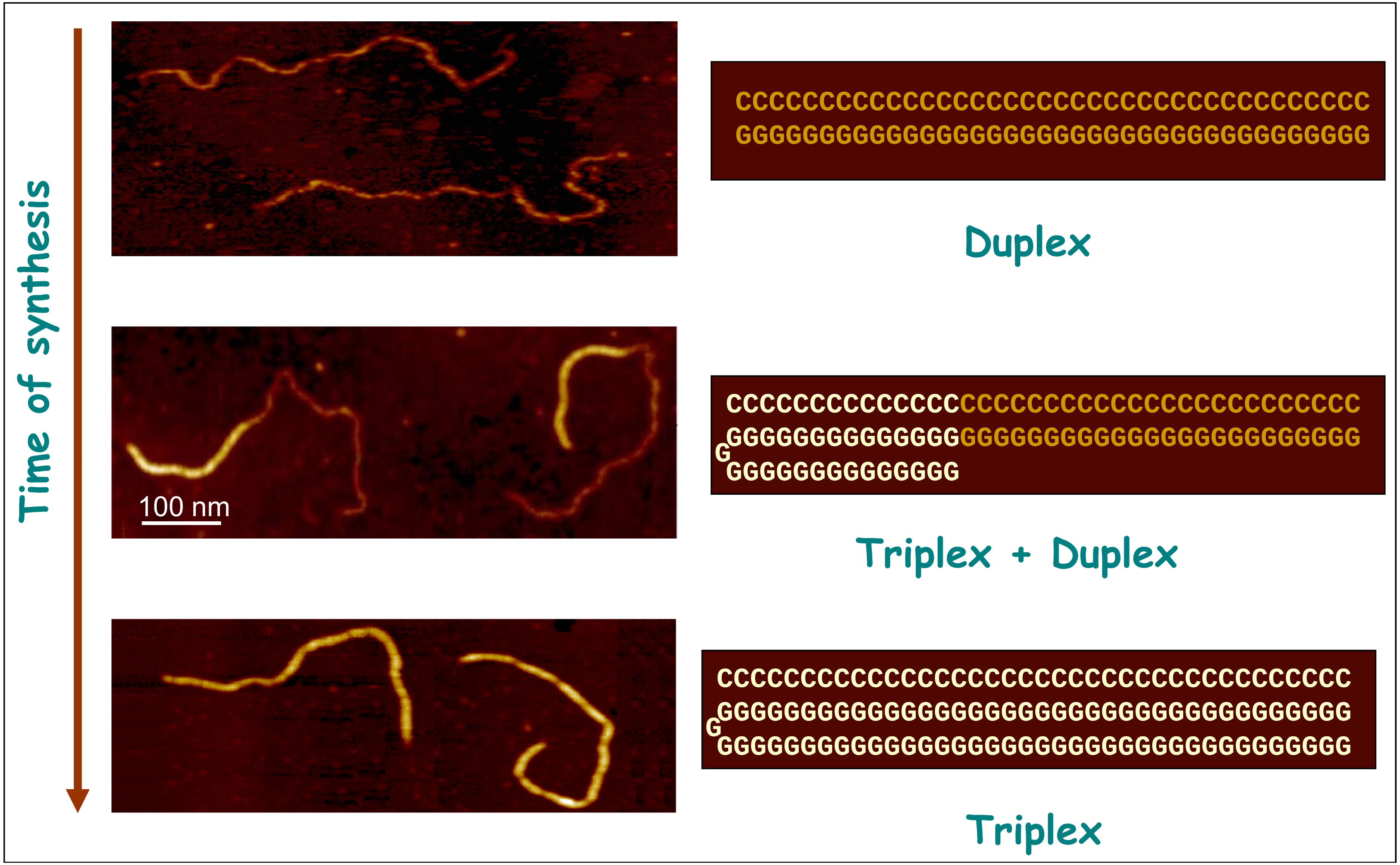
Current research

- New DNA derivative: Triplex-DNA (Kotlyar et al)



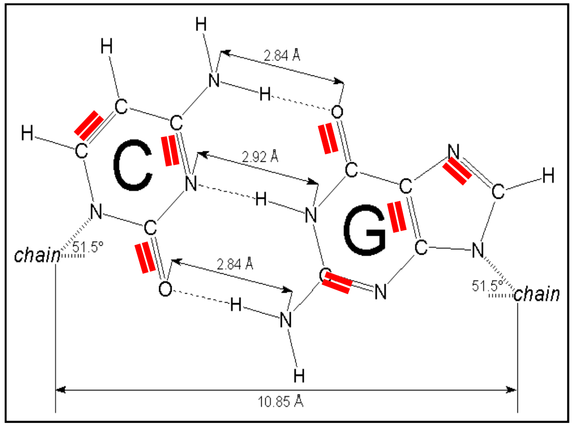
Current research

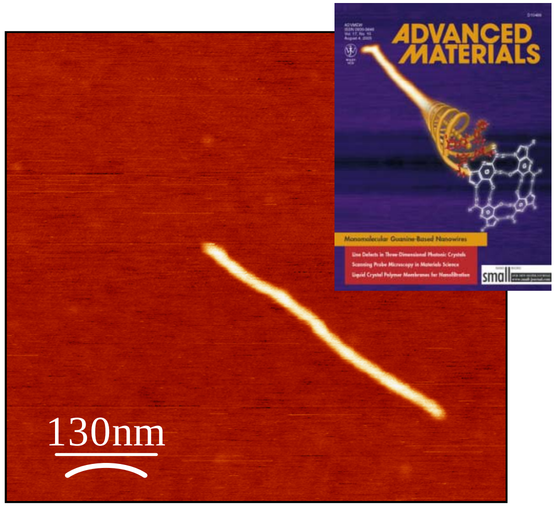
- New DNA derivative: Triplex-DNA (Kotlyar et al)

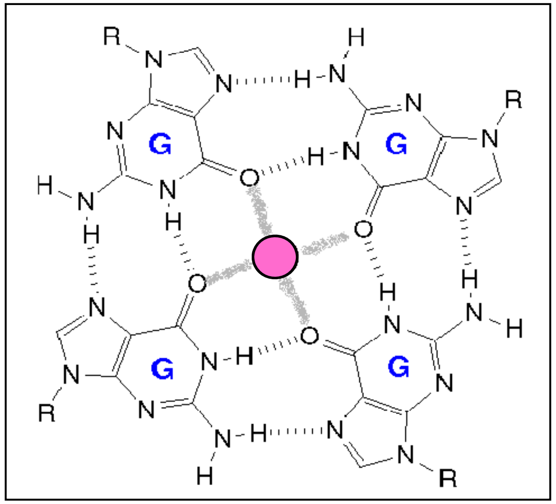


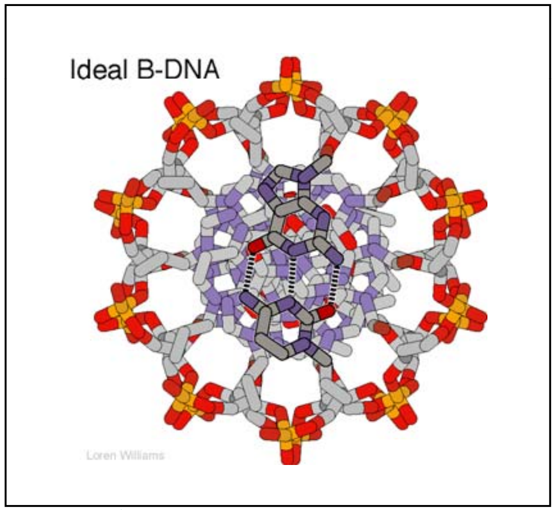
Current research

- New DNA derivative: G4 DNA (Kotlyar et al)

