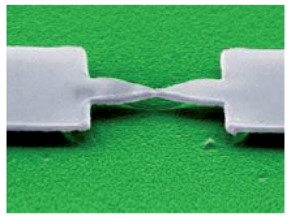
Current Transport in nanoscale molecular junctions

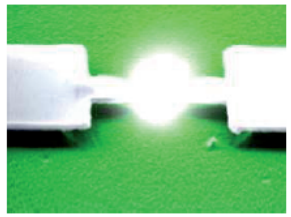
Artur Erbe

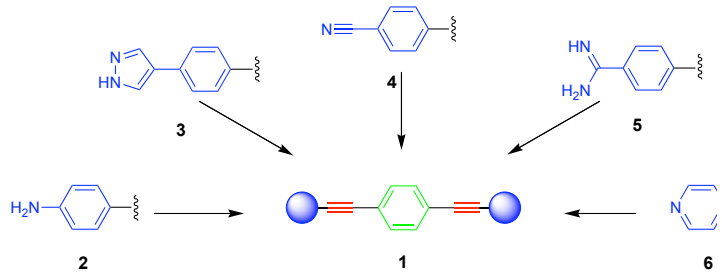
Outline

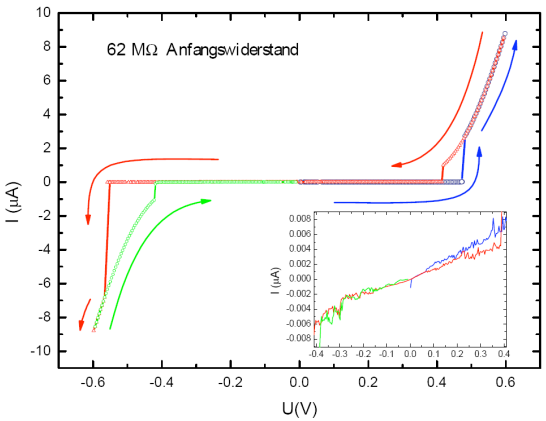
- Mechanical break junctions in liquid environment
- Resonant tunneling model for *I-V* curves
- Current through molecules with varying anchoring groups
- Transport through single DNA molecules
  - linker groups
  - DNA Quadruplex

Molecular electronics

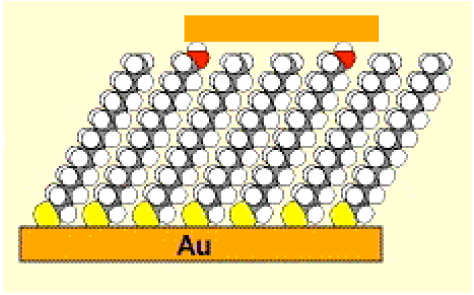


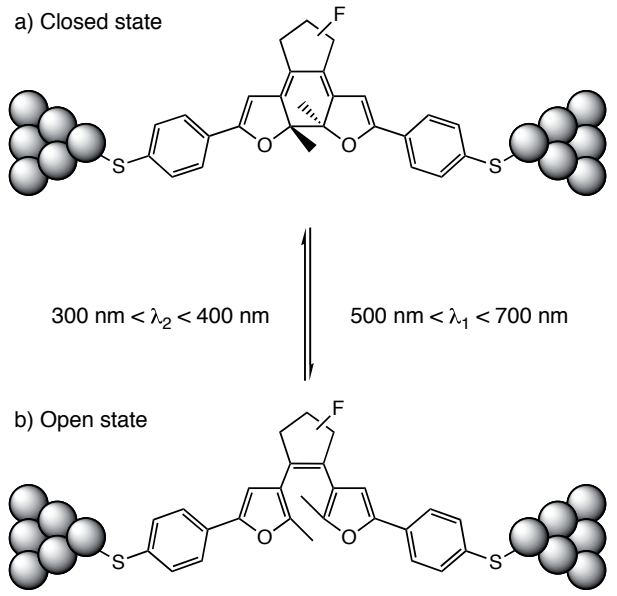






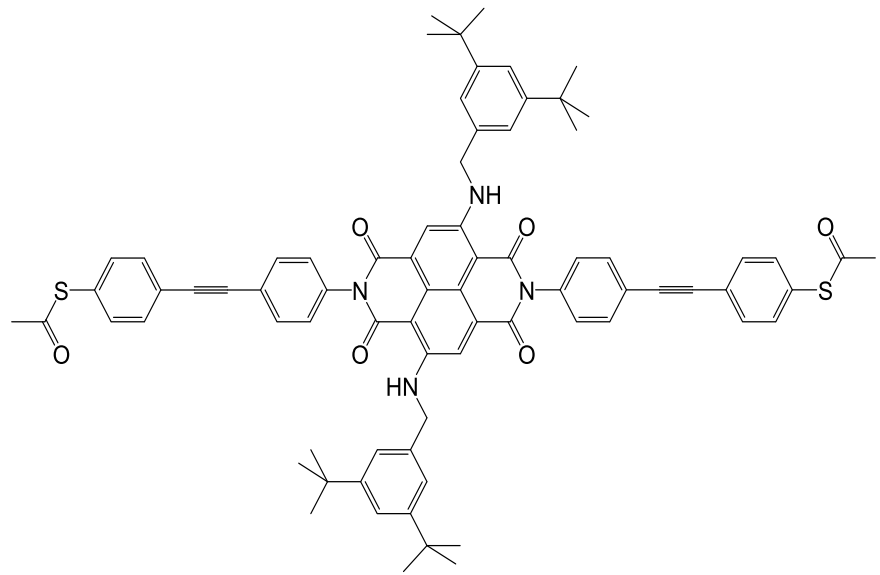
Molecular Device





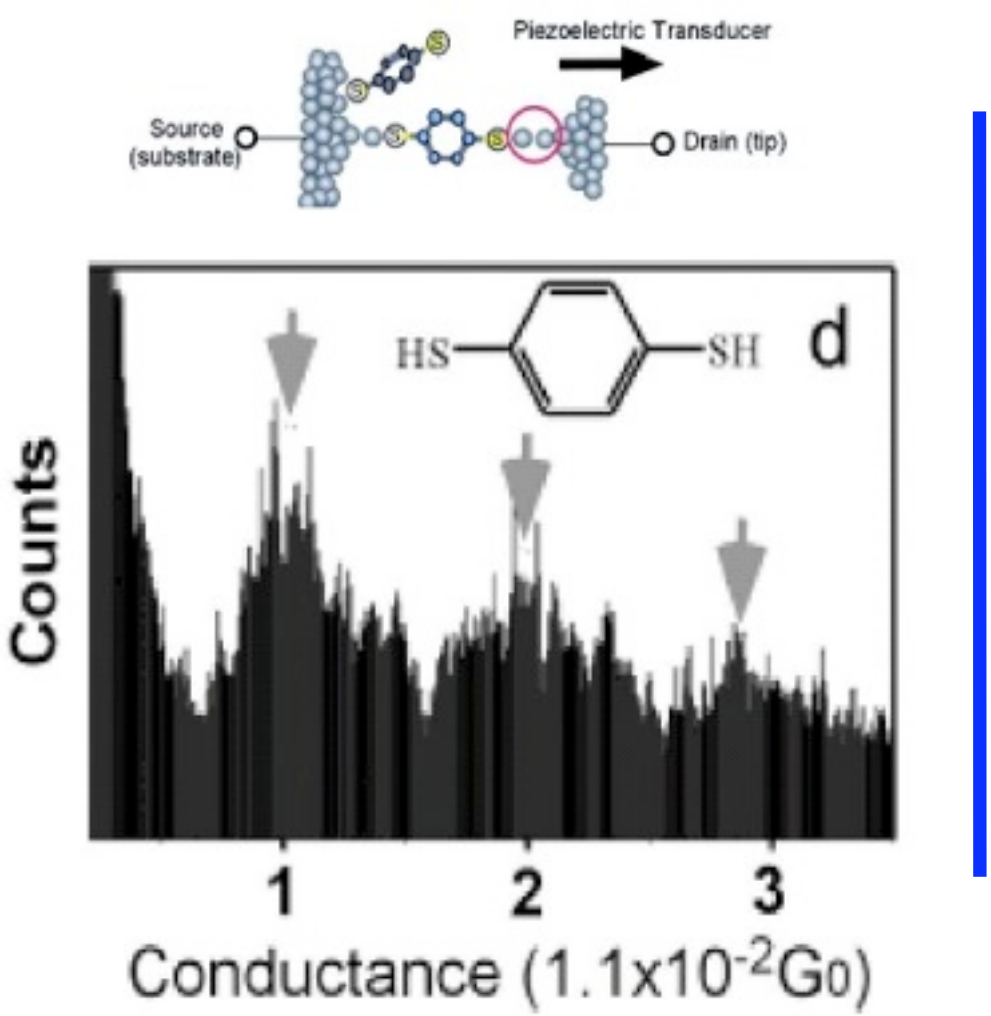
Typical molecules

- Alkanes
- Conjugated molecules
- “Complicated” molecules



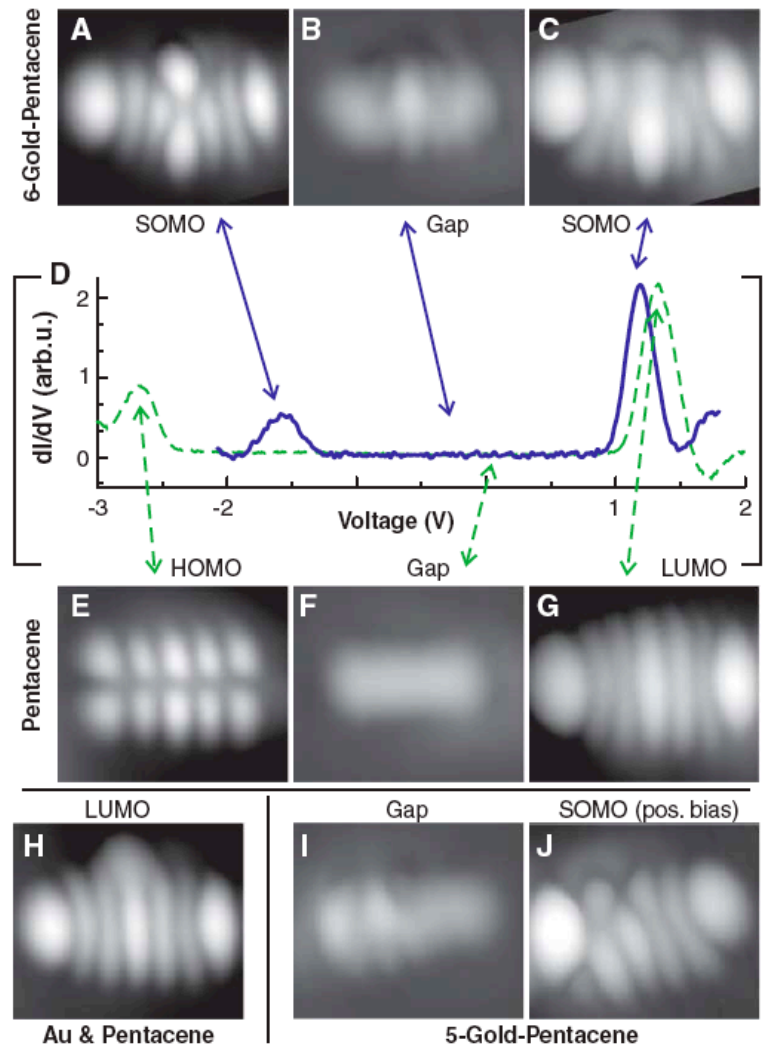
Contacting techniques

Scanning tunneling microscopy



Tao *et al.* Nano Lett (2004)

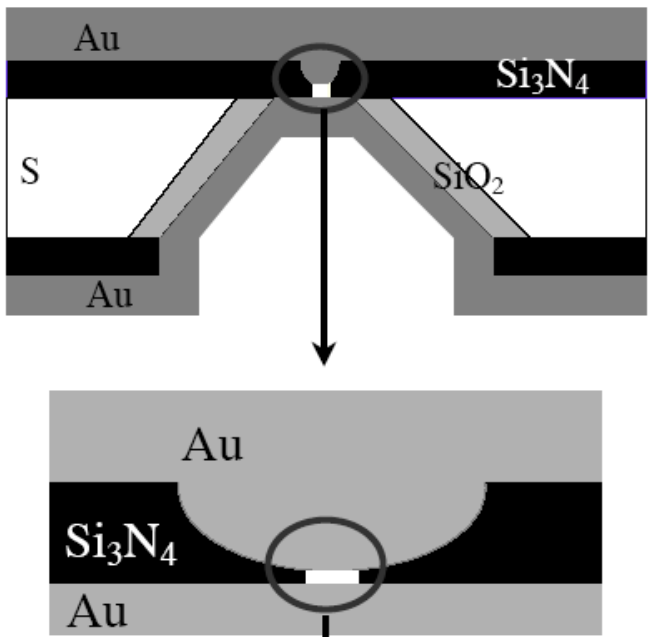
Imaging molecules by STM

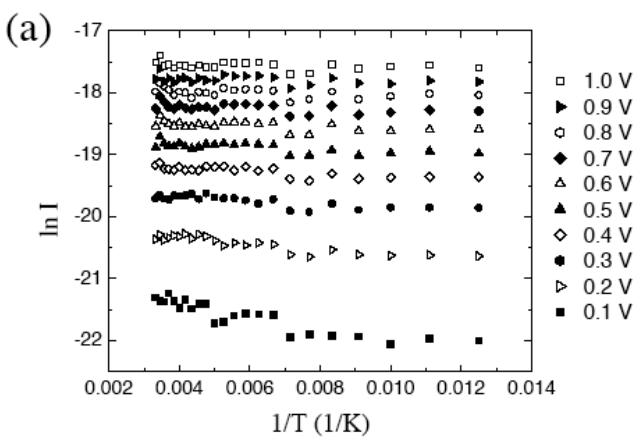


J. Repp *et al.* Science (2006)

Contacting techniques

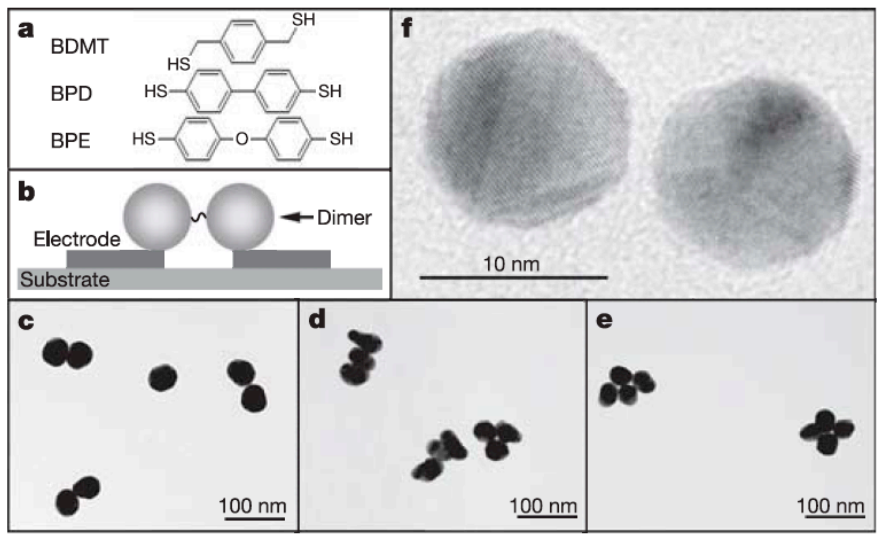
Silicon nanopores on Alkanethiols

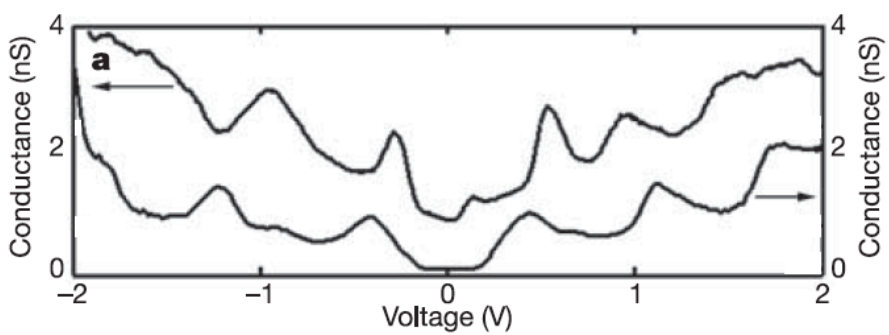




Wang et al. PRB (2003)

metallic clusters bound to molecular linking groups

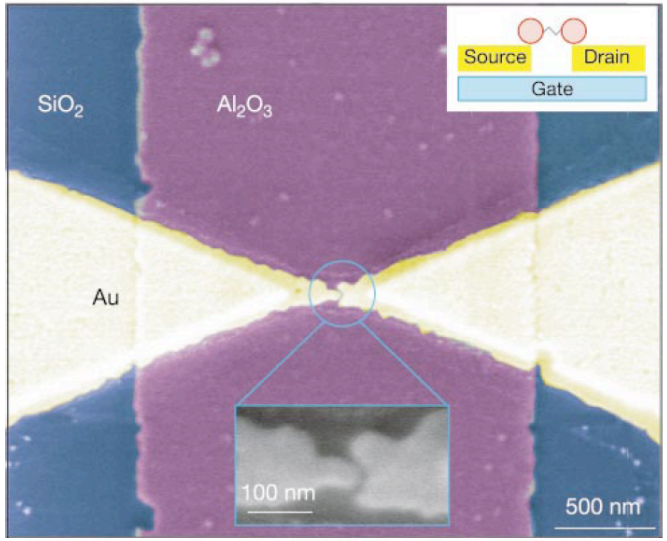


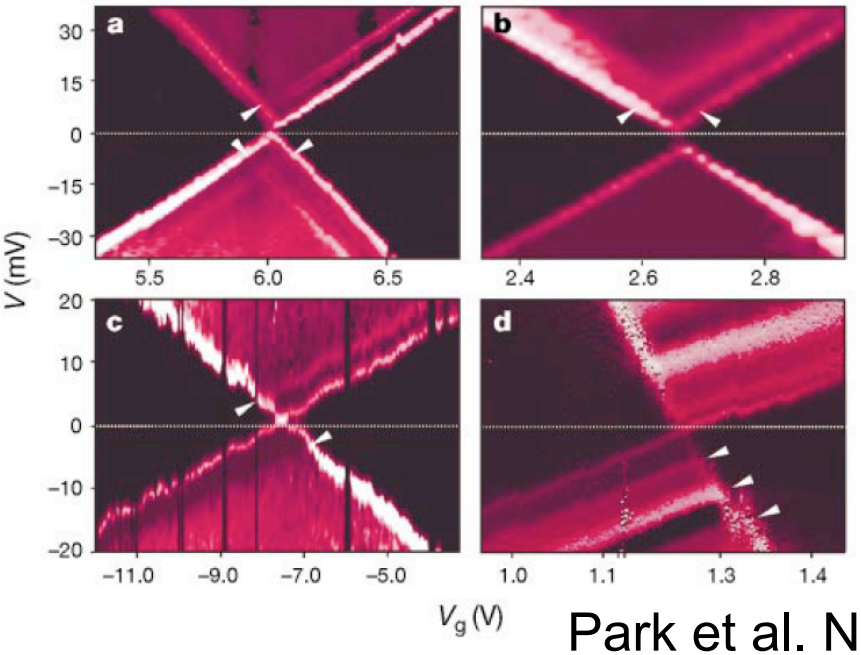


Dadosh et al. Nature (2005)