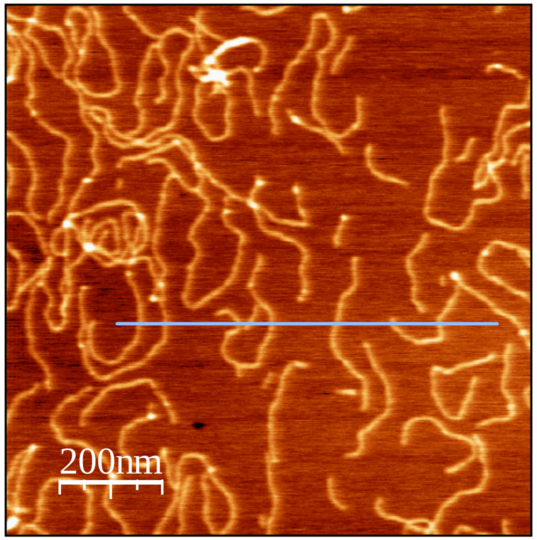


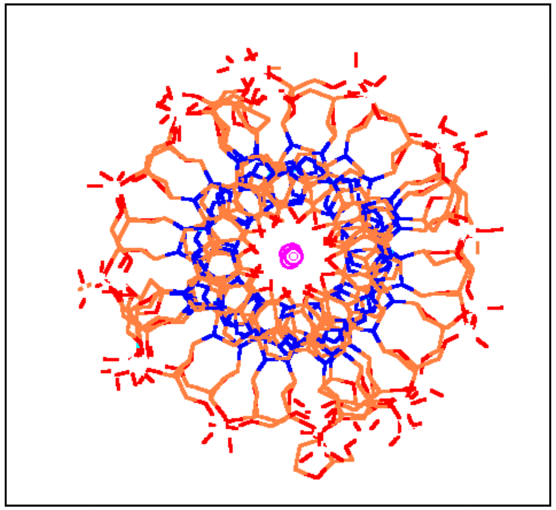






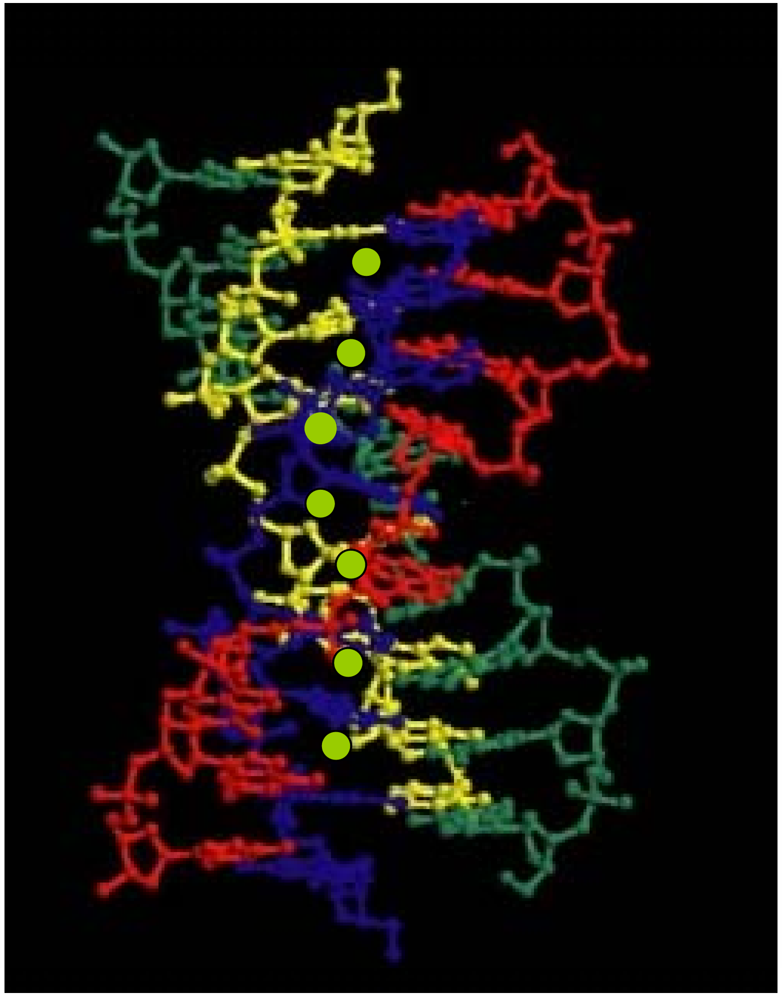
2.1 nm

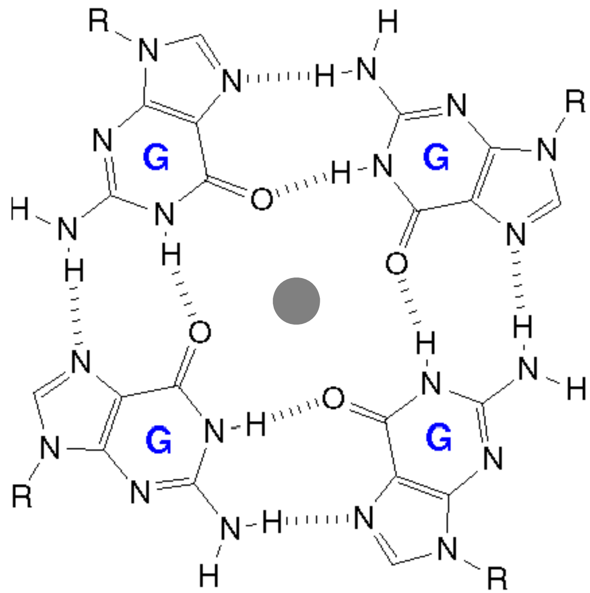




2.3 nm

The Structure of G-quadruplex (4G) DNA

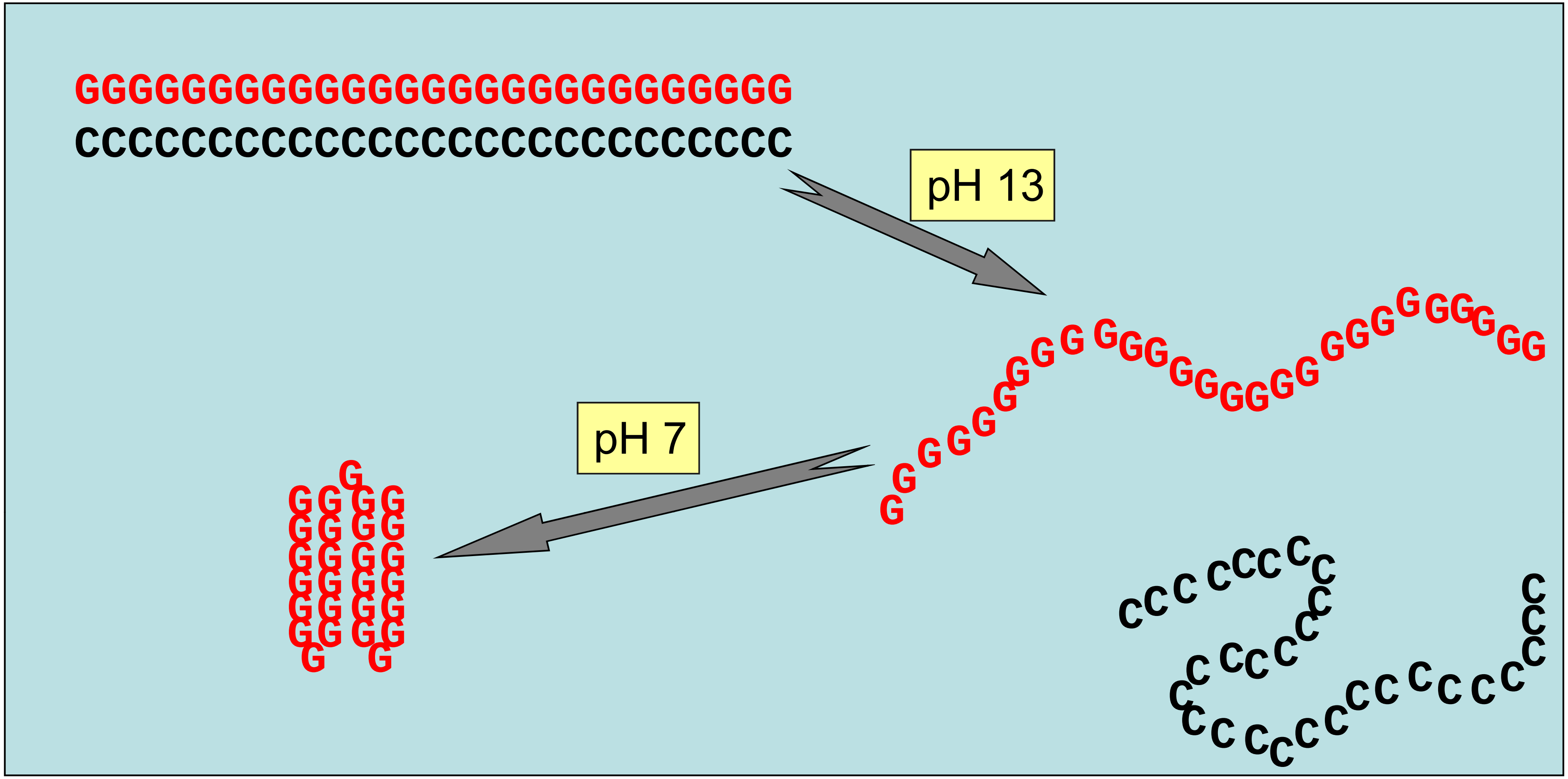




● — K^+ or Na^+

Current research

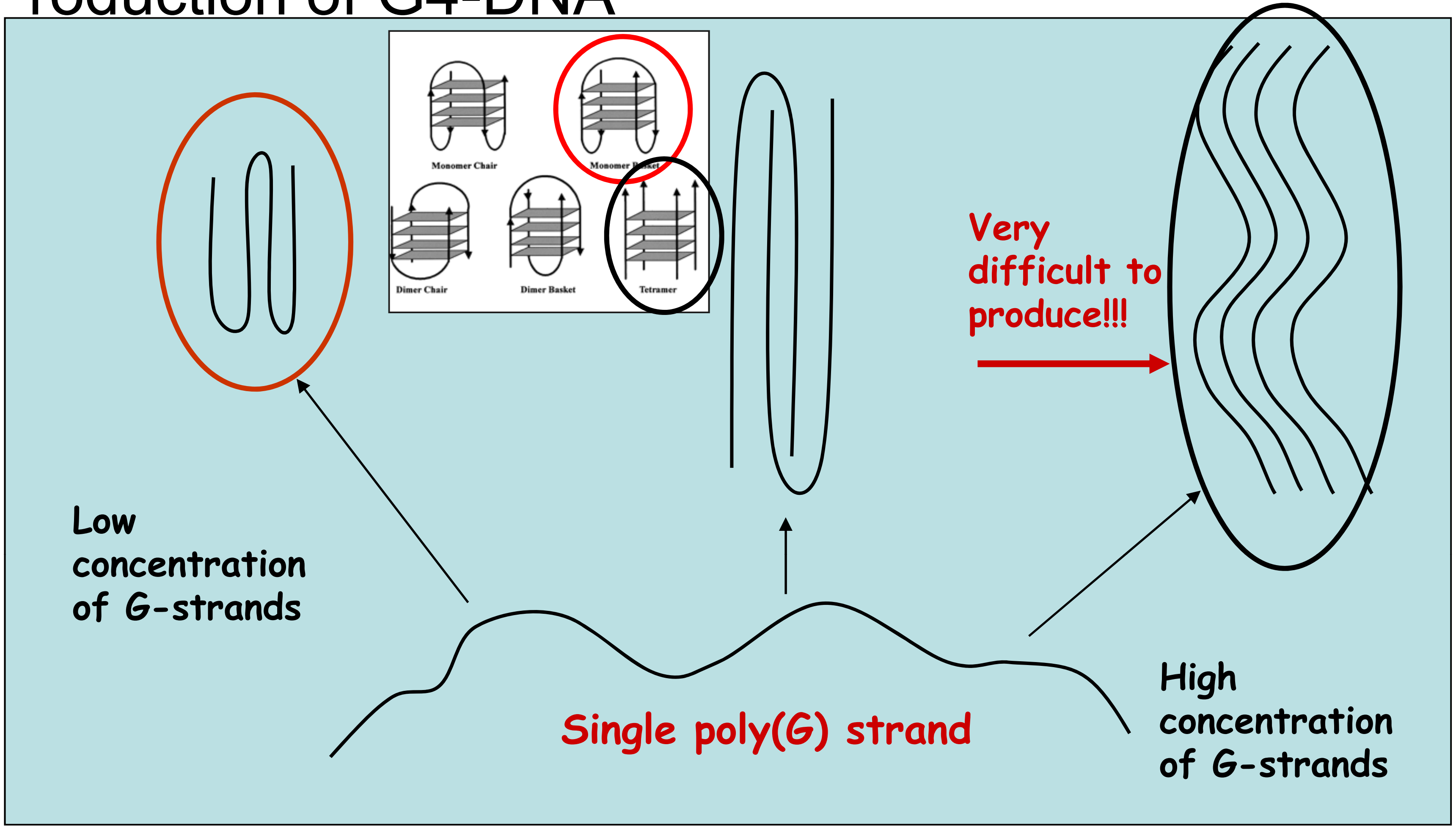
- Production of G4-DNA