Contacting techniques

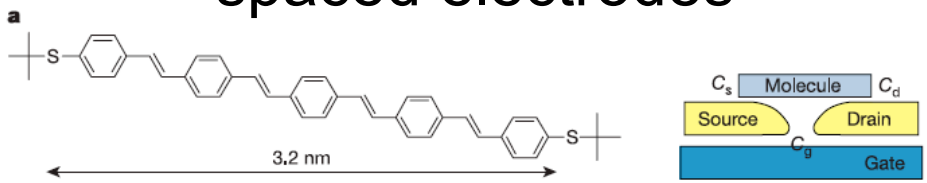
electromigrated junctions

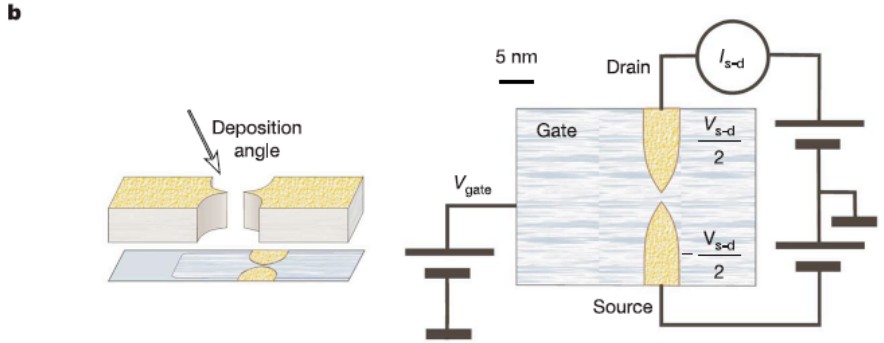


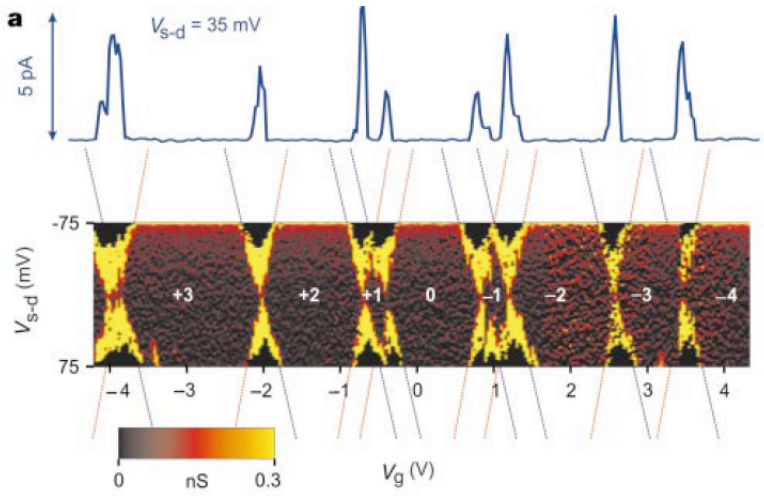


Park et al. Nature (1999)

molecules deposited on closely spaced electrodes

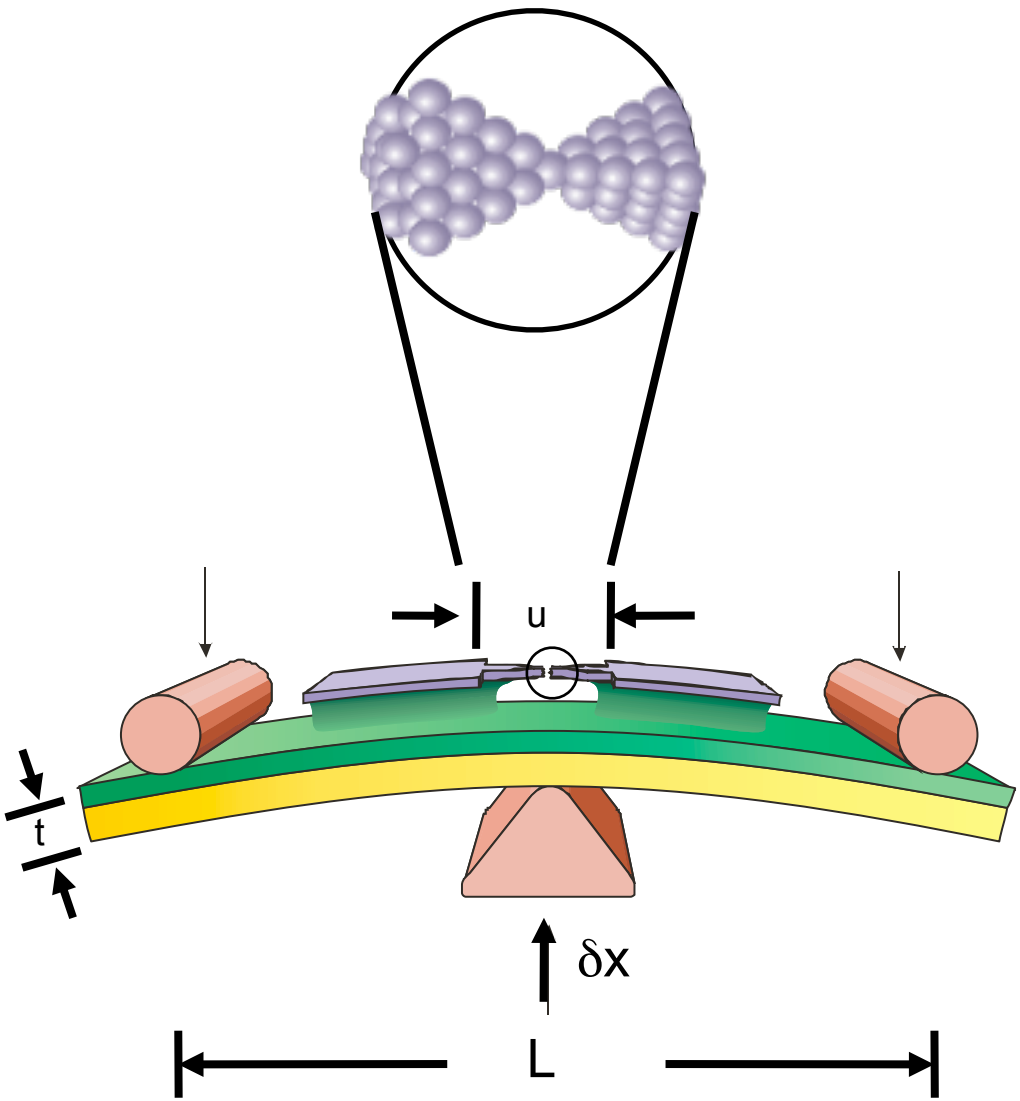






Kubatkin et al. Nature (2003)

Mechanically Controllable Break-junction



Realization of Single-Atom:
Bending by δx results in a lateral stretching of δu = r δx, where

$$r = \frac{6tu}{L^2}$$

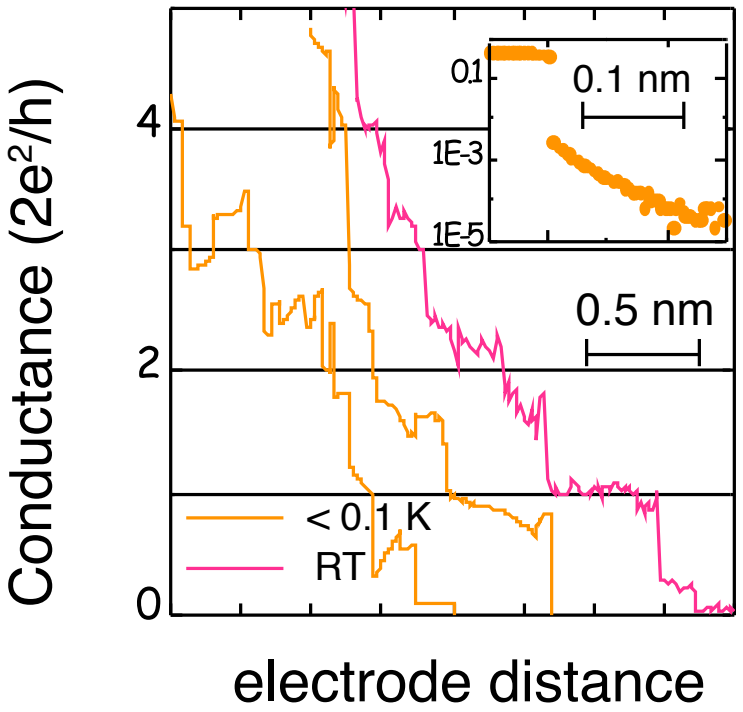
$$r \approx 10^{-4} \ldots 10^{-5}$$

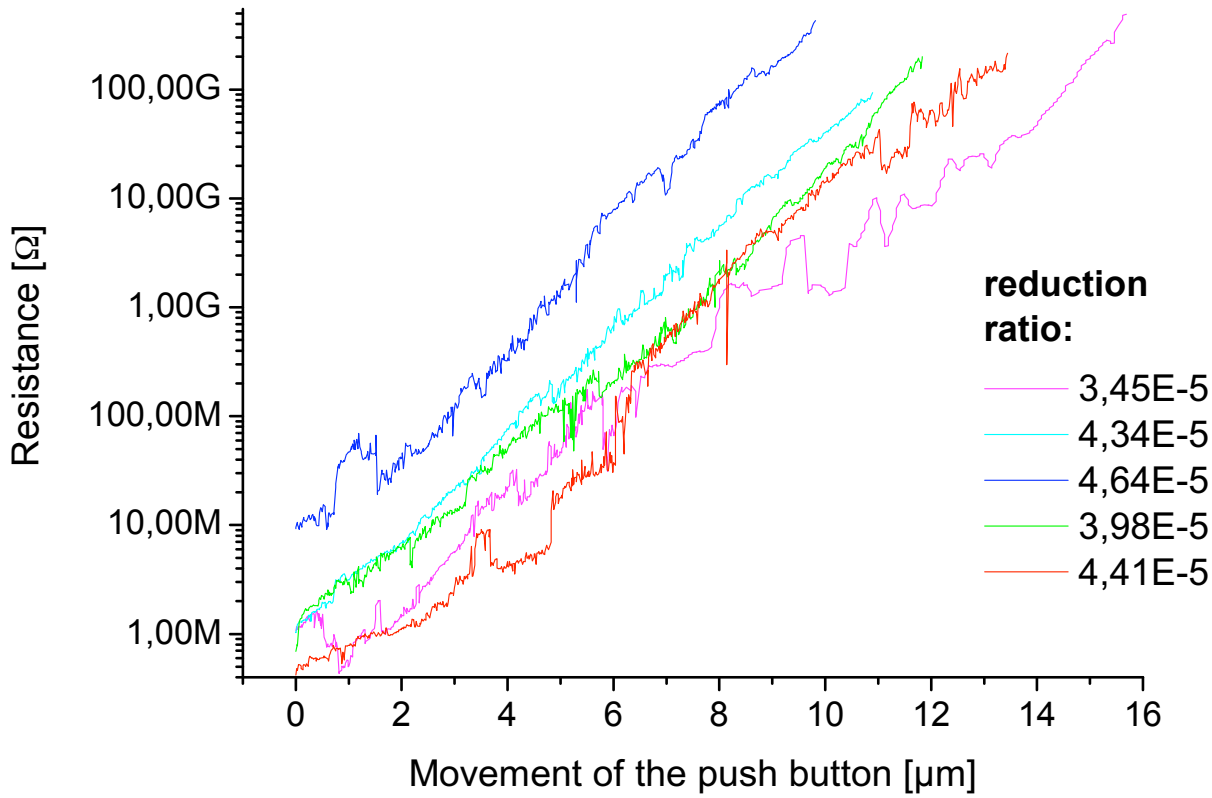
⇒ Atomic resolution possible with "simple" mechanics

Characterization of the gold break junction

- Conductance steps due to atomic configuration
- Tunneling regime is used for calibration of the displacement

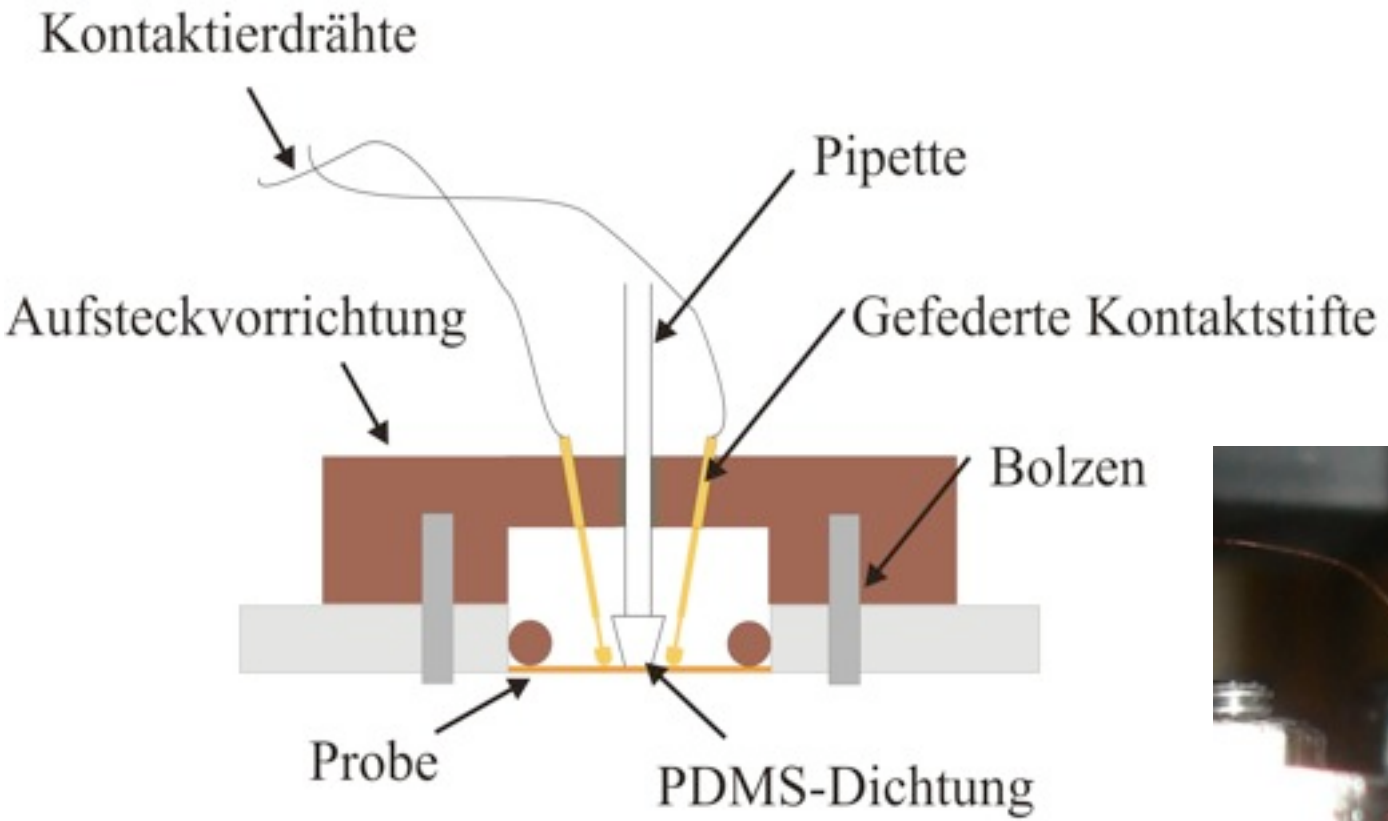
$$R \propto \exp\left(\frac{2}{\hbar}\sqrt{2m\Phi}\cdot d\right)$$

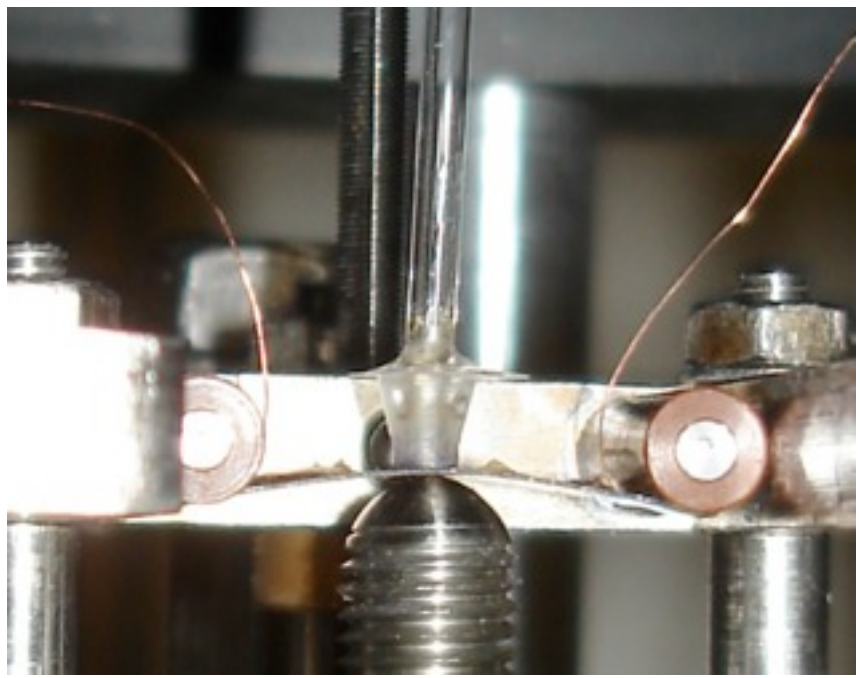




Mechanically controllable break junctions

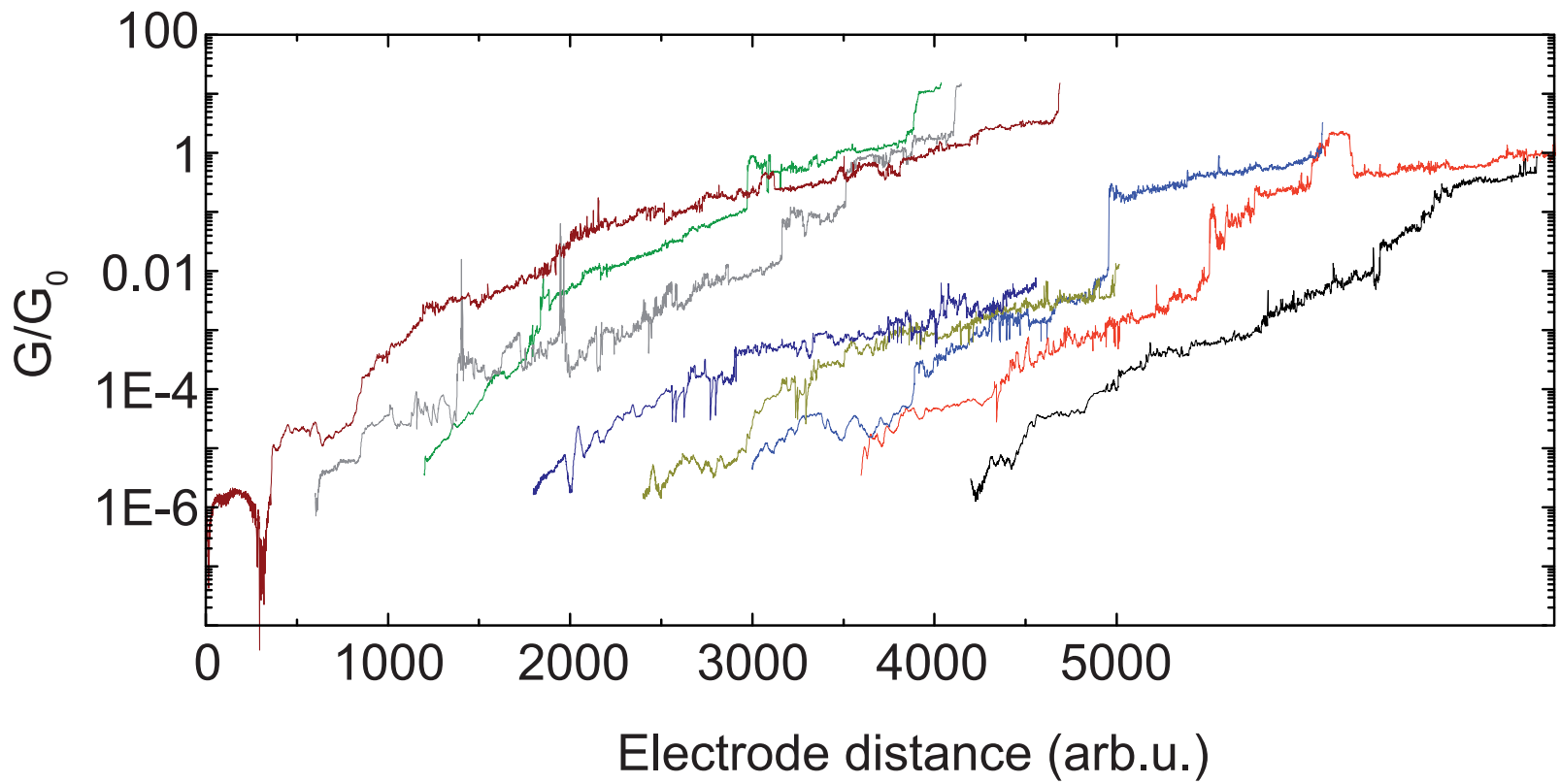
Characterization of molecules in liquid environment





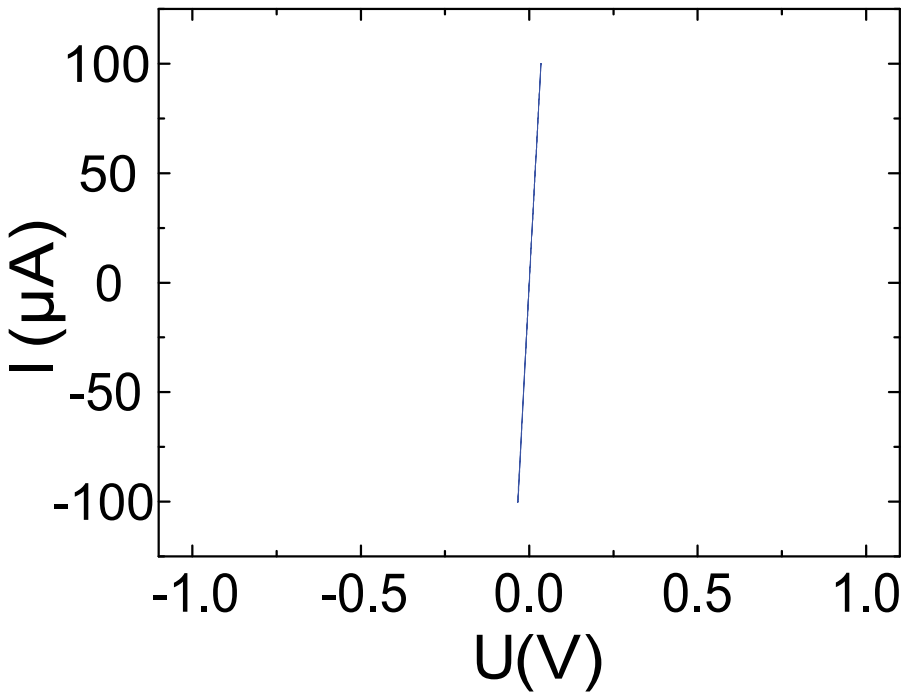
Characterization of pure solvent

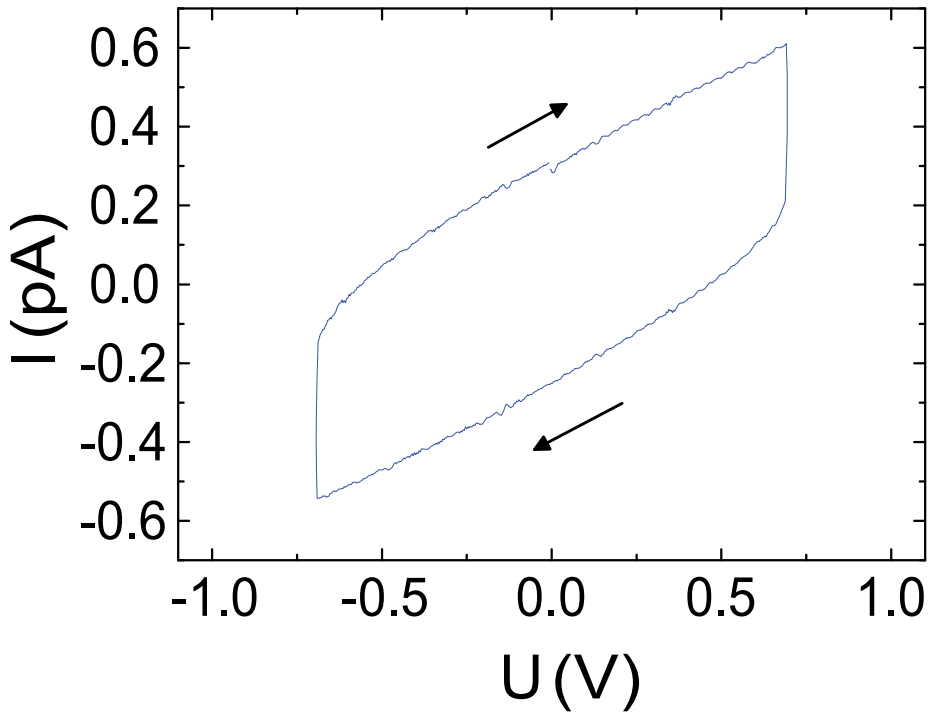
- No clear steps visible
- Rearrangements of the gold contacts possible
- Distance calibration only qualitatively



S. Verleger, Diploma Thesis (2006)

IV-curves in pure solvent

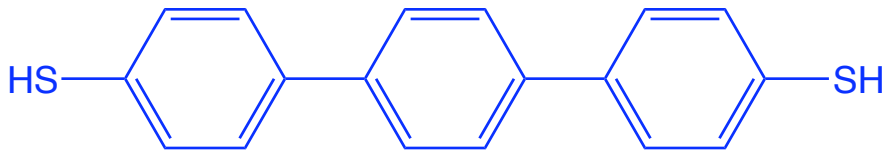


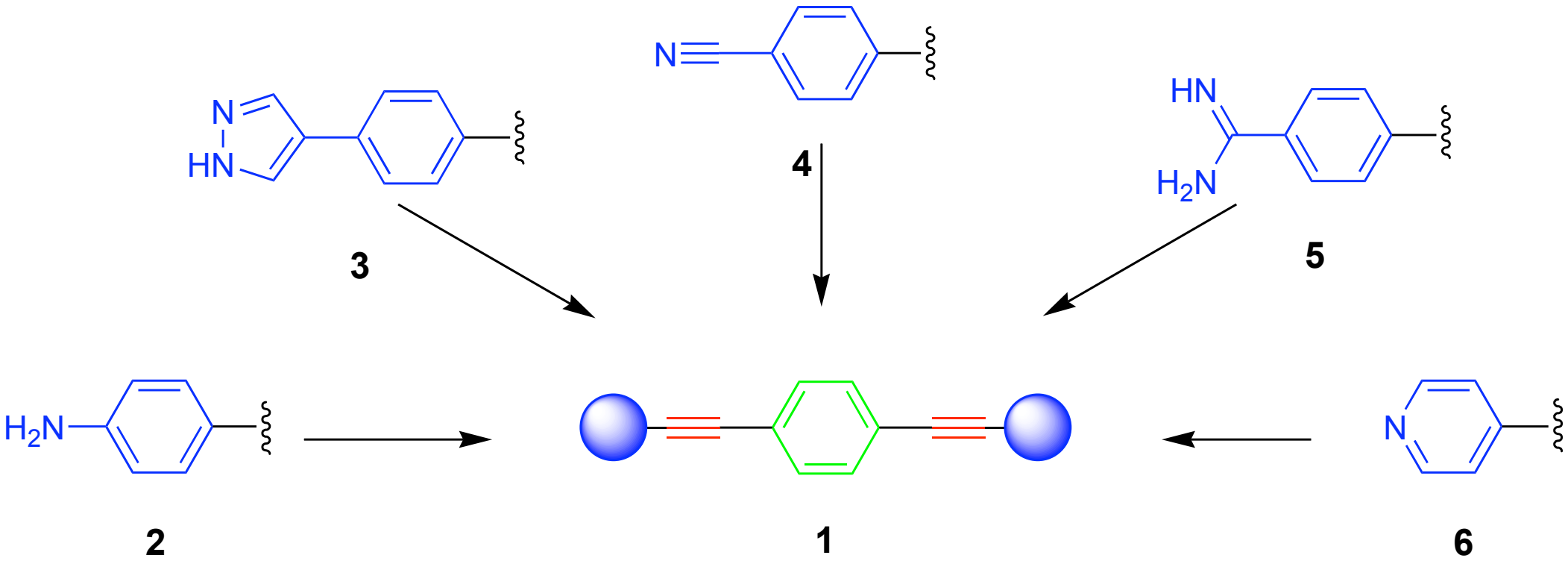


- linear (direct tunneling or metallic contact)
- hysteretic effects due to solvent (small current)

Contacting “simple” molecules

- Basic molecule: Conjugated => highly conductive
- Change of linker groups
- Traditional: thiol-gold bond
- Nitrogen based chemistry more reliable?

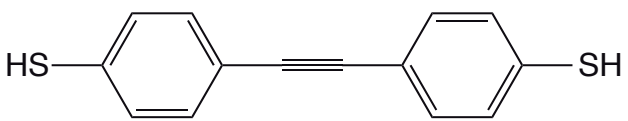




Characterized molecules

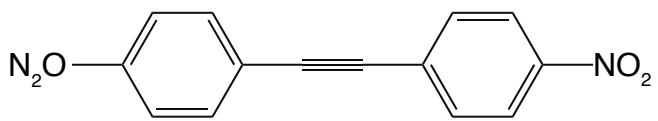
- Various anchoring groups on the same short and conjugated center

BTT



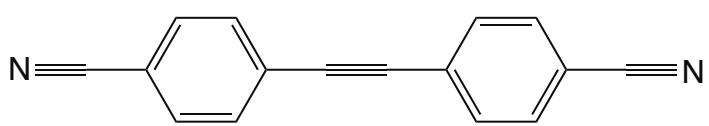
4,4’-bisthiotolane

BNT



4,4’-bisnitrotolane

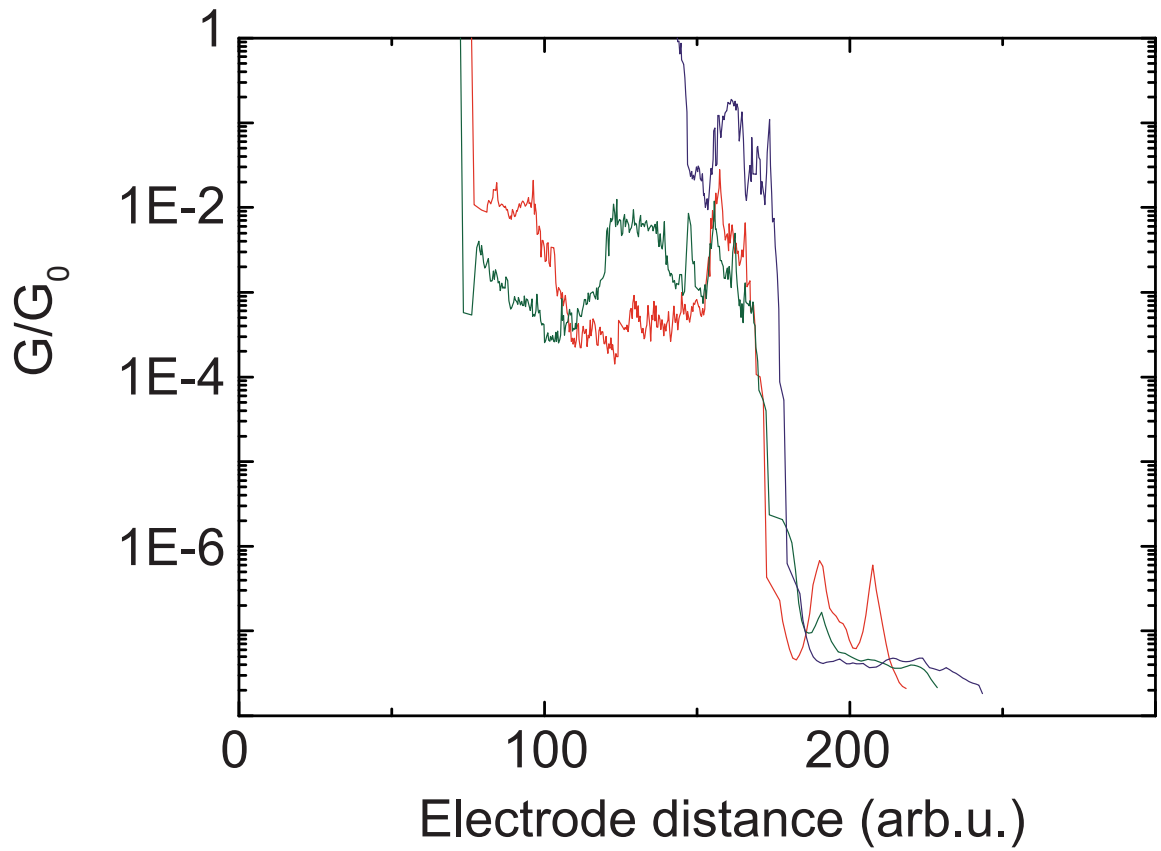
BCT



4,4’-biscyanotolane

Characterization of molecular junctions

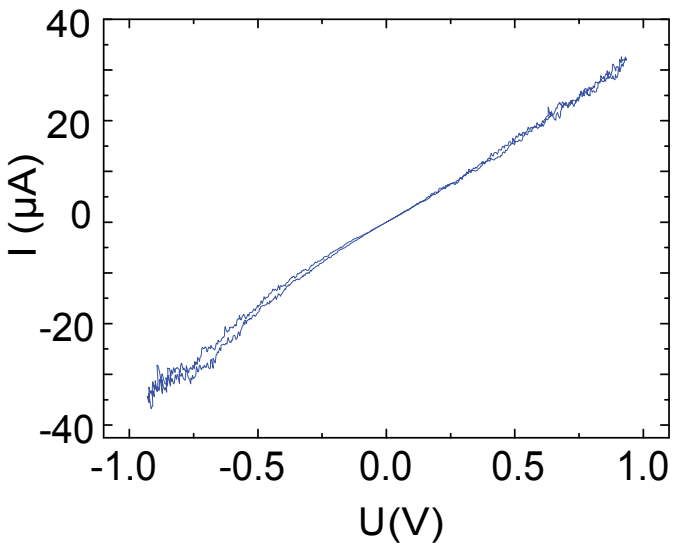
- Steps below $1G_0$ (BCT in Toluol)

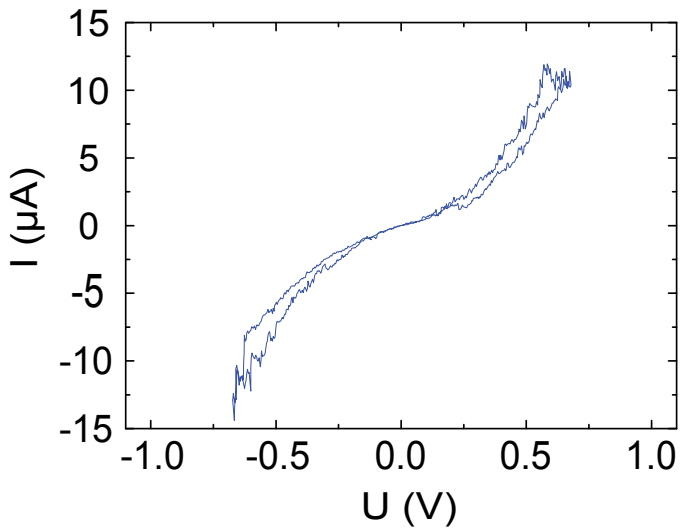


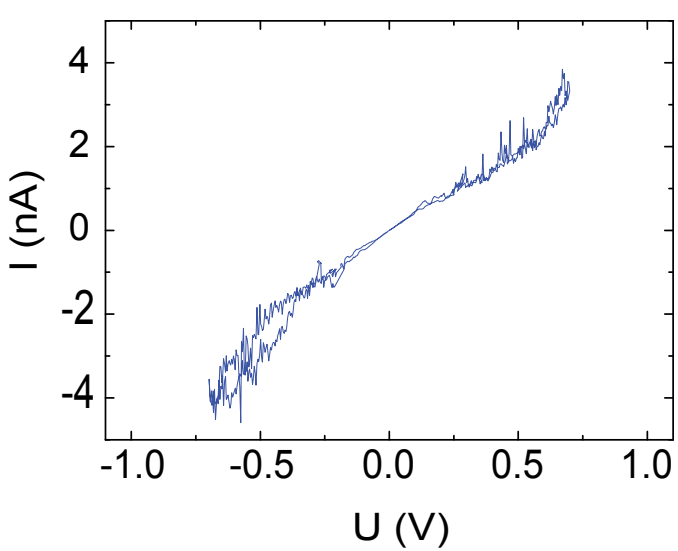
Th. Kirchner, Diploma Thesis (2008)