- Dissociation Poly(G) and Poly(C) strands at high pH
- Folding the PolyG strand into G4-DNA upon lowering pH

Current research

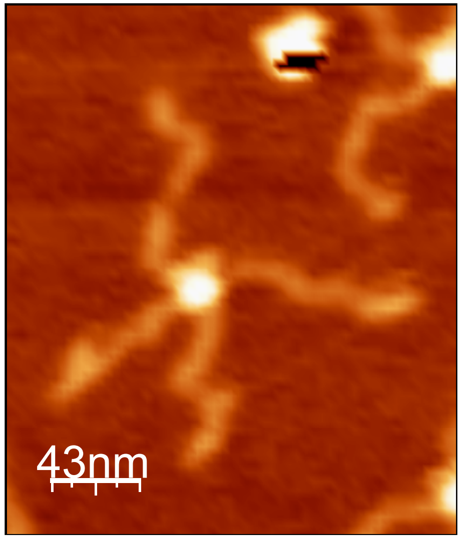
- Production of G4-DNA

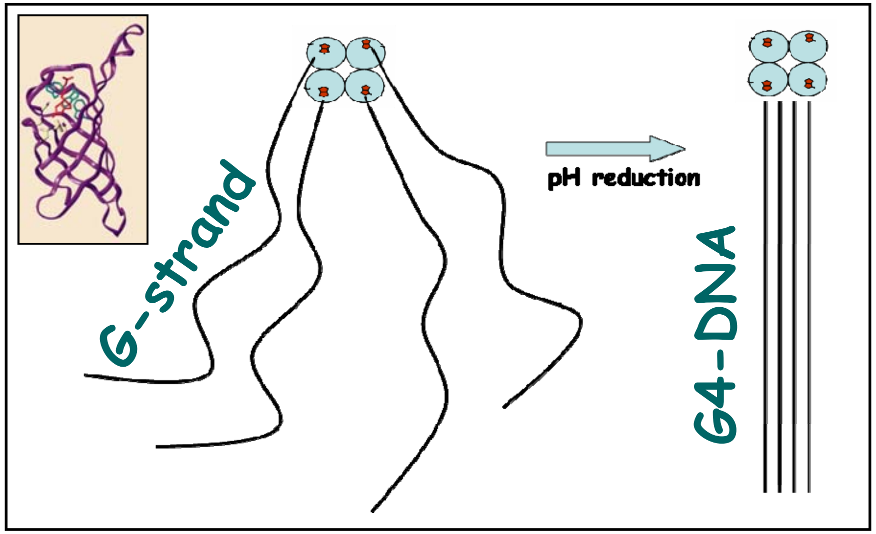


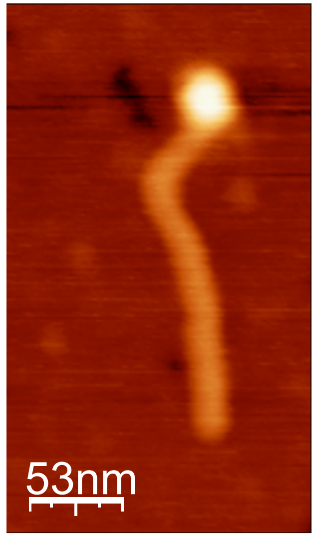
- Note the 4:1 length-ratio => intra-molecular 4-folding
- Length-ratio is consistent with AFM characterization (shown later)