Characterization of molecular junctions

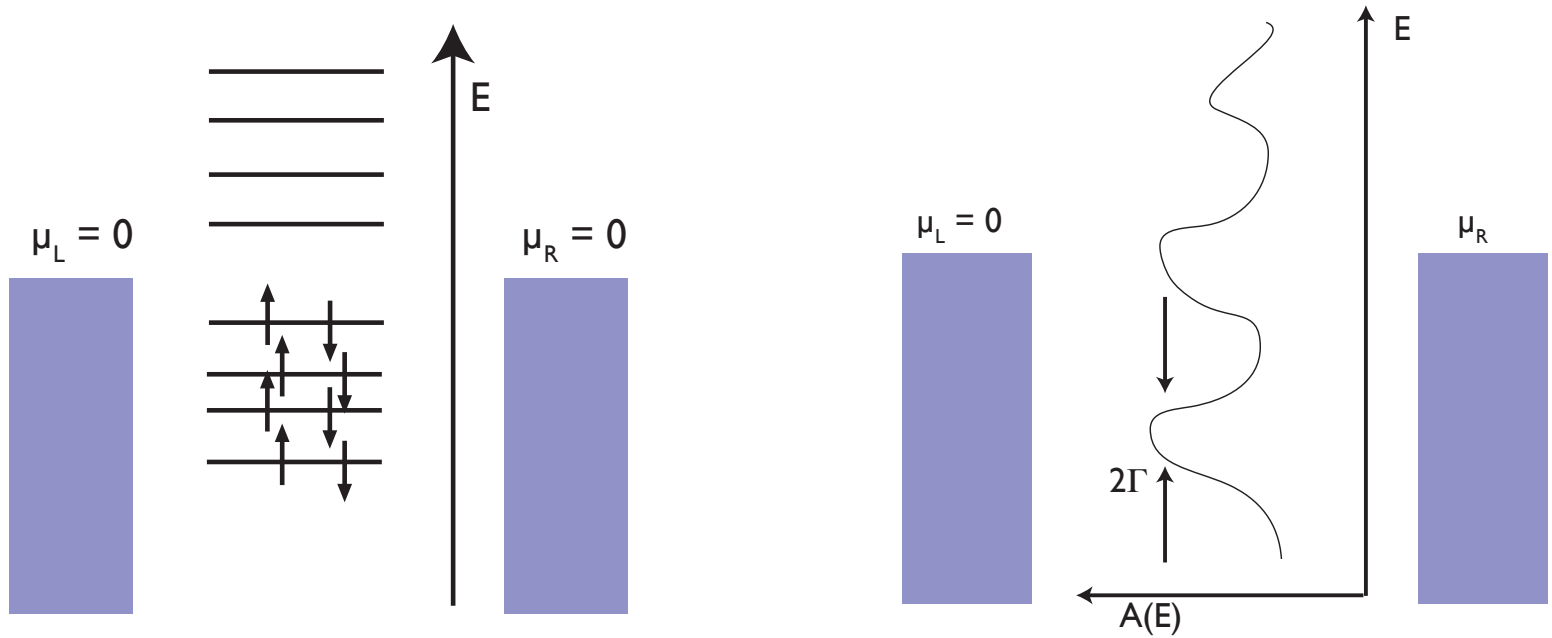
- *IV*s vary from
  - purely metallic to
  - resonant tunneling through molecules to
  - tunneling through solvent







Understanding *I-V*-curves

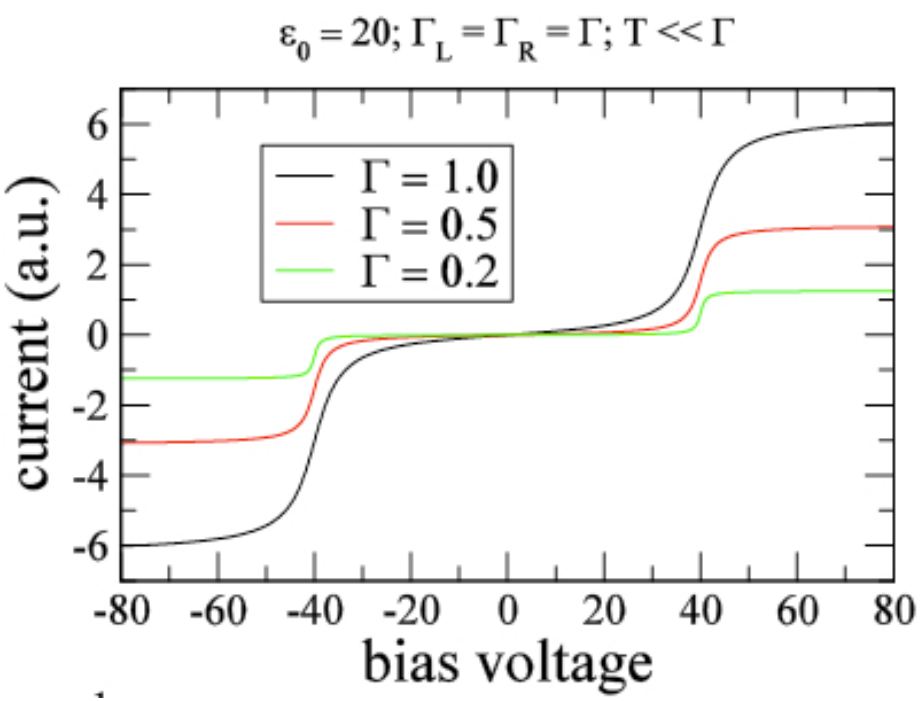


- Toy model: Single level between metallic leads
- coupling to leads: level broadening

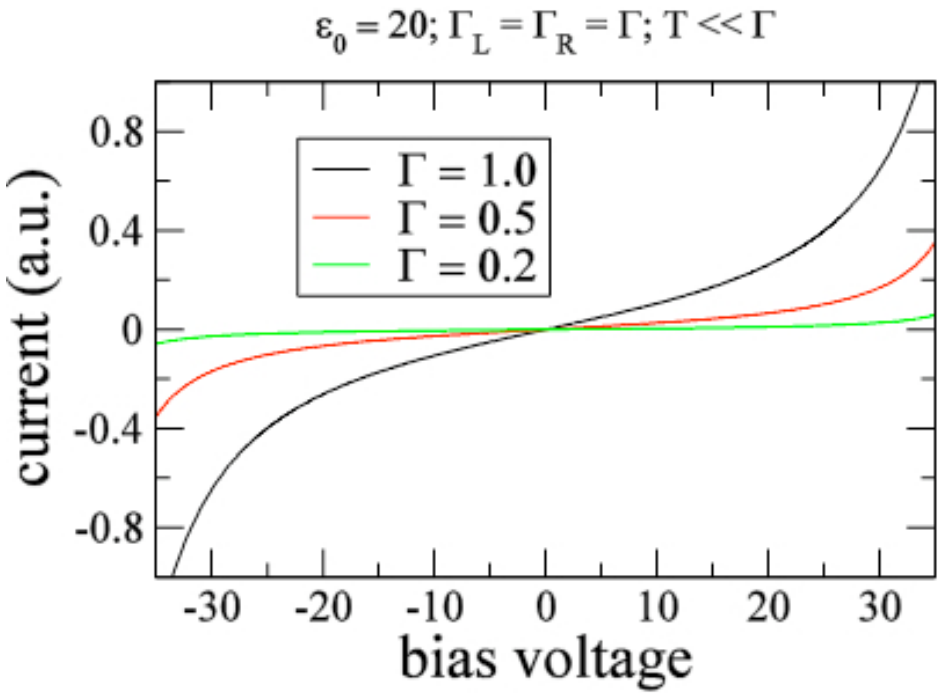
$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE\, T(E,V)\,[f_L - f_R] \qquad T(E) = \frac{4\Gamma_L \Gamma_R}{(E-\epsilon_0)^2 + (\Gamma_L + \Gamma_R)}$$

Resonant tunneling

- Resonant case: Transport through molecular level



- Off resonant case: Molecules as tunneling junctions



J.C. Cuevas (2007)

IV-curves with various linkers

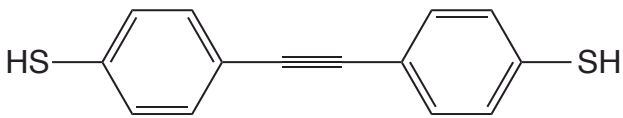
Fit to single level model works well for all three molecules

$$\Gamma_L = \Gamma_R = 0.065\text{eV} \quad E_0 = 0.4\text{eV}$$

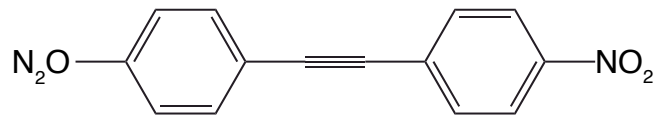
$$\Gamma_L = \Gamma_R = 0.094\text{eV} \quad E_0 = 0.29\text{eV}$$

$$\Gamma_L = \Gamma_R = 0.85\text{meV} \quad E_0 = 0.54\text{eV}$$

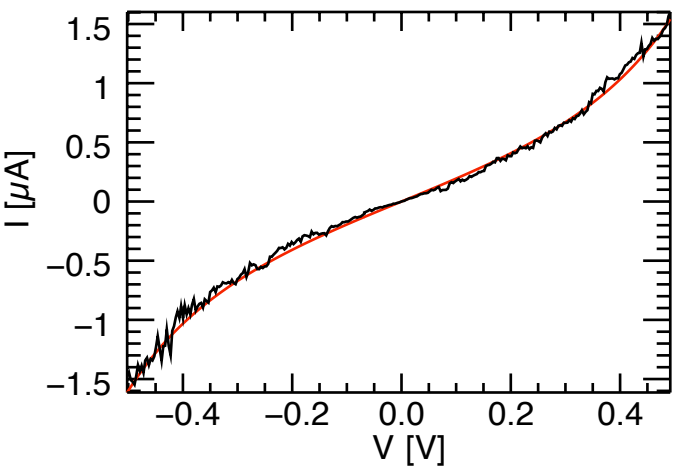
BTT

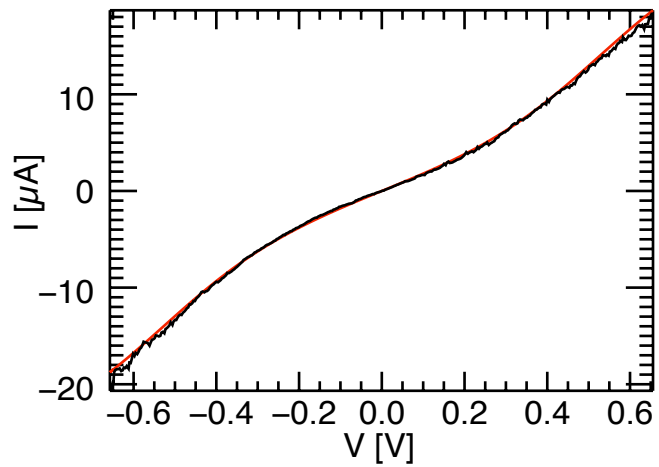


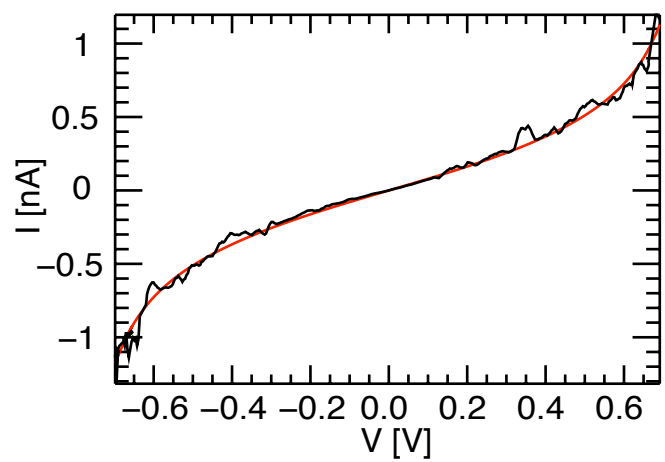
BNT



BCT







L. Zotti *et al.*, Small (2010) accepted

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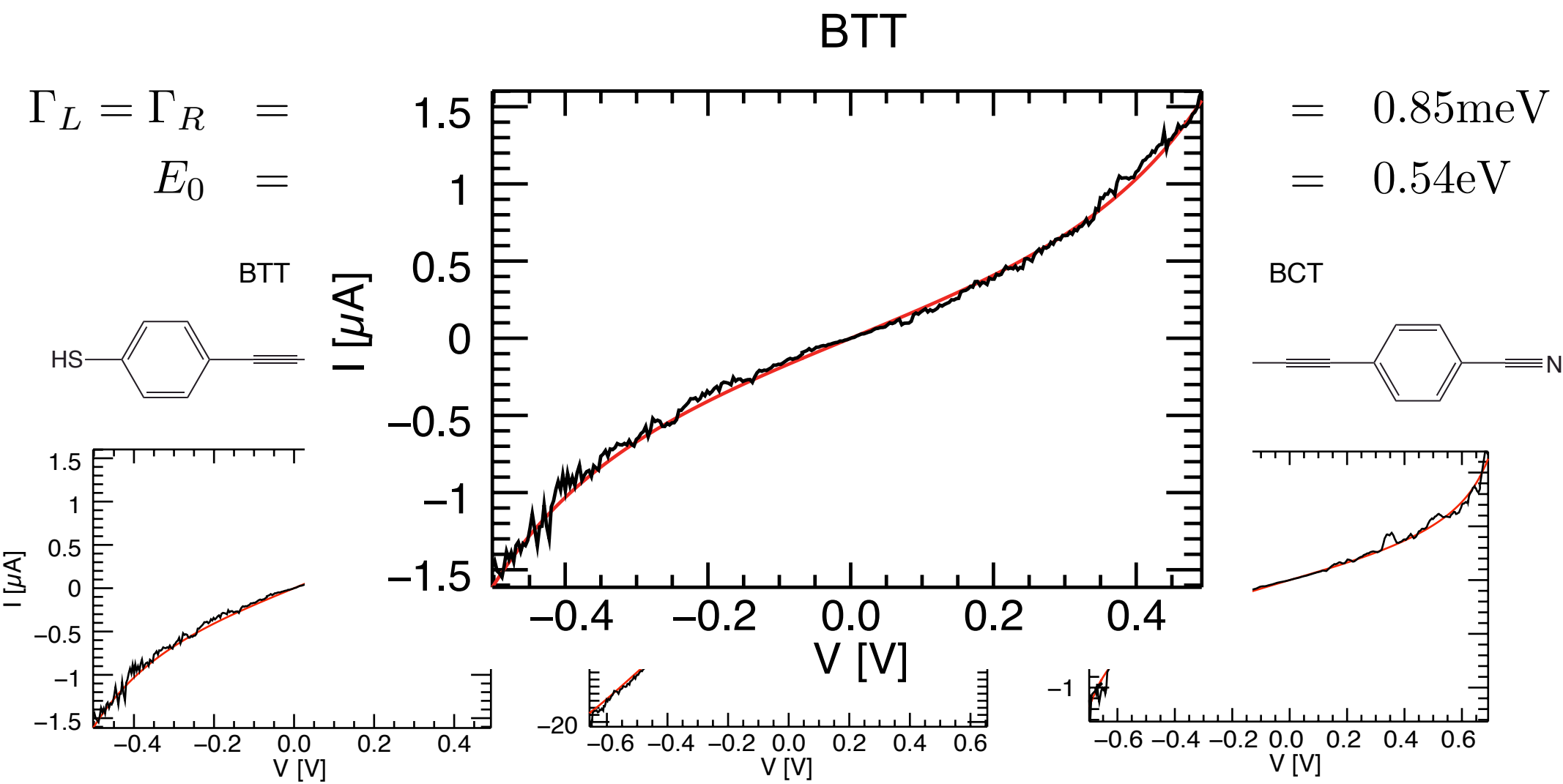

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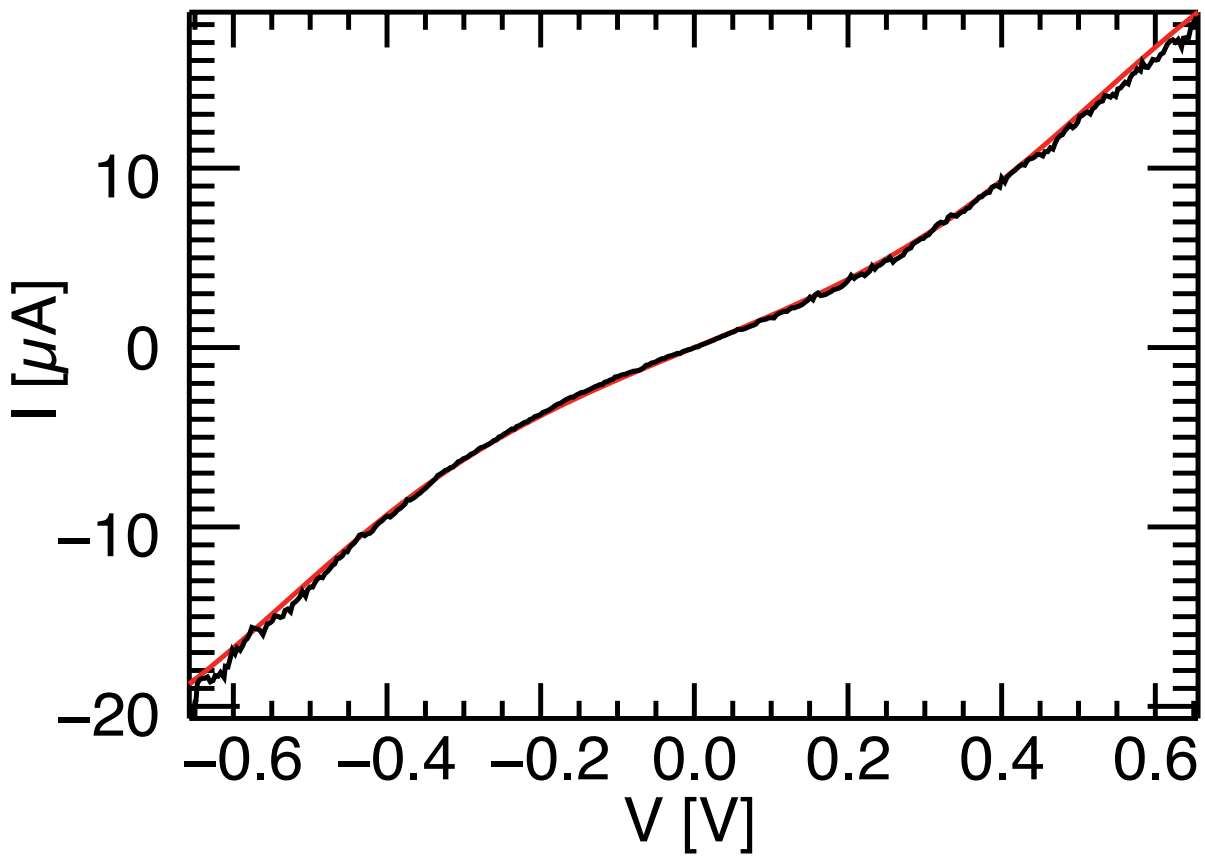

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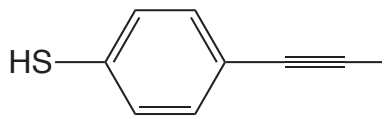

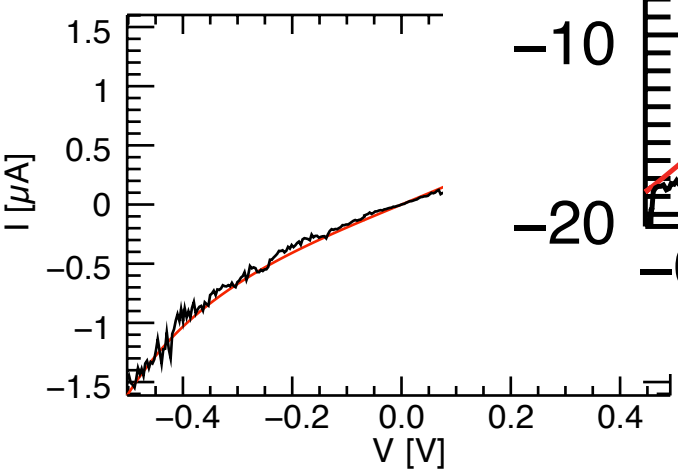

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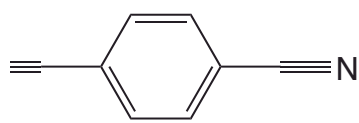

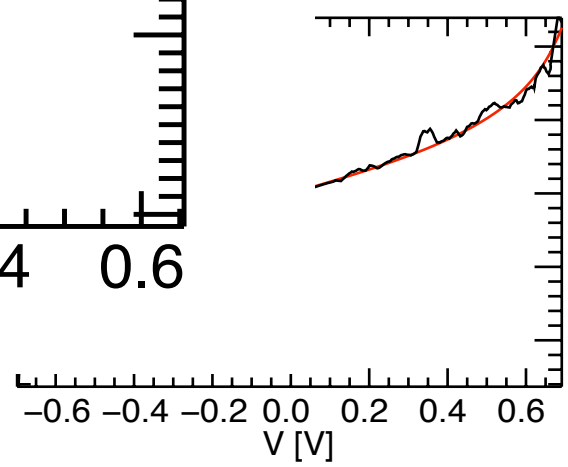

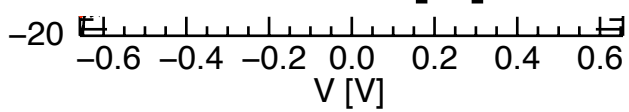

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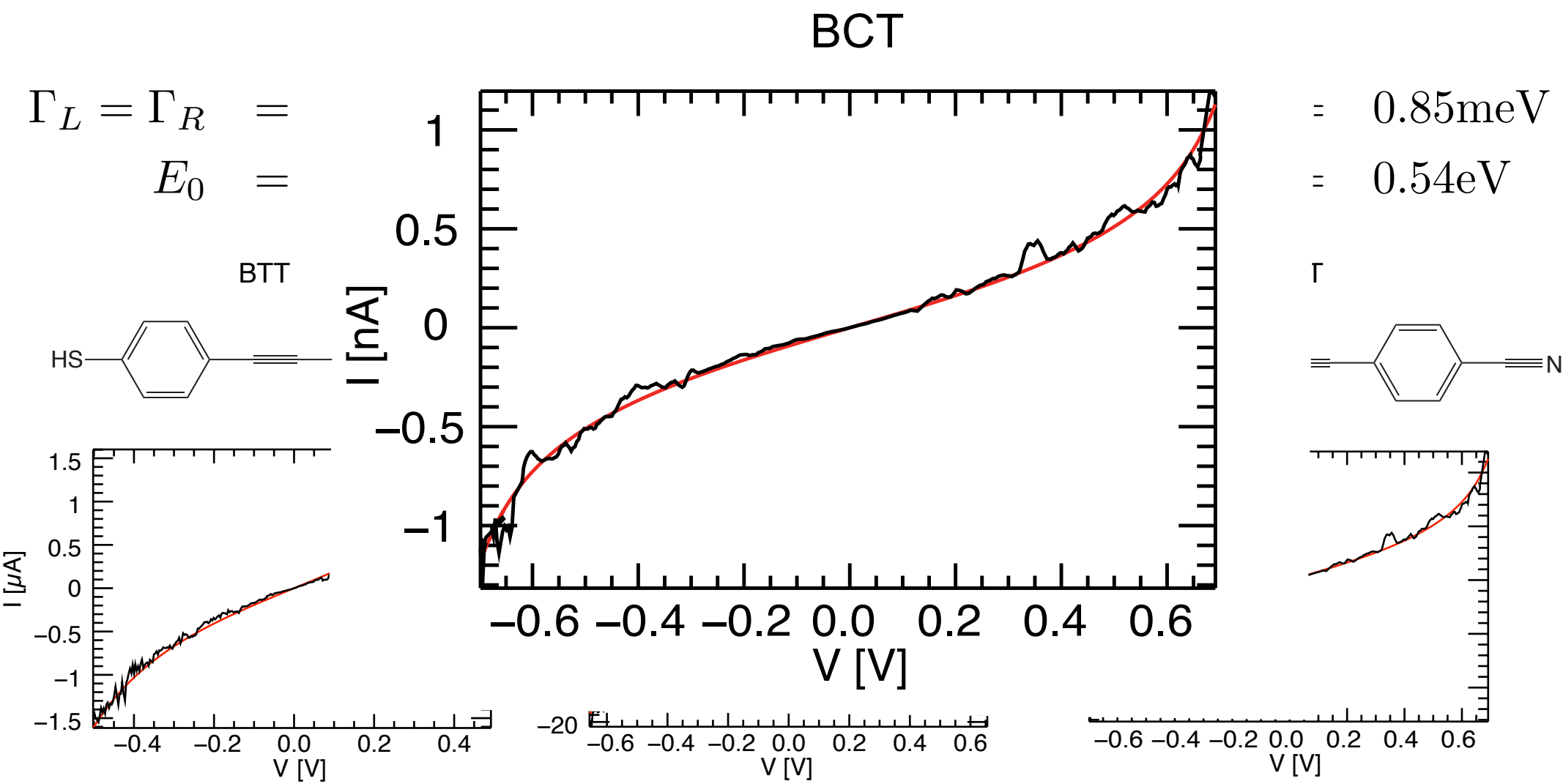

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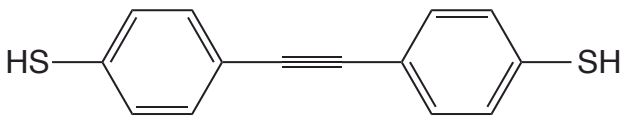

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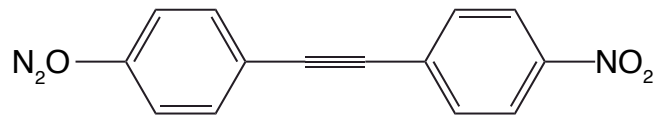
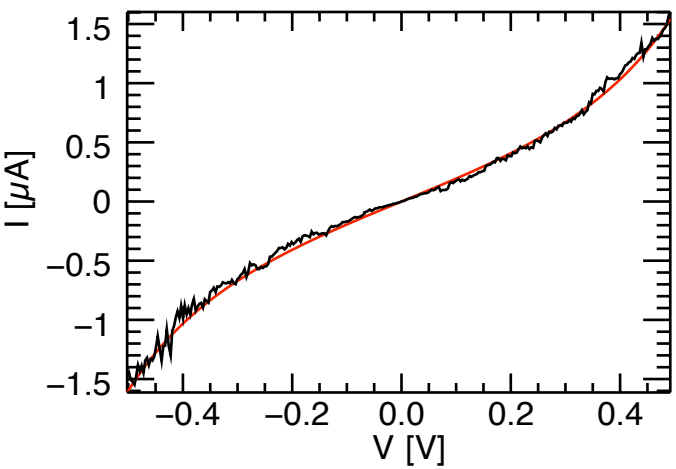
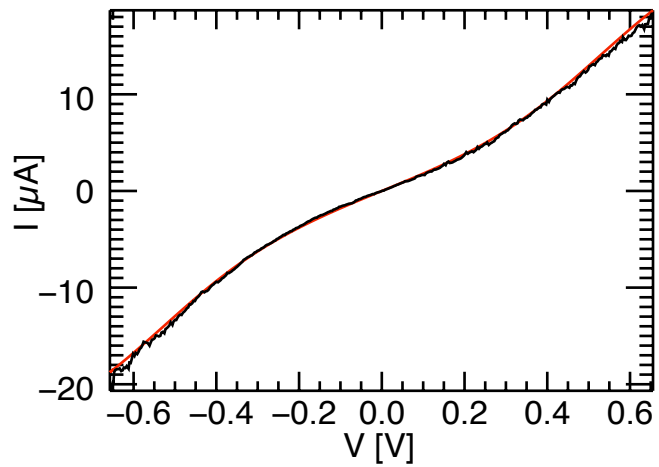
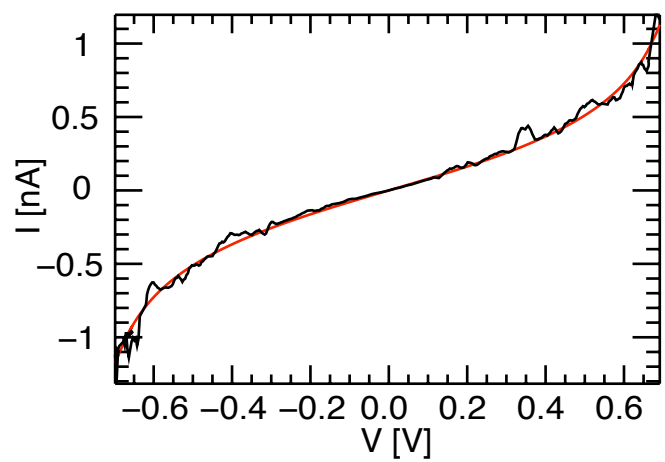