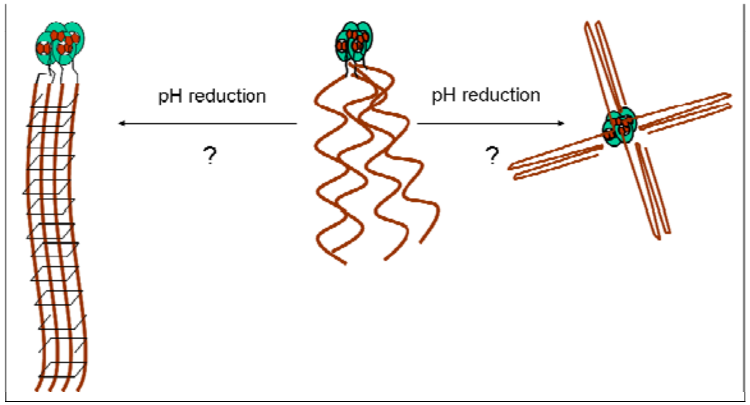
Current research

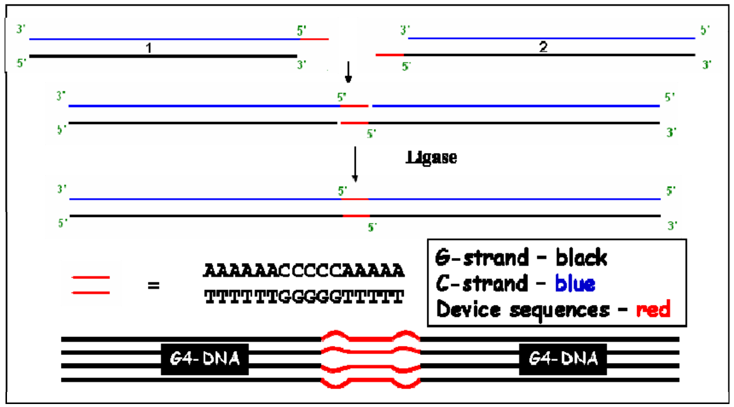
- Production of G4-DNA:4-Stranded G4-DNA with Biotin-Avidin











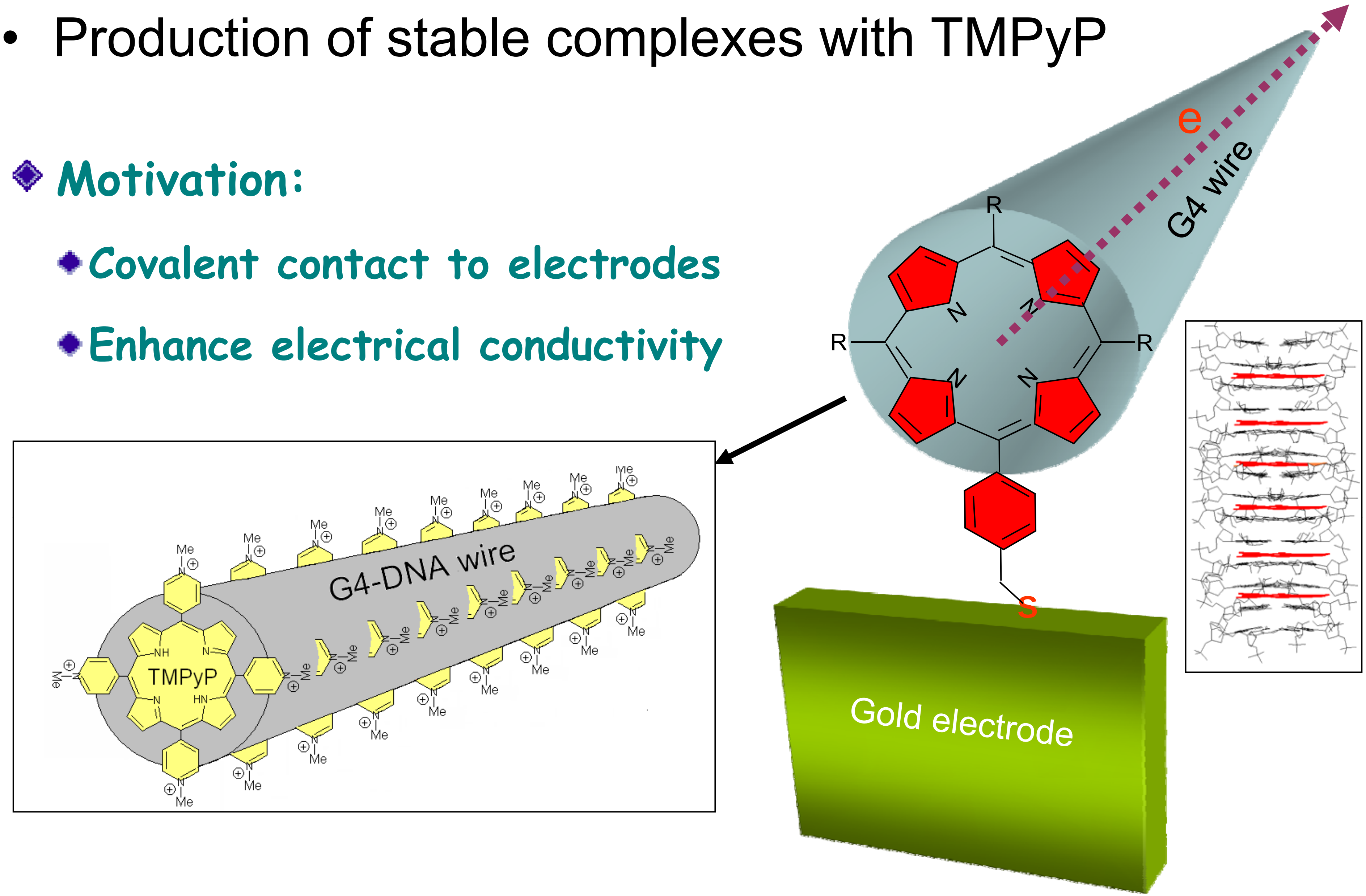
- Our solution for 4-stranded G4-DNA construction
- Potential junctions…