BCT





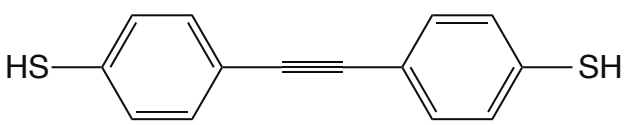


L. Zotti *et al.*, Small (2010) accepted

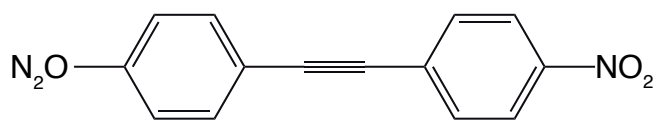
Parameters for anchoring groups

- largest coupling for BNT
- smallest coupling for BCT

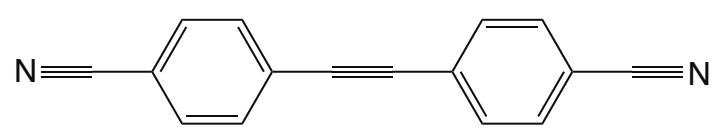
BTT

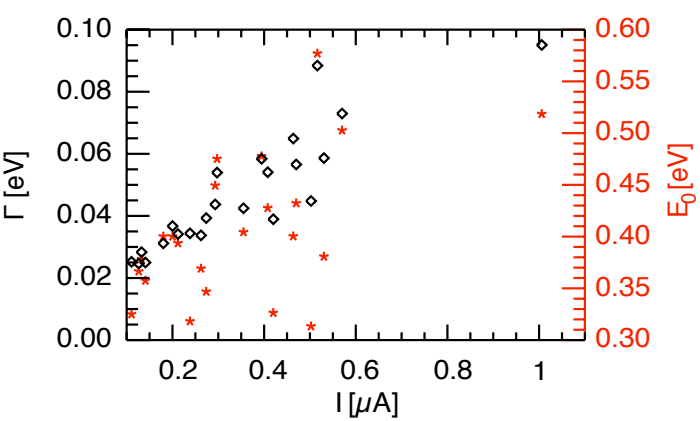


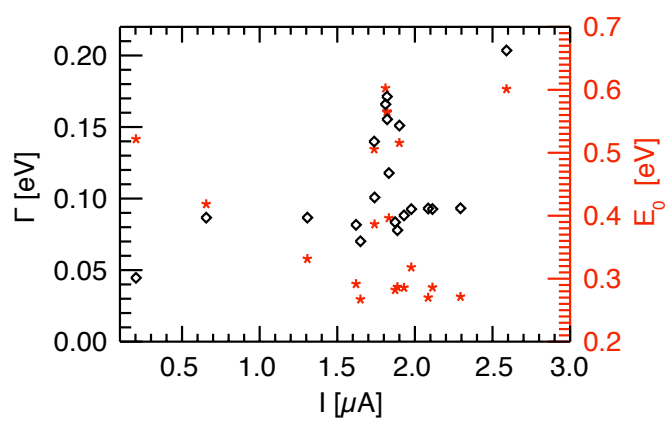
BNT

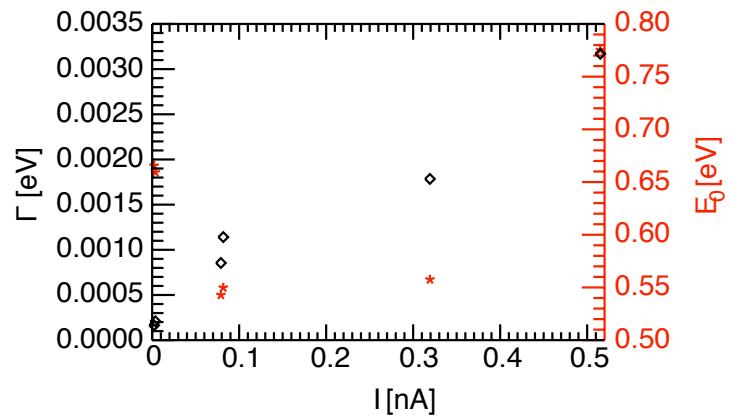


BCT



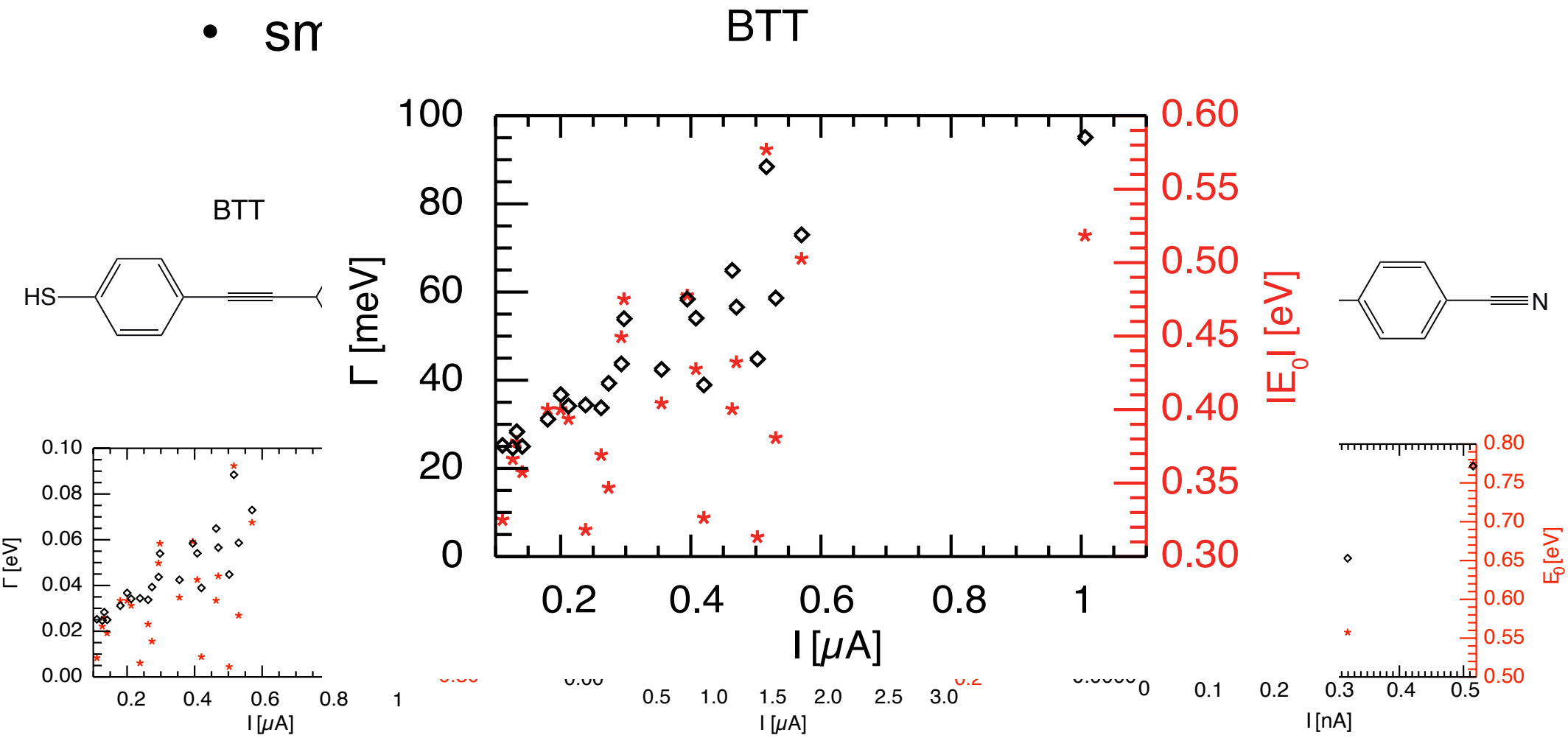






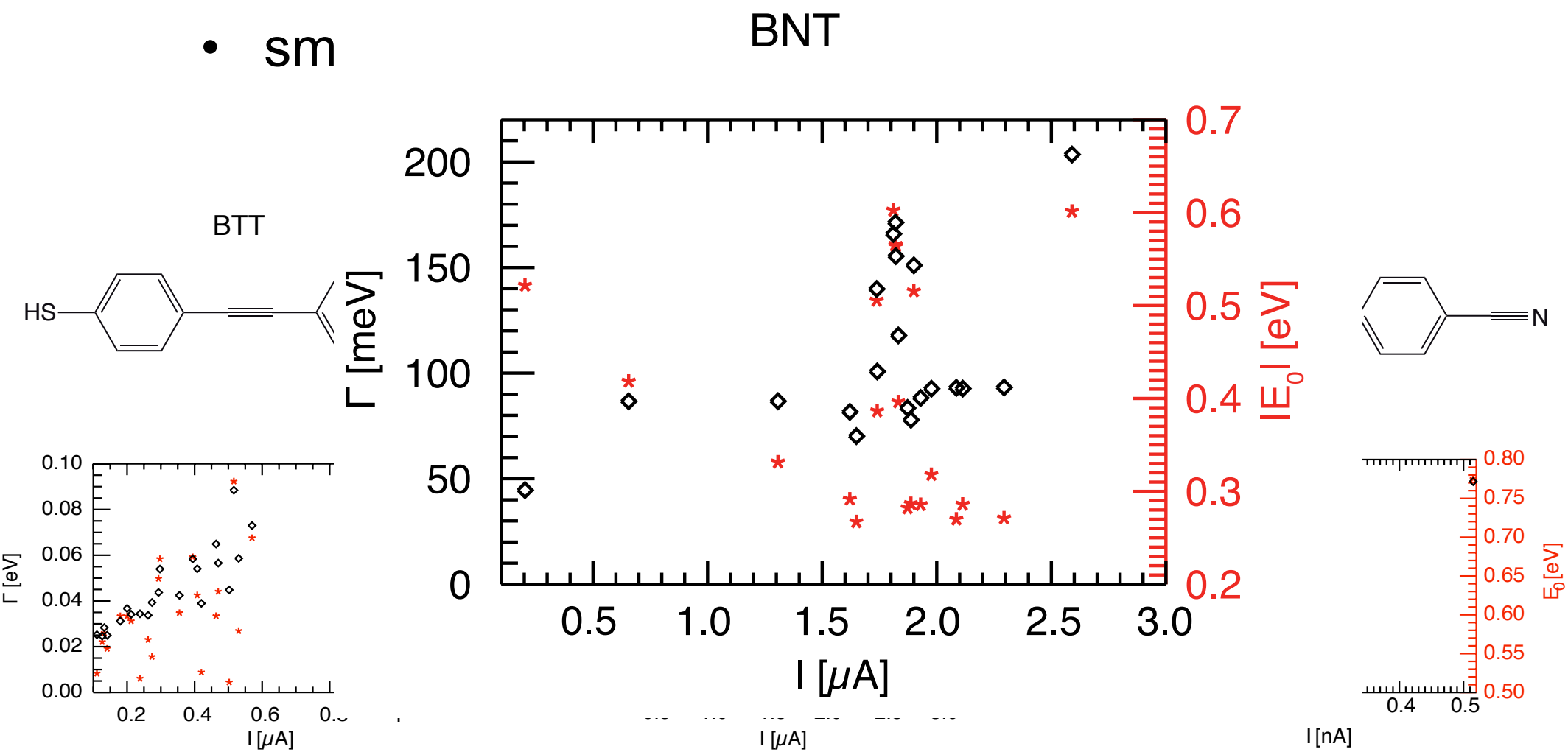
Parameters for anchoring groups

- largest coupling for BNT
- sm



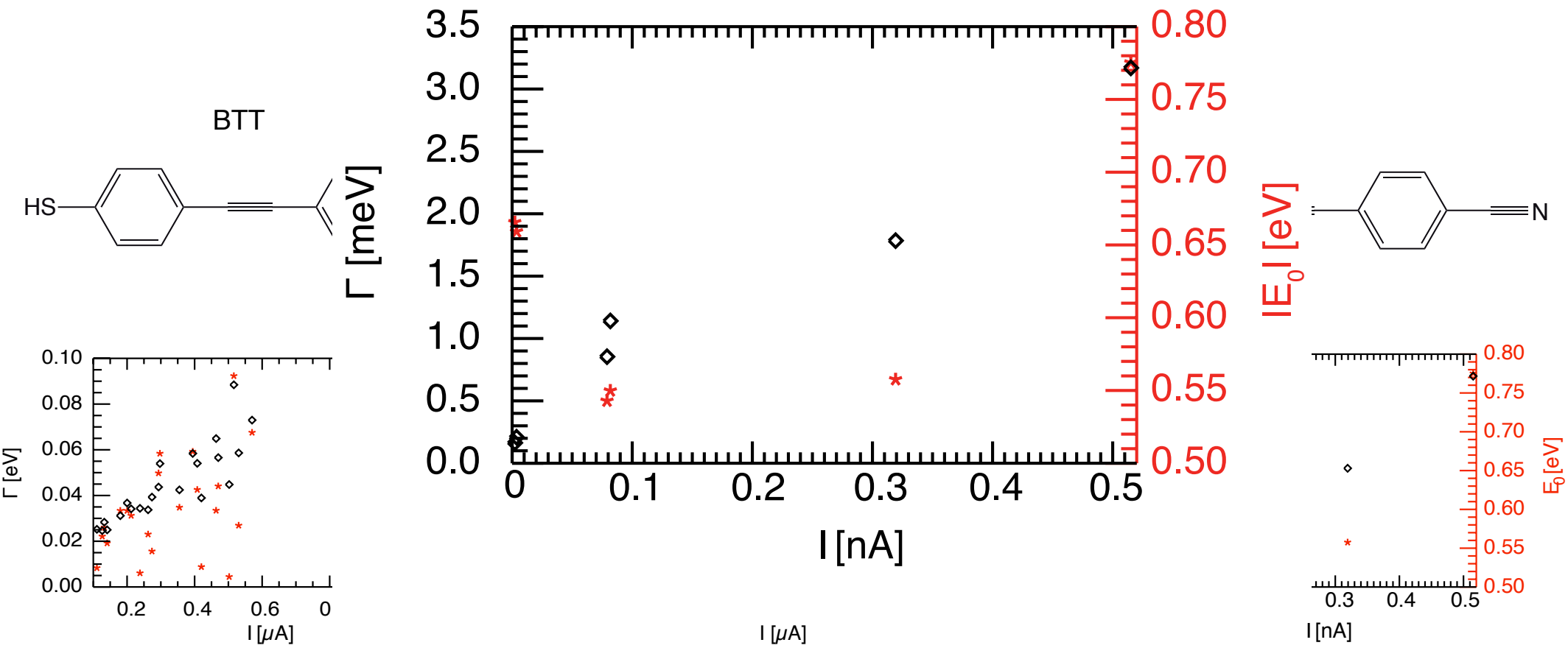
Parameters for anchoring groups

- largest coupling for BNT
- sm



Parameters for anchoring groups

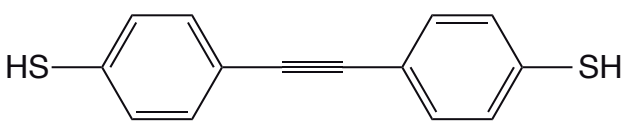
- largest coupling for BNT
- sm



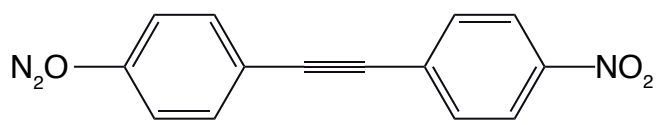
Parameters for anchoring groups

- largest coupling for BNT
- smallest coupling for BCT

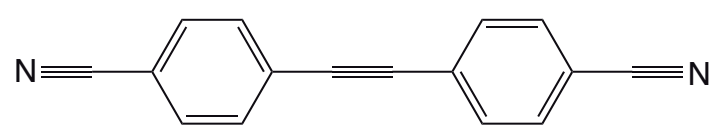
BTT

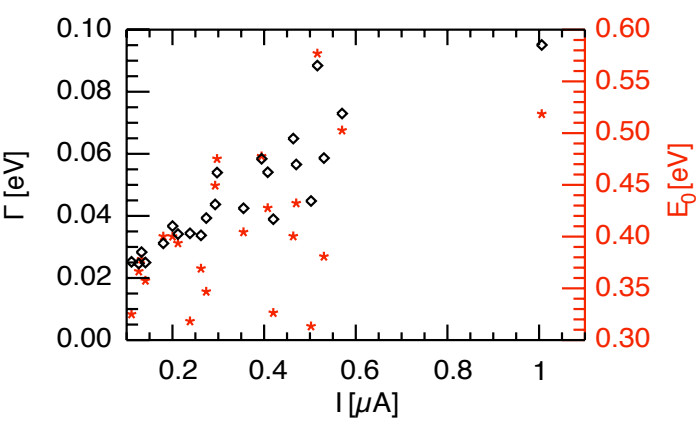


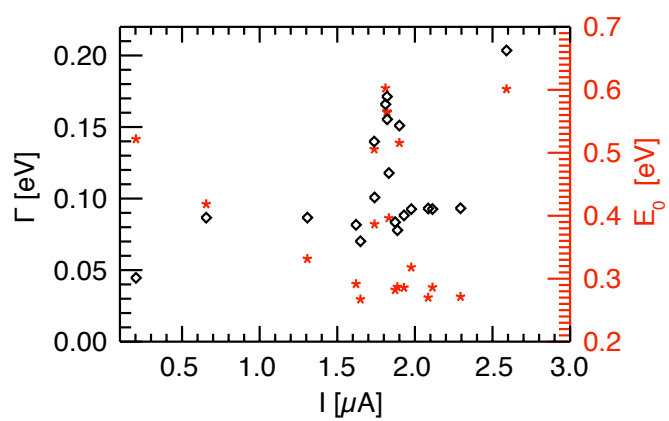
BNT

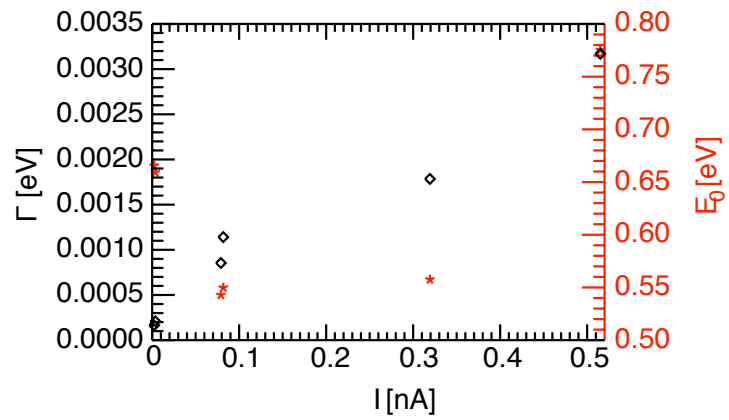


BCT





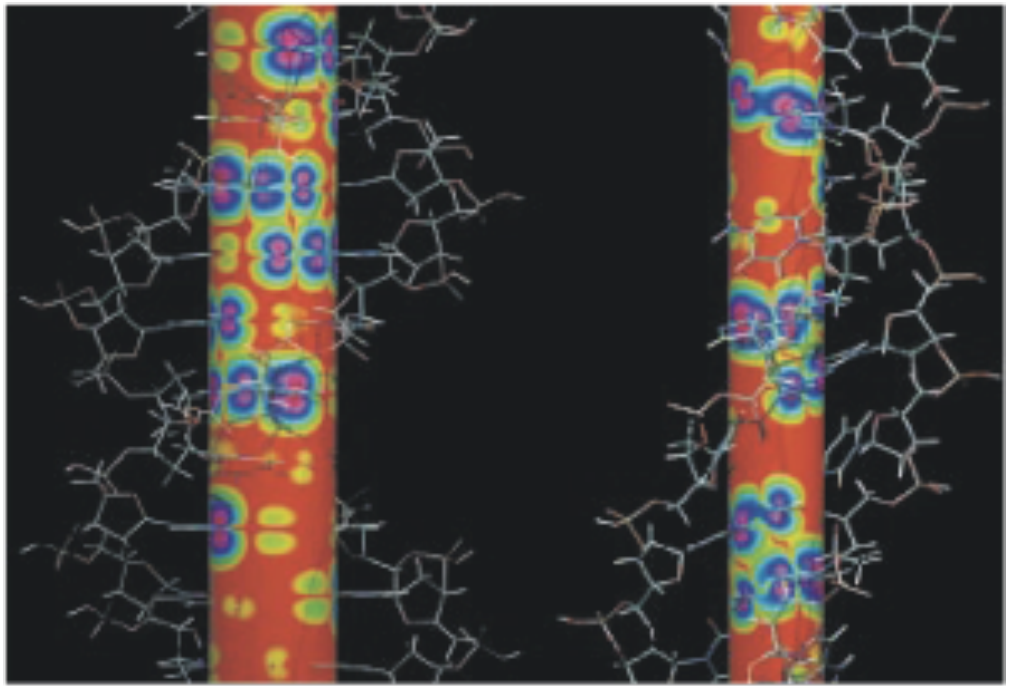




Conclusions

- Influence of anchoring groups clearly visible
  - thiol most stable
  - nitro most conductive
  - cyano unstable and poorly conducting
- *IV*-curves fit resonant tunneling through single level
- Comparison with DFT calculations

DNA structure and charge transfer



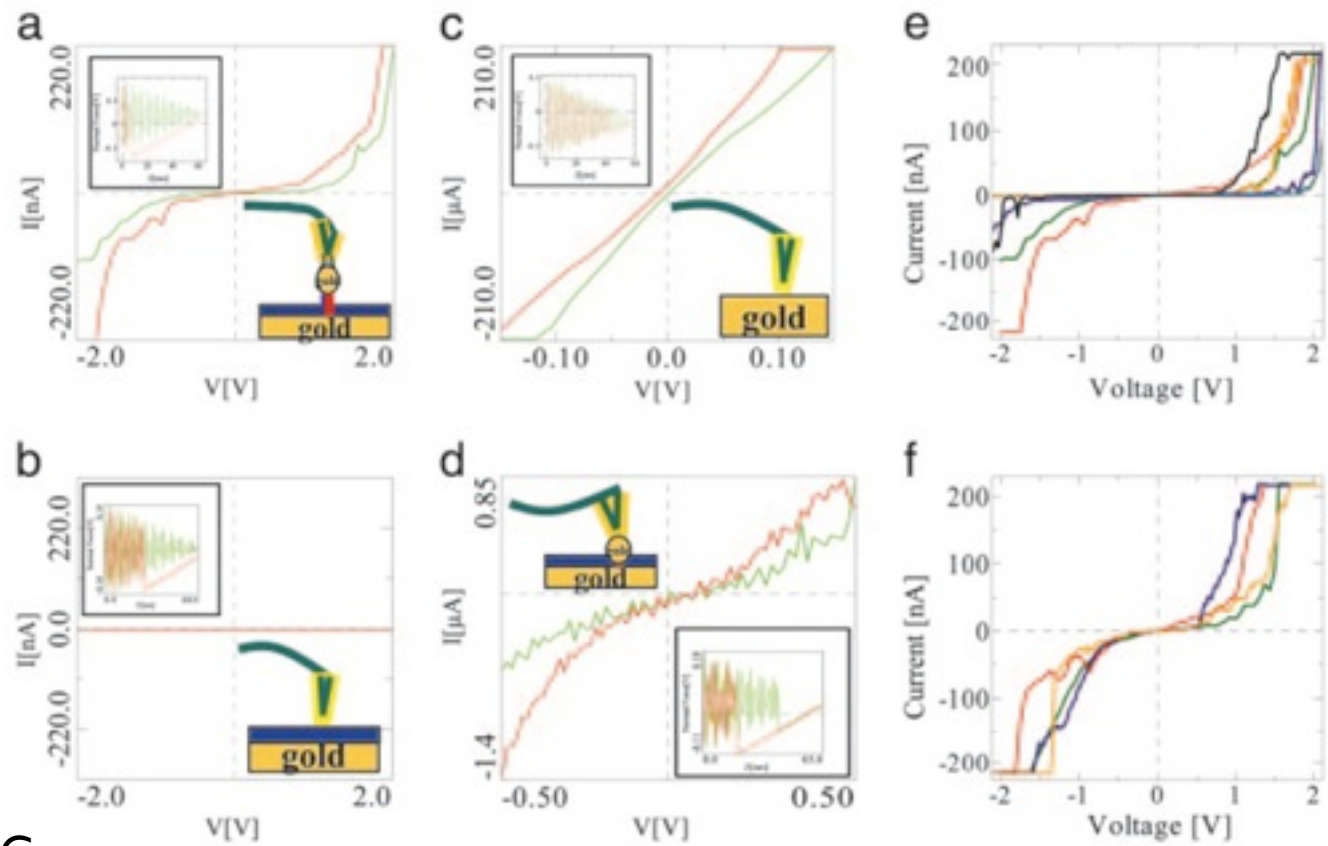
P. Maragakis *et al.* Phys. Rev. B **66** 241104 (2002)

- conformational change:
  - normal DNA – overstretched DNA
  - relevant for transport properties of DNA
- experimental test:
  - stretching DNA during *I-V*-measurement
  - control of other parameters

➡ DNA in mechanical break-junction (MCB)

Binding molecules to gold

- Thiol linkers immobilize molecules on gold
- Standard method for DNA: coupling through thioalkyl linkers

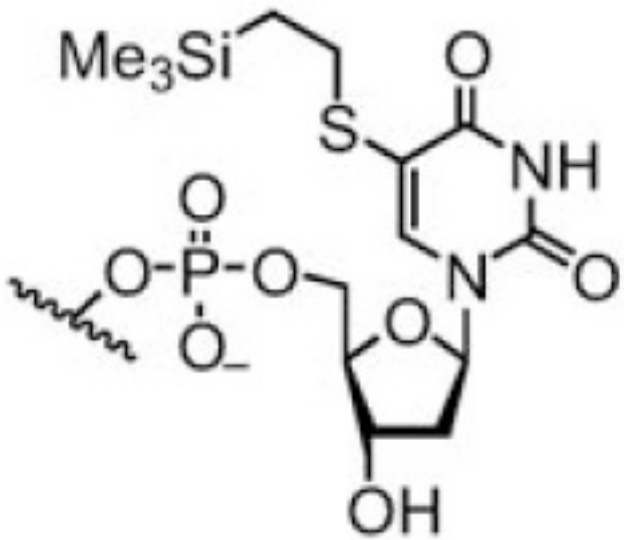


5'-CAT TAA TGC
TAT GCA GAA AAT CTT AG-3'-C3H6-SH

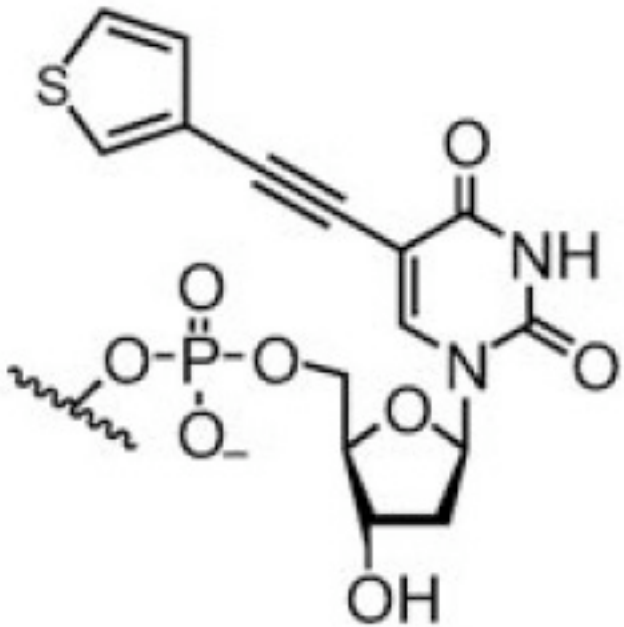
H. Cohen *et al.* PNAS (2005)

Thiolated Nucleotides

- Goals:
  - Improved conductivity by better coupling to π-system
  - Higher reliability of immobilization



1

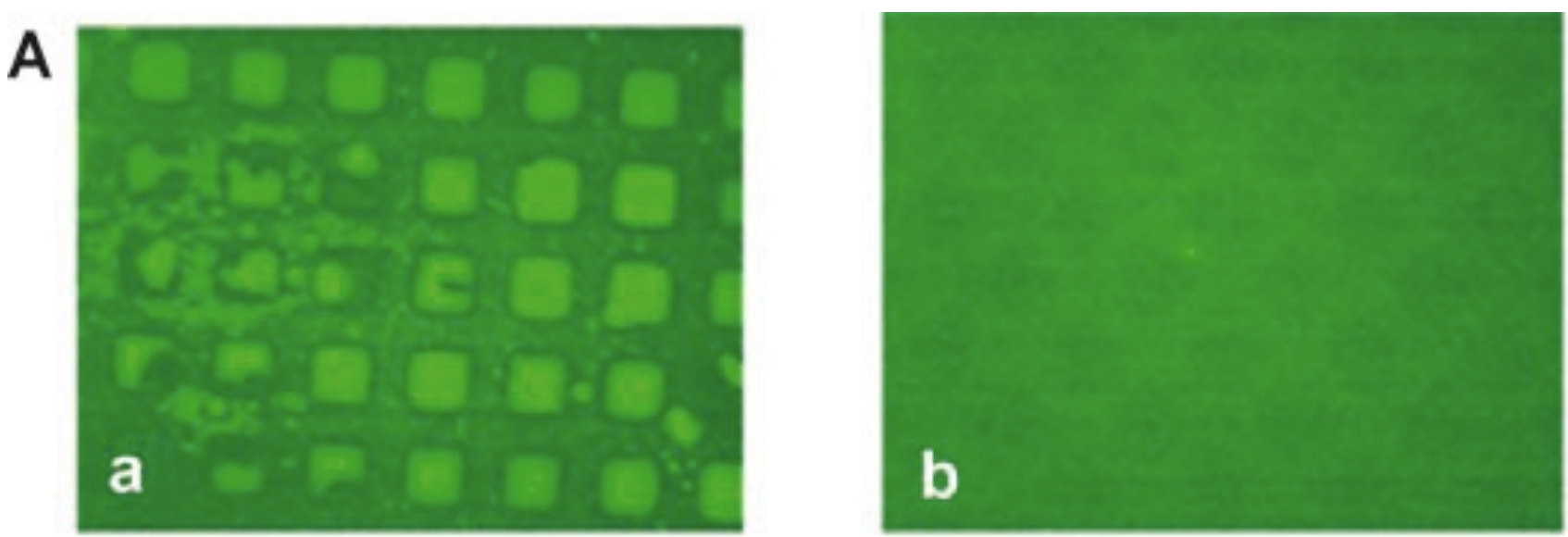


2

Fluorescence microscopy

- Comparison thiolated (ON2b) vs.non-thiolated (ON1b)
- gold pads fabricated by shadow-mask evaporation
- fluorescence of the molecules observed

ON1b: 5'-FAM-CGT TGG TCC TGA AGG AGG AT
ON2b: 5'-FAM-CGT TGG TCC TGA AGG AGG A**1**

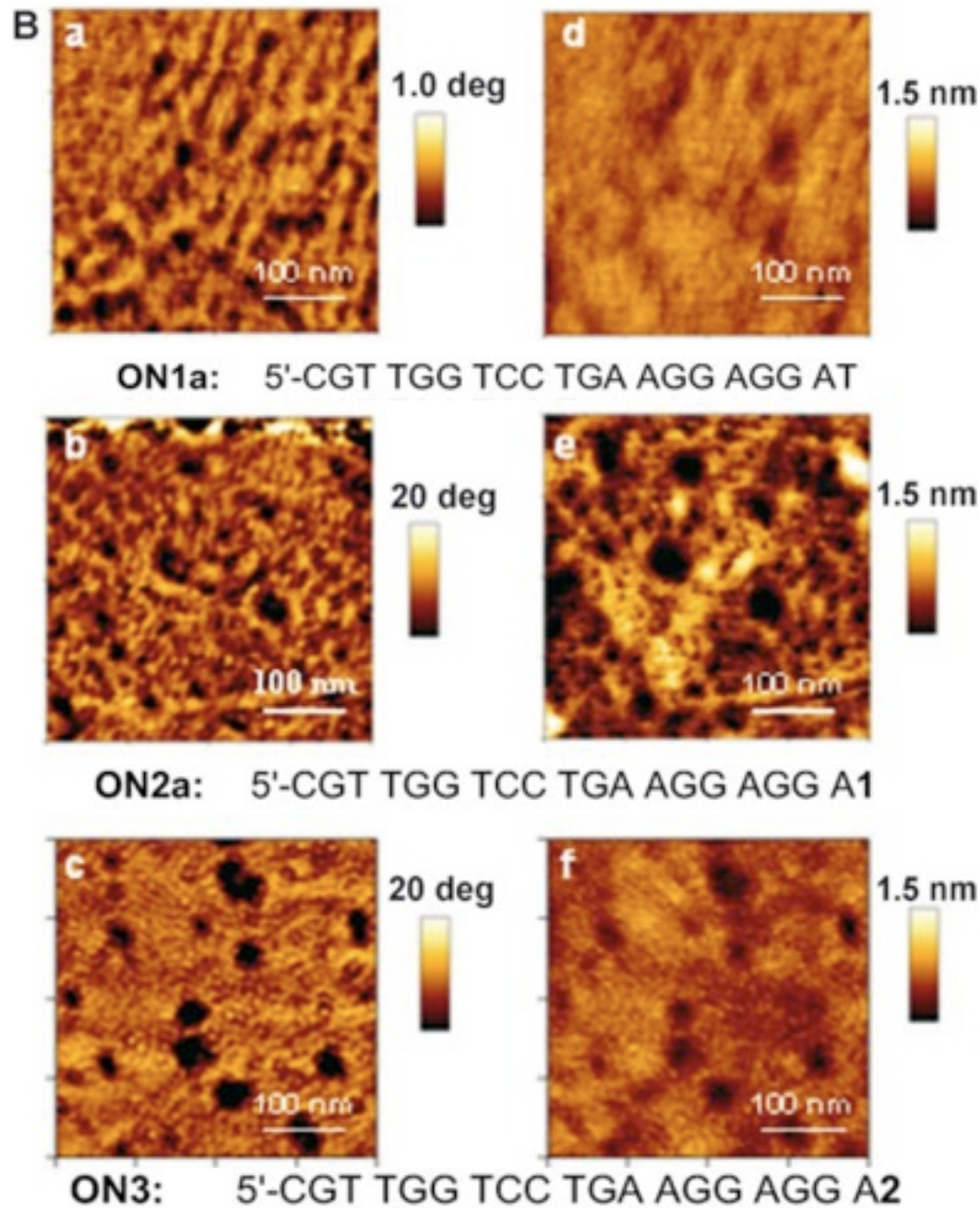


ON2b ON1b

Liu *et al.* ChemPhysChem (2008)

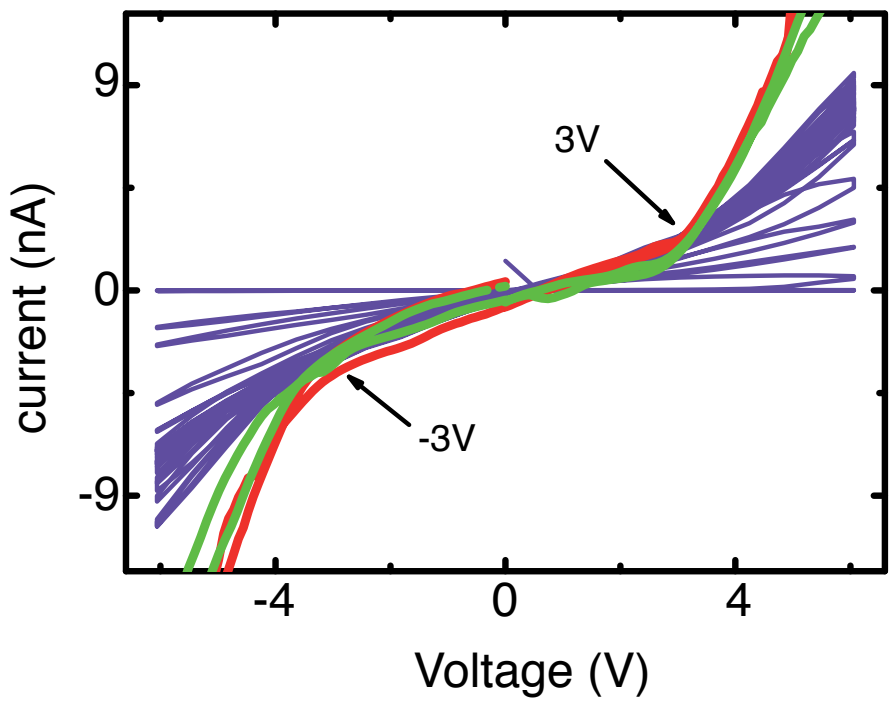
AFM measurements

- Topography (left) and phase contrast
- protected thiol binds
- thiophene binds
- no binding for
  - unprotected thiol (not shown)
  - un-thiolated



*I*V*s* in liquid environment

- complex sequence
  - 5'thiol-dG GGCGGCGACCTTCCCGCAGCTGGTACGGAC

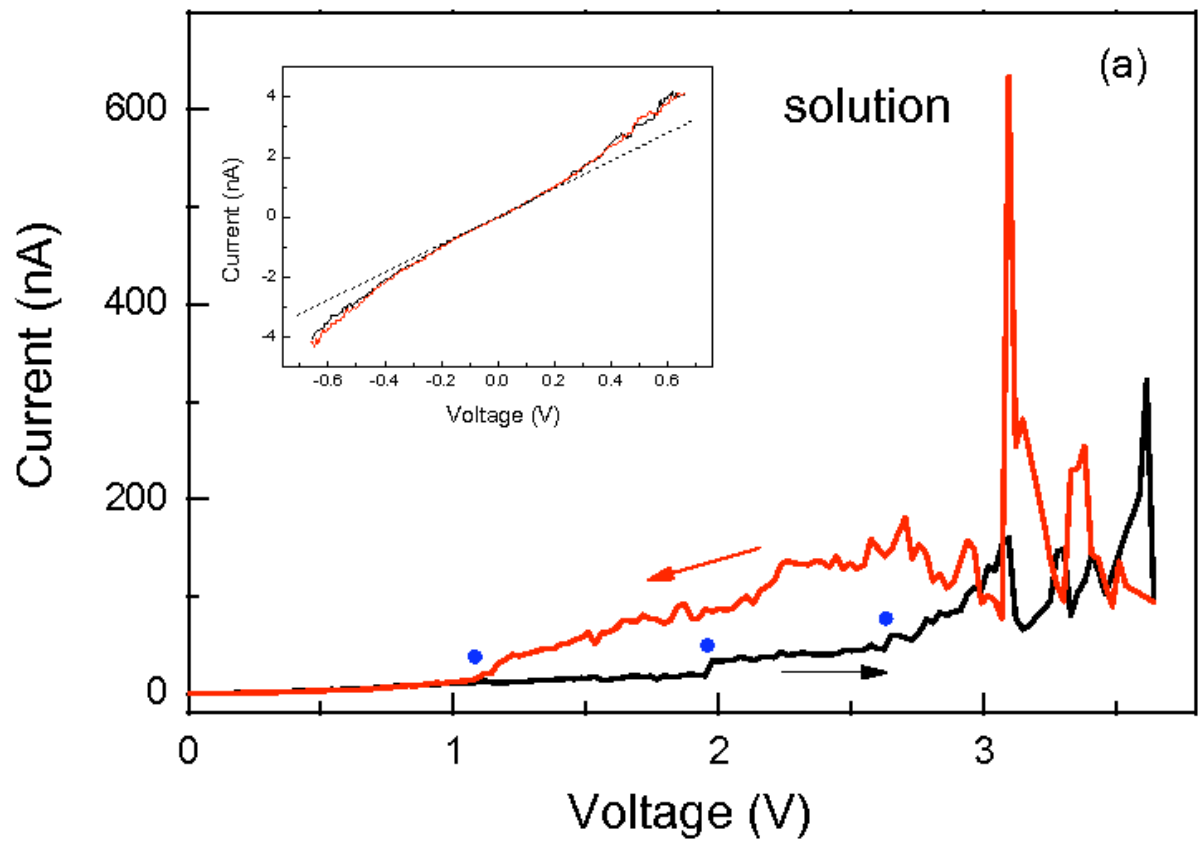


- degradation while continuously sweeping voltage

Kang *et al.*, New J. Phys. (2008)

NDR in liquid environment

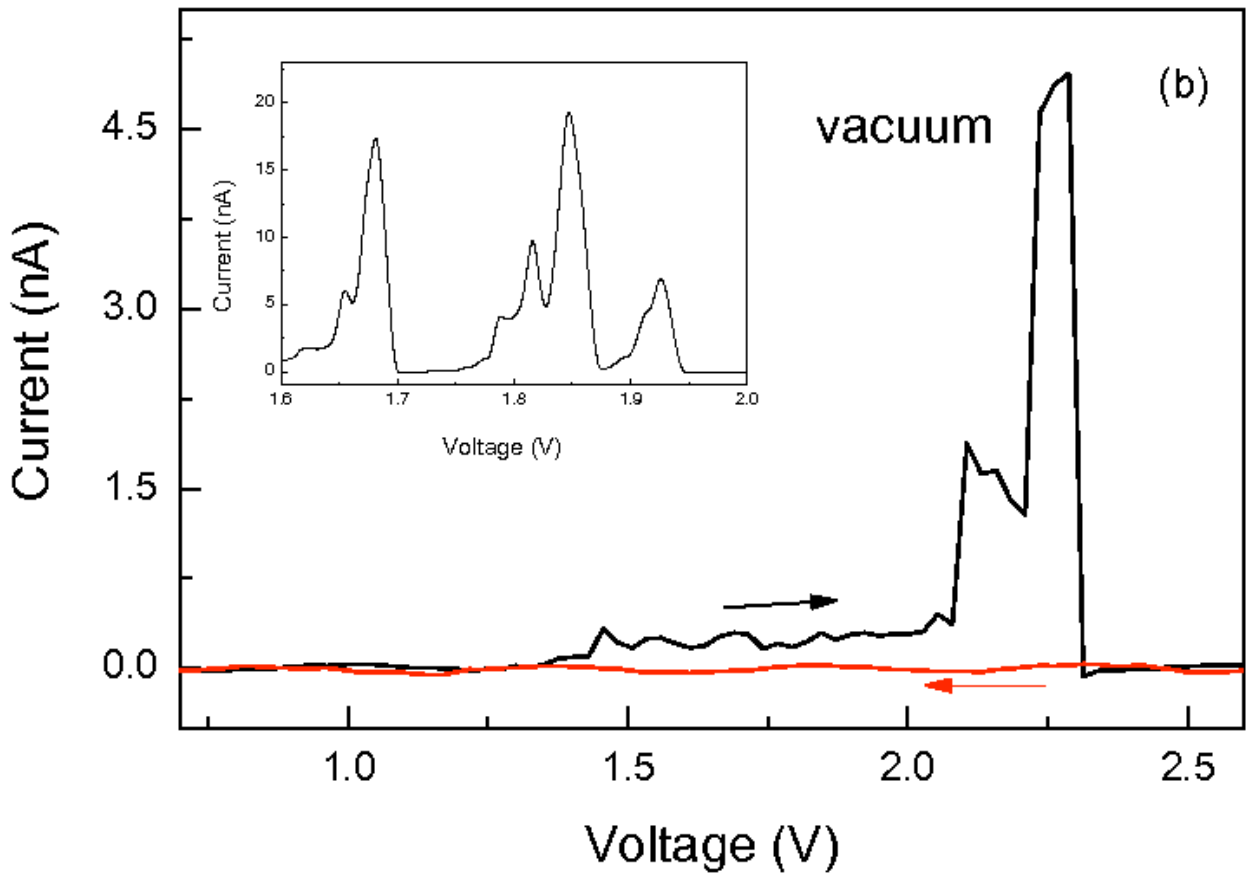
- nonlinear behavior at $V_{sd} > 0.5V$
- step-like behavior at $V_{sd} > 1V$
- hysteretic negative differential resistance (NDR) at large voltages



Kang *et al.* APL (2010)

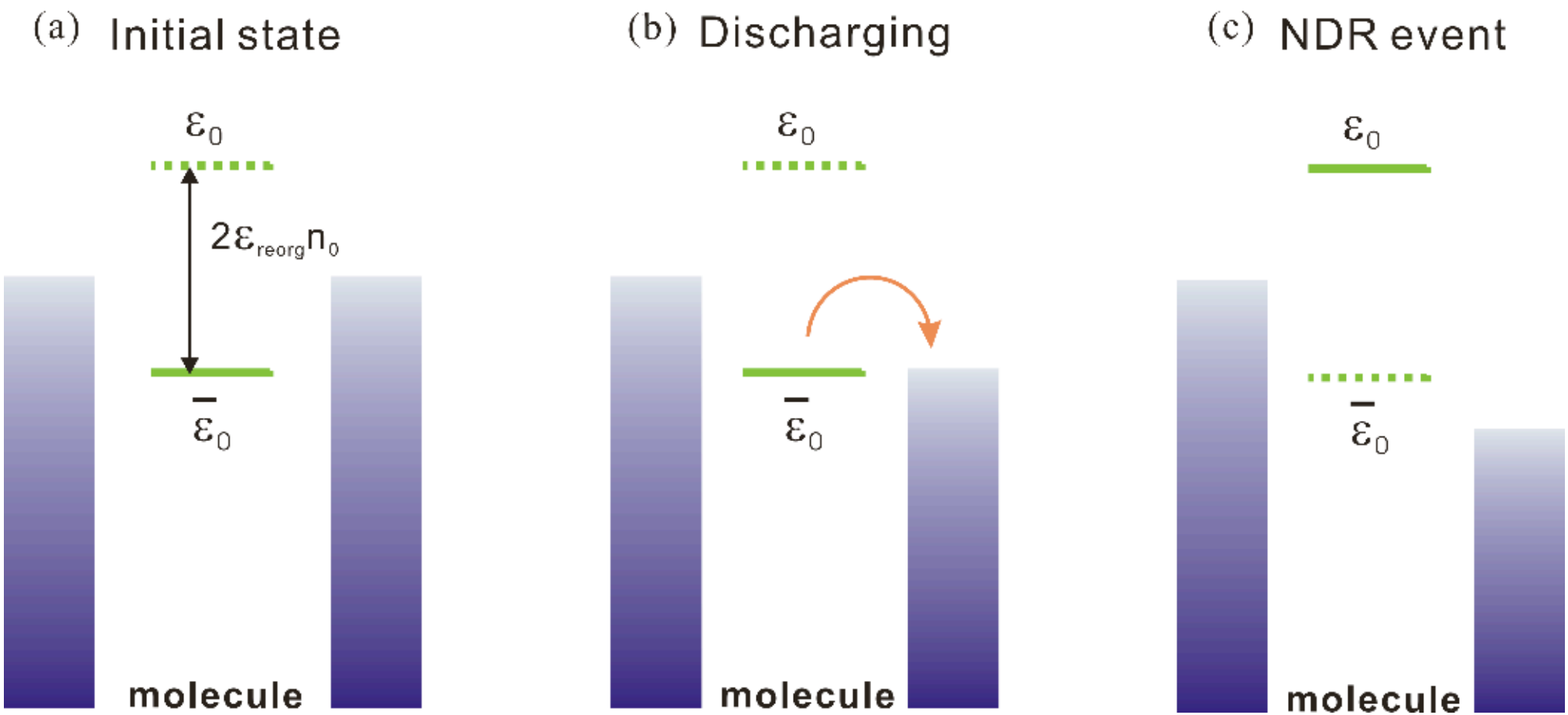
NDR in vacuum

- multiple peaks in forward direction
- no peaks in backward direction



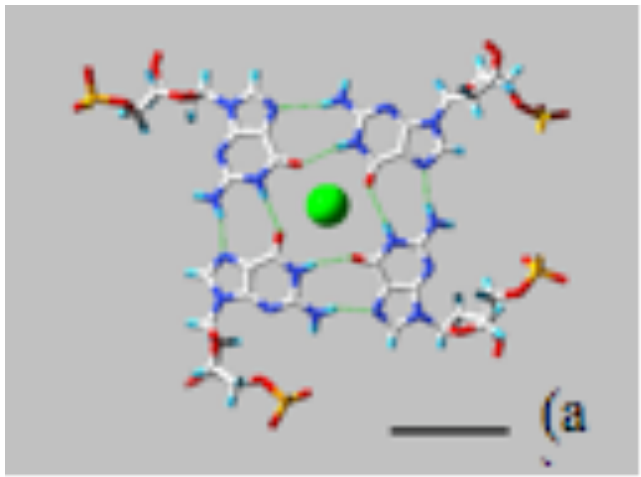
Formation of polarons?