Current research

- Production of stable complexes with TMPyP

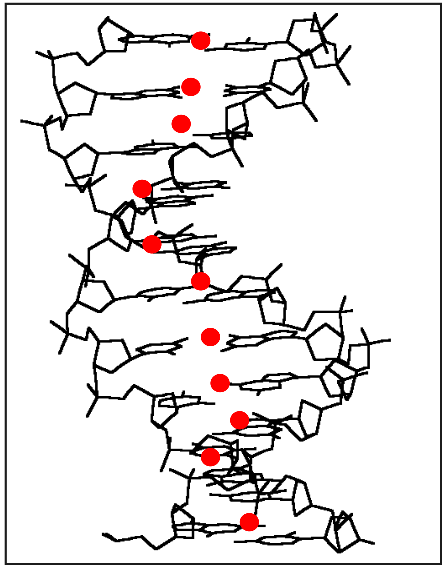
◆ **Motivation:**

- ◆ *Covalent contact to electrodes*
- ◆ *Enhance electrical conductivity*

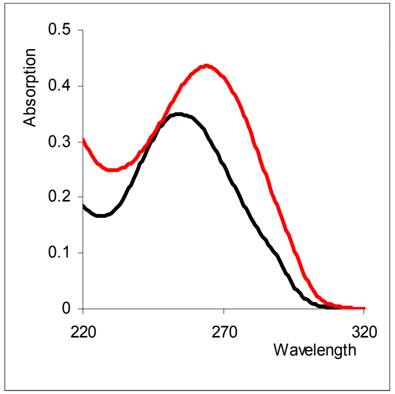


Current research

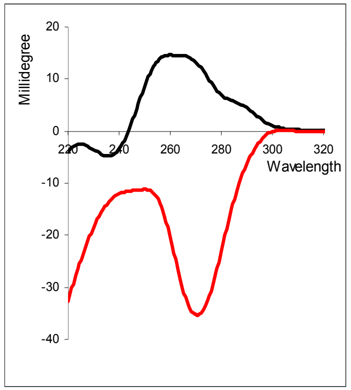
- DNA derivative: M-DNA



- Enzymatic production of long Poly(G)-Poly(C)
- Complexation with Ag^{1+} and Cu^{1+}
- Stoichiometry: 1 ion:1 bp
- High stability

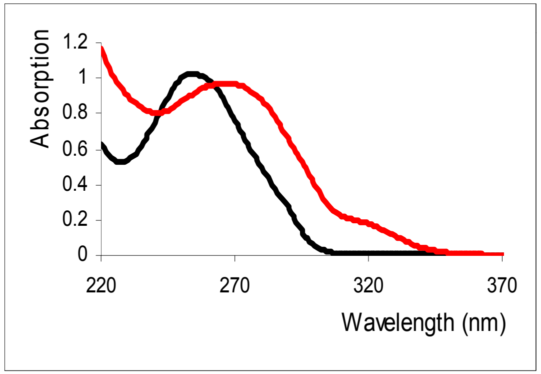


Absorption

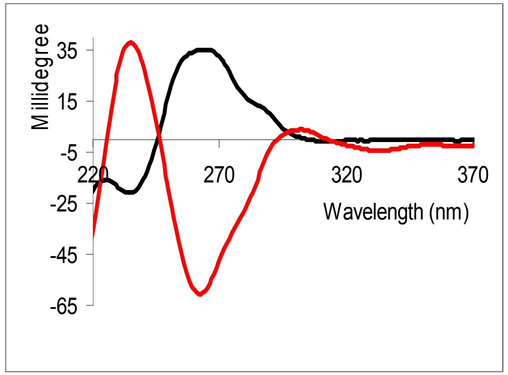


CD

Poly(G)-Poly(C) + Ag^{+1}



Absorption

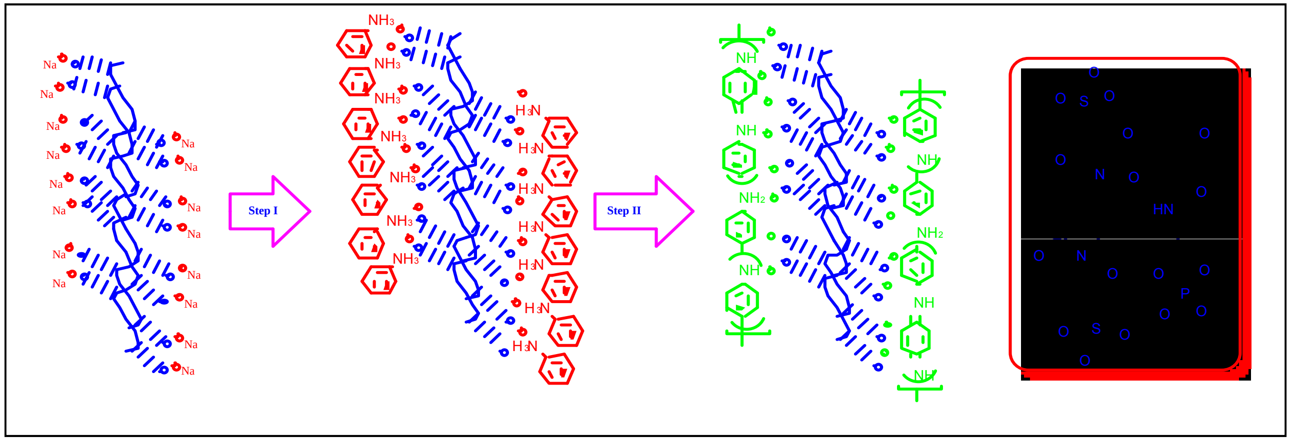


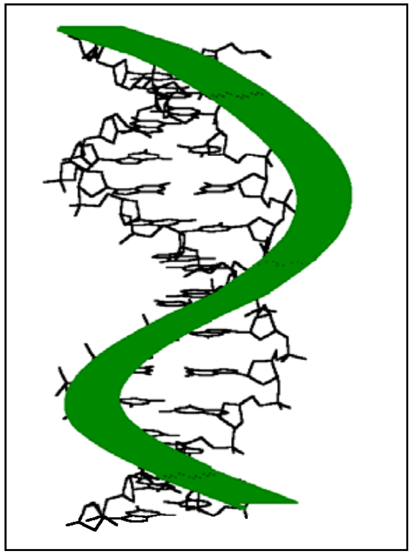
CD

Poly(G)-Poly(C) + Cu^{+1}

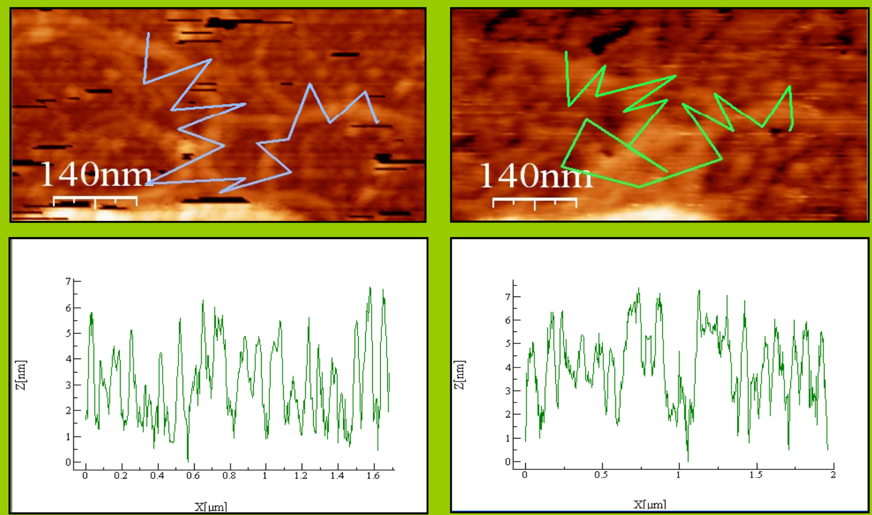
Current research

- Polyaniline coating (poly(G)-Poly(C) (S. Yitzchaik et al)





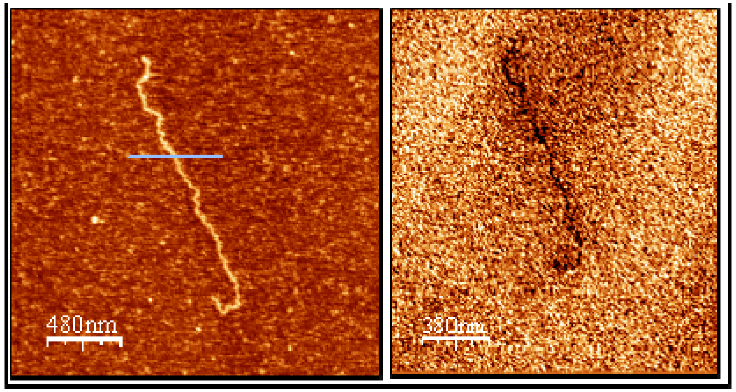
- Two synthetic routes (Oxidative and photochemical)
- Mechanistic and Photo-electrochemical investigation

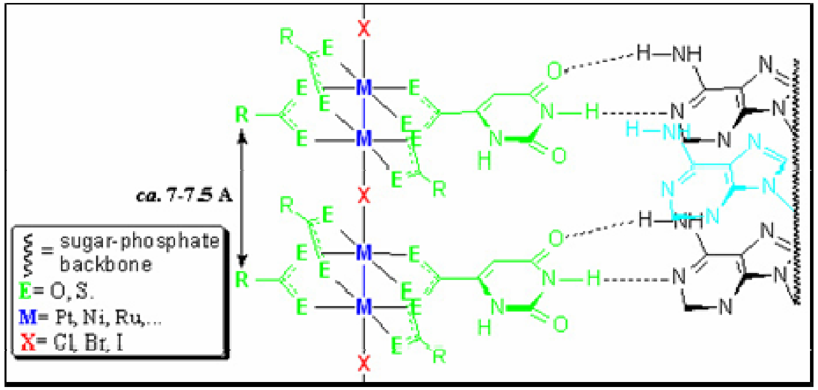


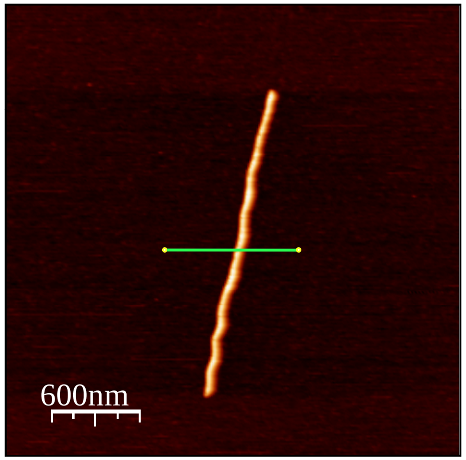
Before PAN: <h>~4 nm After PAN: <h>~5 nm

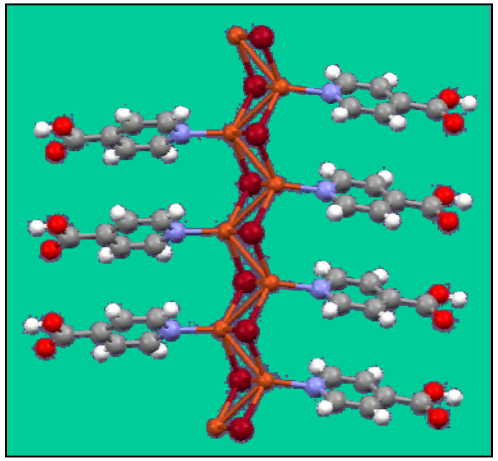
Current research

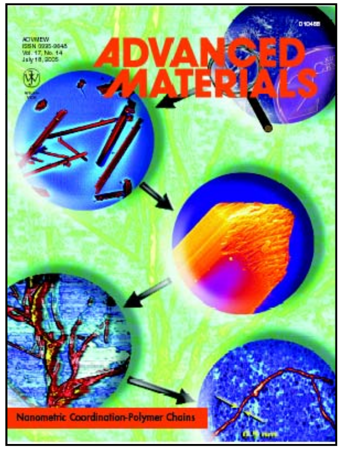
- MMX-polymer – DNA hybrids (F. Zamorra et al)