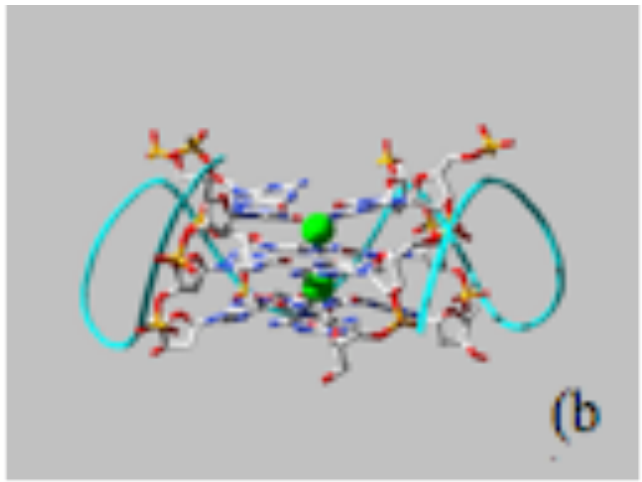
- Polaron formation can lead to multiple NDR peaks

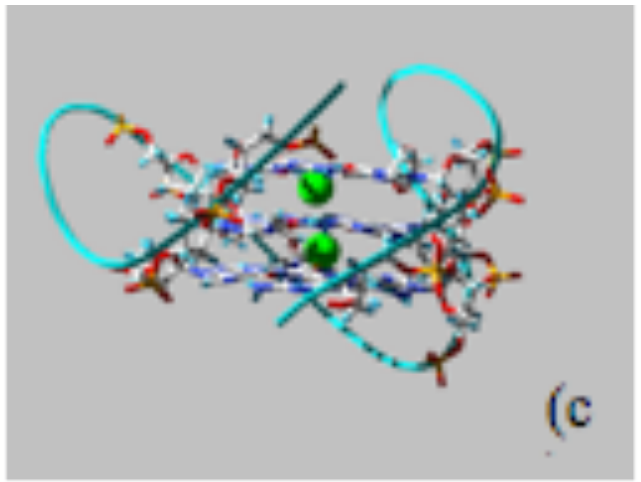


DNA Quadruplexes

- Poly-GC wires show higher conductance than DNA with AT
- G4 quadruplexes stack G-bases
- thiol groups to bind to electrodes



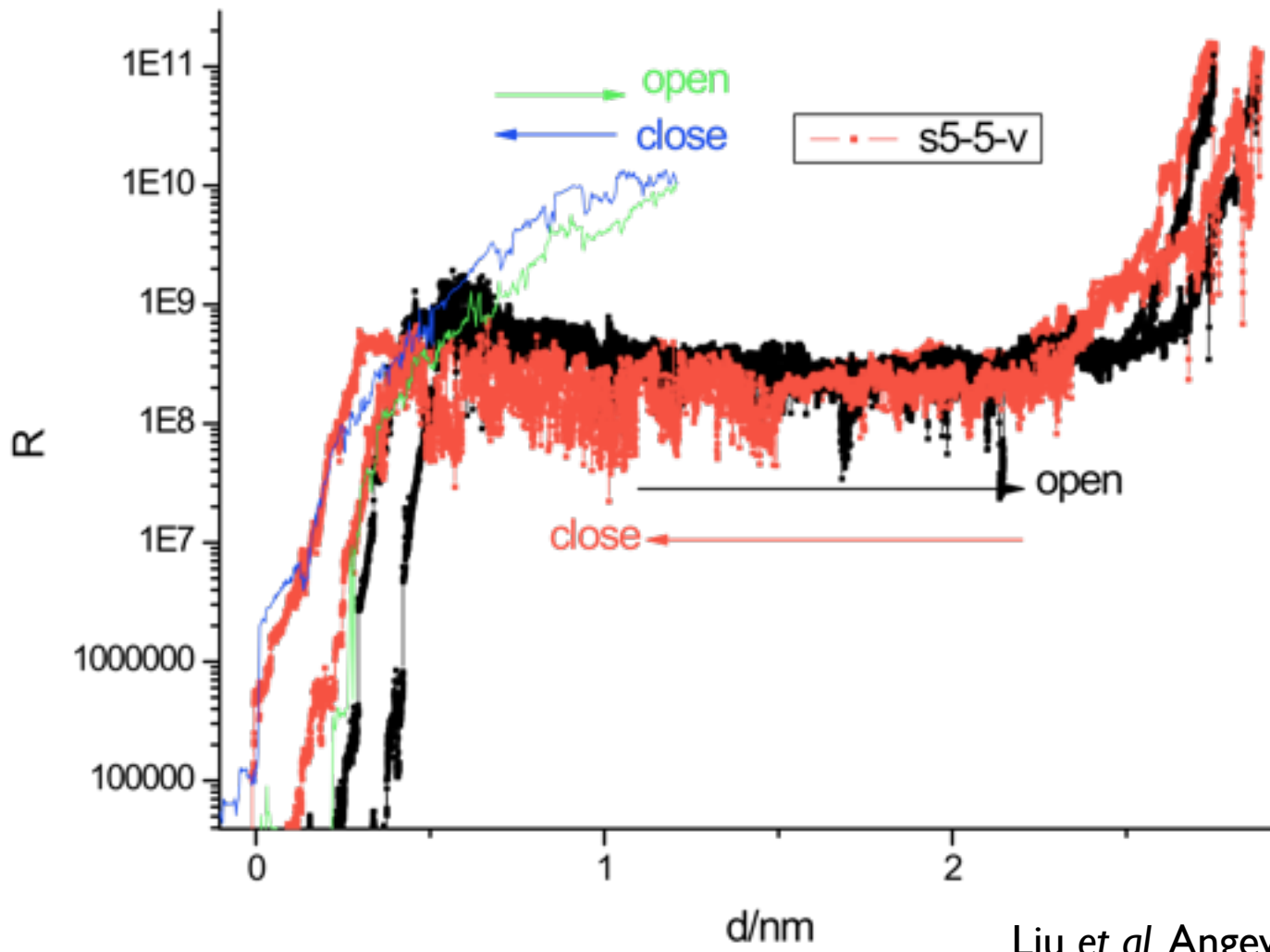




5’-(T*G_3[TTAGGG]$_3$T*)-3’

Opening and closing curves

- large plateaus if quadruplex with thiol endgroups are present



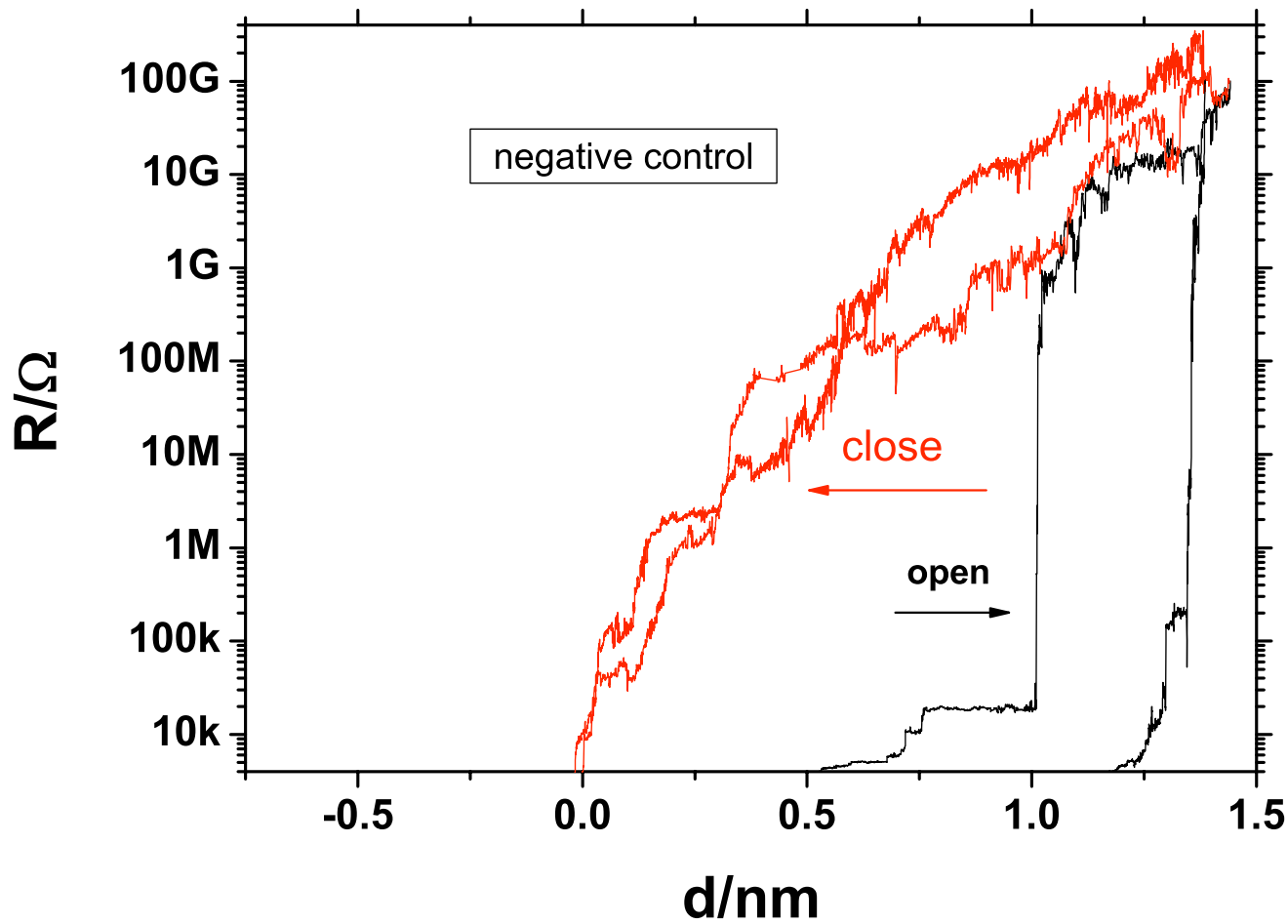
Liu *et al.* Angewandte Chemie (2010)

Control sample

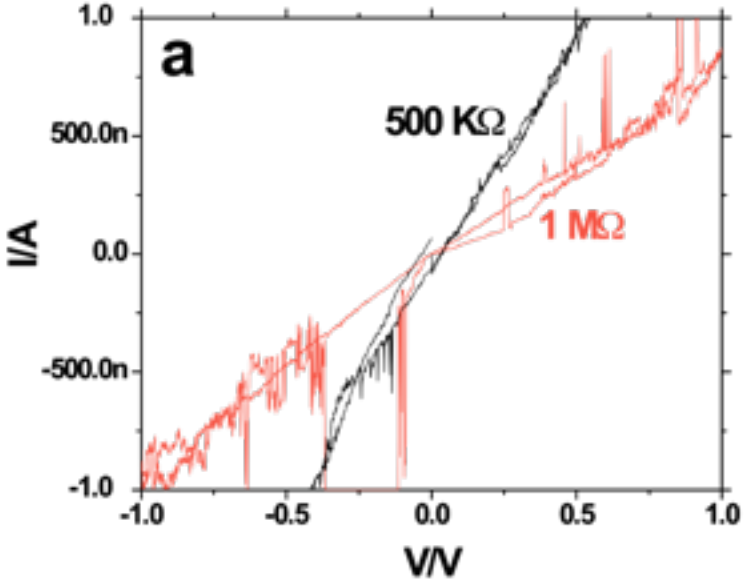
- transport measurement on structure that does not form Quadruplexes:

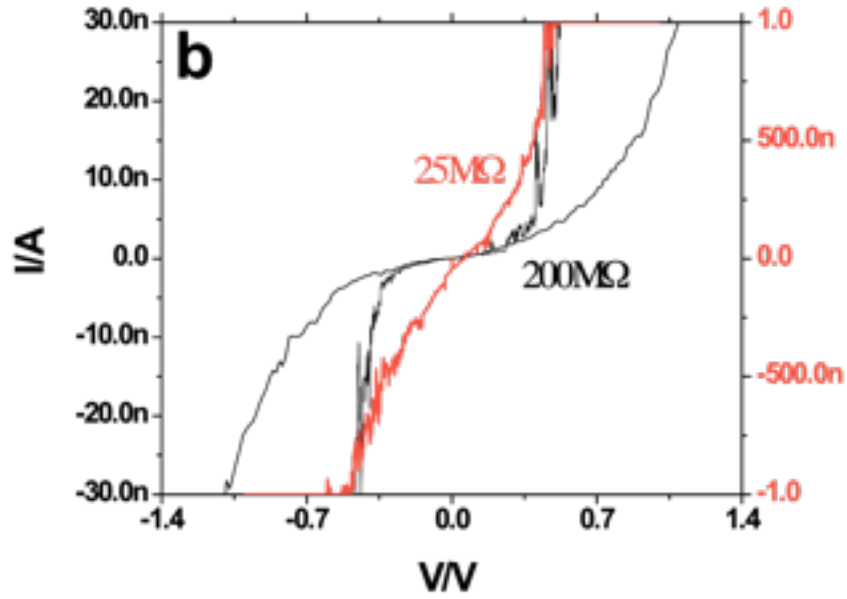
  5’-d($T^*C_3[TTACCC]_3T^*$)-3’

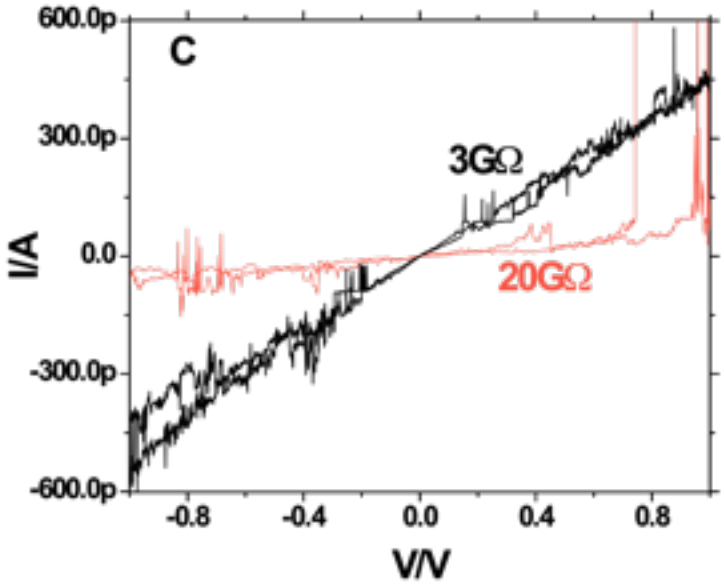
- no long plateau observed

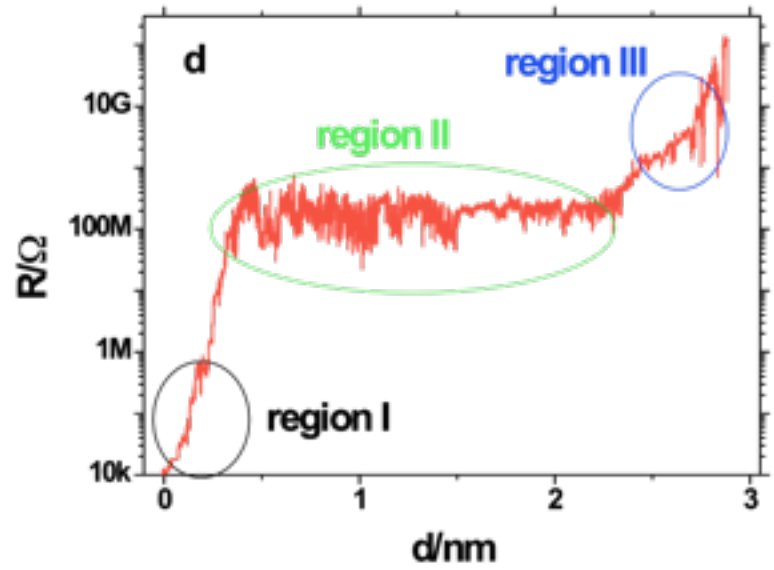


IV-characteristics









Conclusions

- Electrical coupling to DNA by short linker groups
- Mechanical stability proven by fluorescence microscopy and AFM
- Electrical measurements show resistance of 10 - 100 MΩ
- *IV*-curve can be modeled by single level model
- DNA quadruplex shows extraordinary stretching behavior

Thanks

- Uta Eberlein, Thomas Kirchner, Christian Kreuter, Stefan Bächle
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- Tang Zhuo, Benjamin Bornemann, Andreas Marx
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