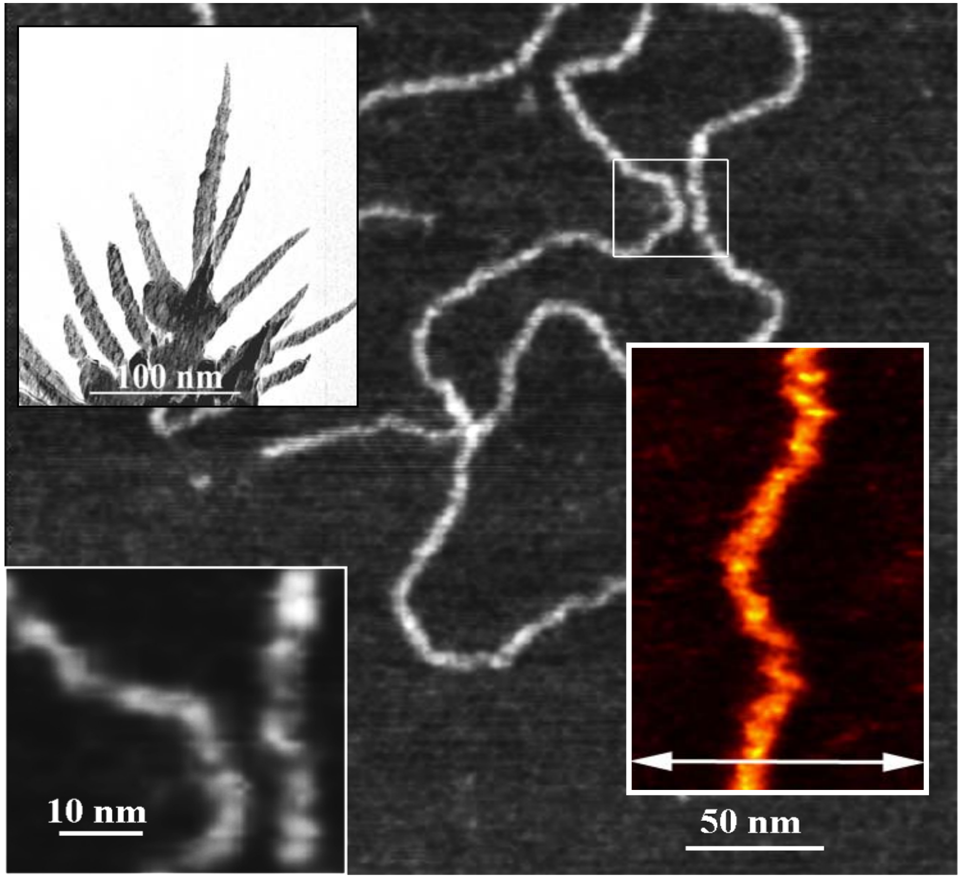




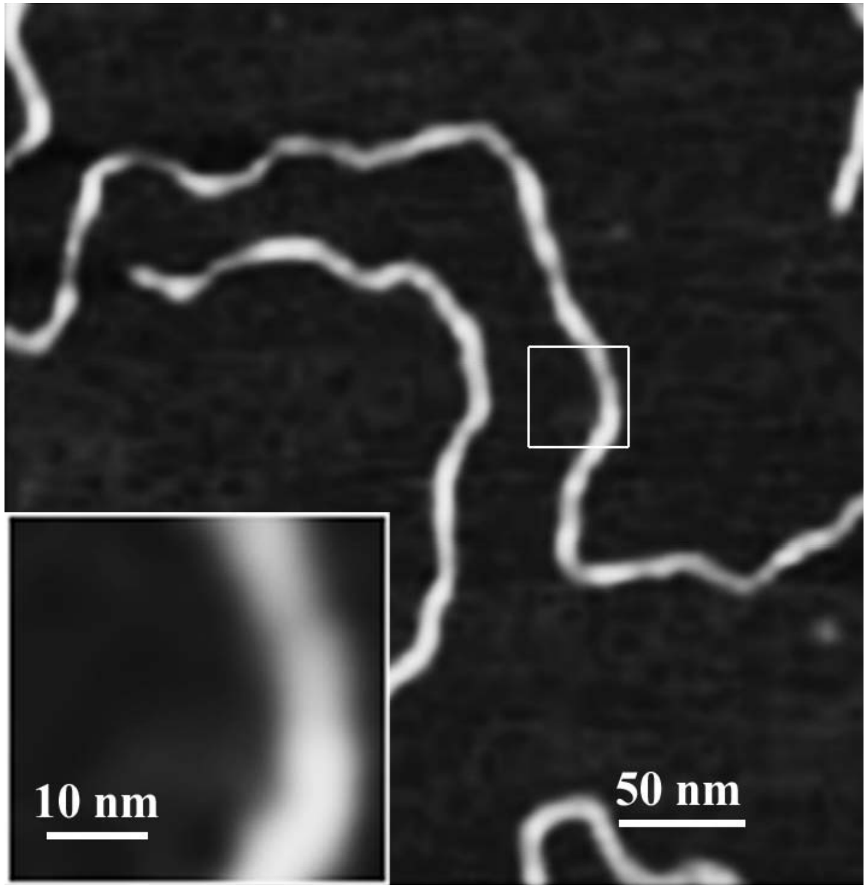
Current research

- AFM characterization with high resolution tips

Ultra sharp tips

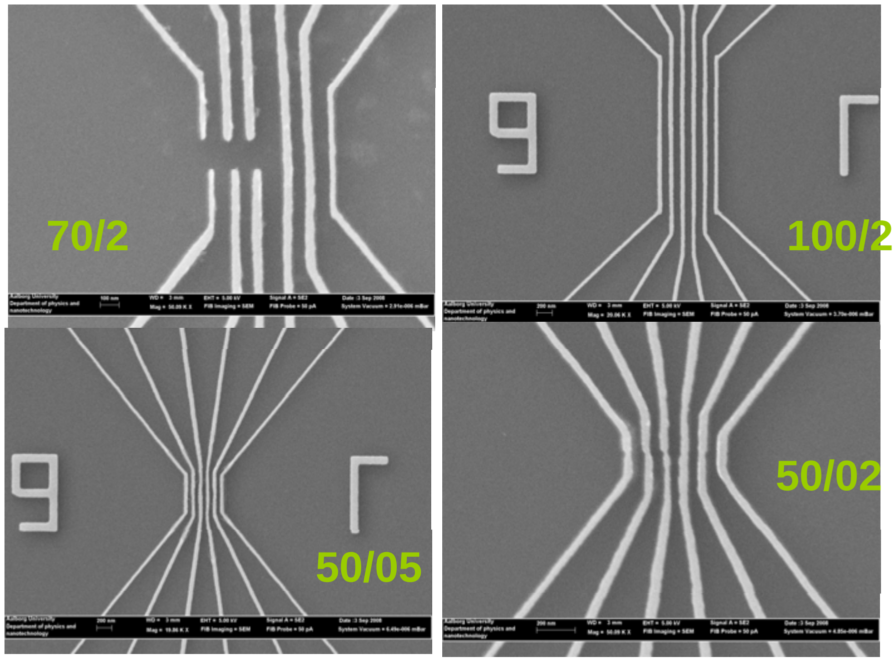


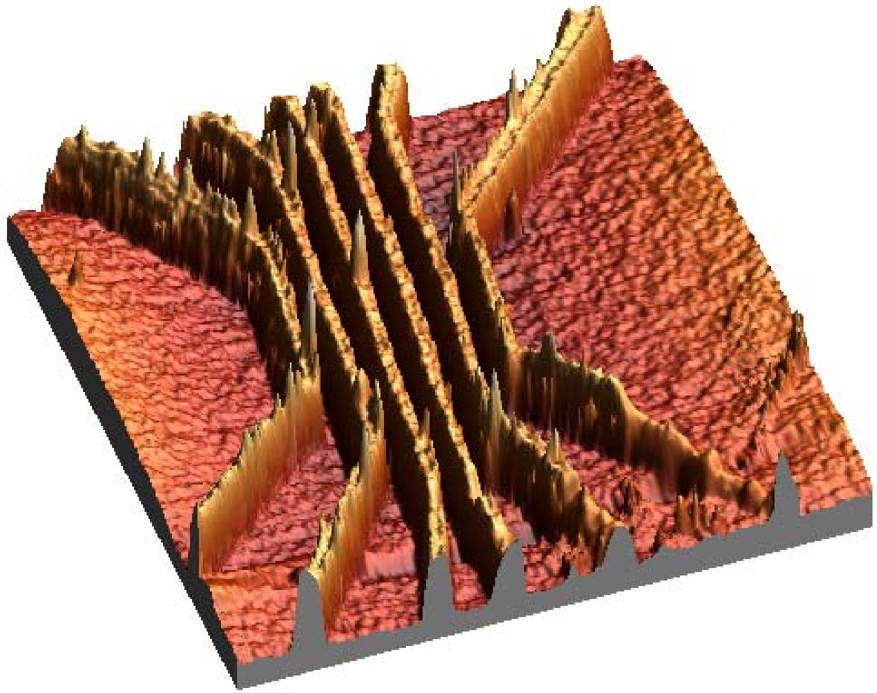
Conventional tips



Our activities

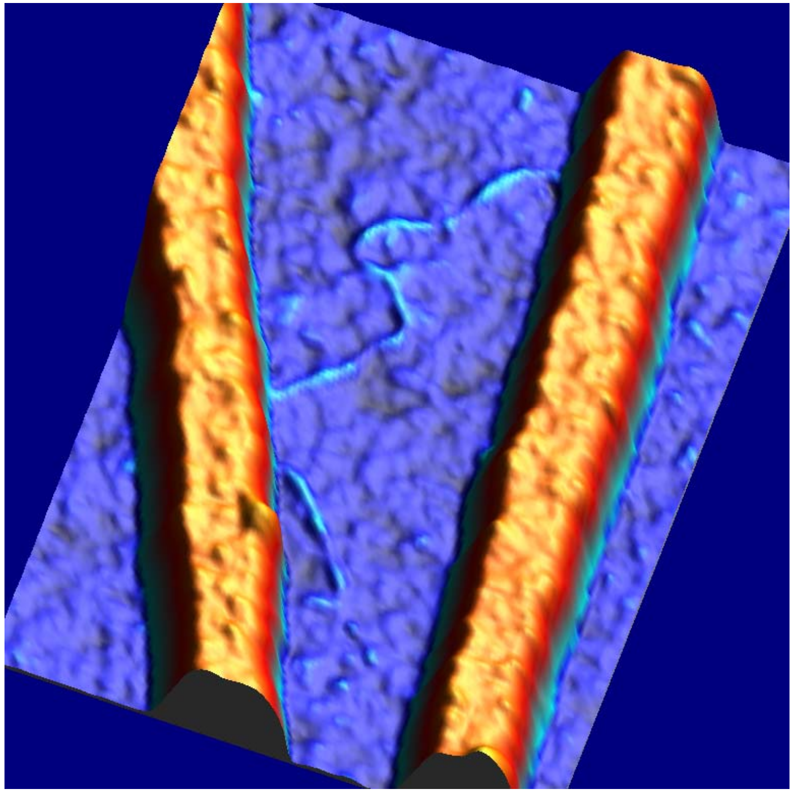
- Electrodes design



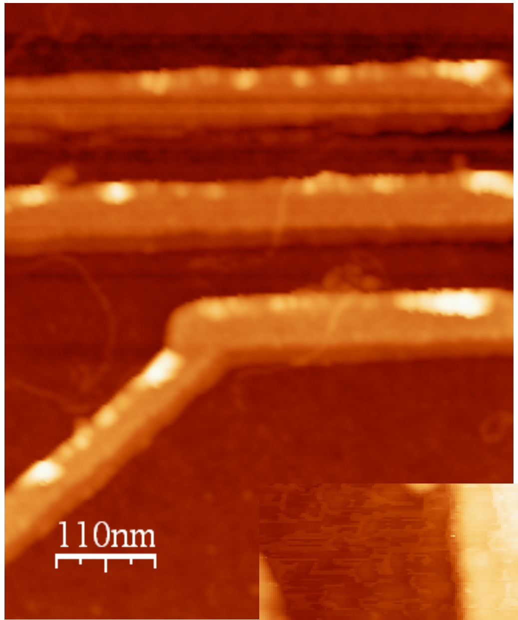


Our activities

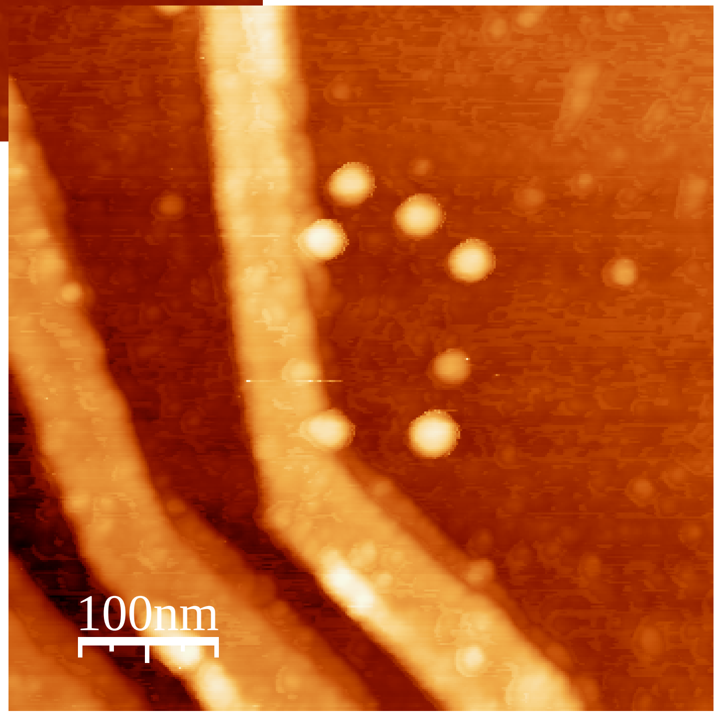
- DNA deposition



phosphothiolated dsDNA
on APTMS surface



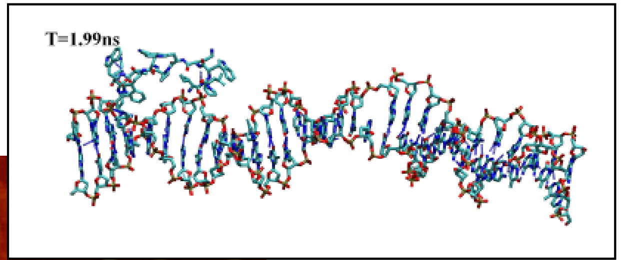
dsDNA
on APTMS
surface

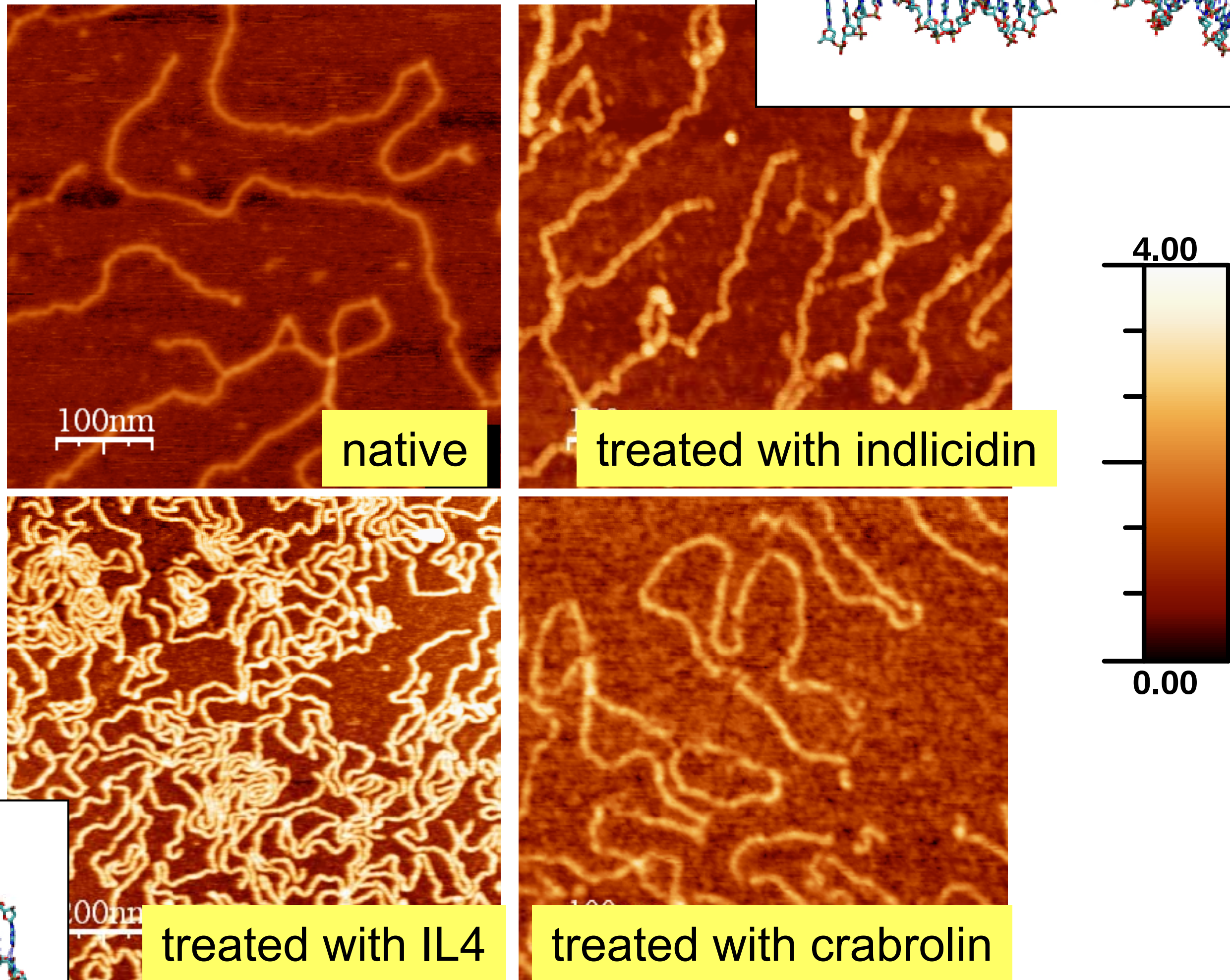


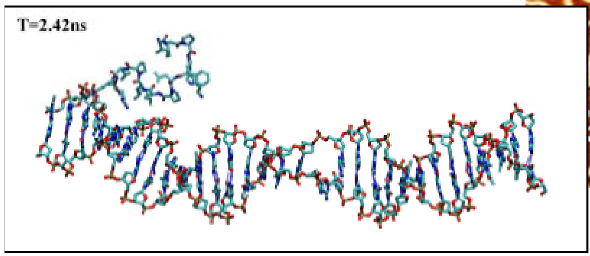
dsDNA-NP dimers
on APTMS
surface

Peptide (AMP) coated DNA

- short AMP and toxin peptides can bind to DNA;
- interaction can be tuned by structure of a peptide
- continuos tube with ~1nm increase in diameter can be formed
- route to functional layer on DNA: coating with short peptides







Binding of IL4 to monomolecular G4