Electrochem 08
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UNIVERSITY OF LIVERPOOL

Medium effects in single molecule conductance measurements.

Edmund Leary[1], Chris Finch[2], Iain Grace[2], Horst Höbenreich[1], Harm van Zalinge[1], Wolfgang Haiss[1], Richard Nichols[1], Colin Lambert[2] and Simon Higgins[1]

[1] Chemistry Department, University of Liverpool
[2] Physics Department, University of Lancaster

Outline

Introduction - ‘single molecule conductance’ techniques.

I(s) technique, exemplified with 1,9-nonanedithiol.

‘Molecular double tunnelling barriers’?

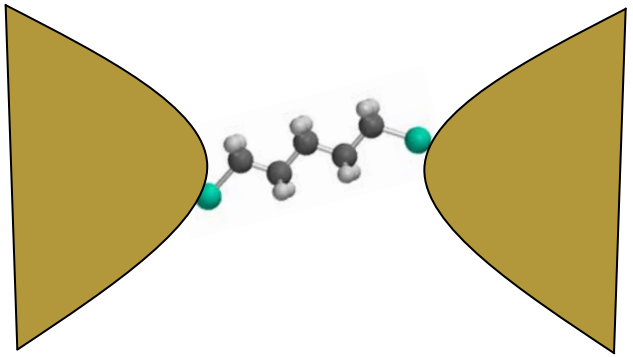
- Chemical control over conductance.
- Electrochemical control over conductance.

Oligothiophenes - *Environmental* effects on conductance.

- Measurements - in air.
- Theory - in vacuum.
- Theory - in ‘ambient’
- Measurements - under argon and vacuum.

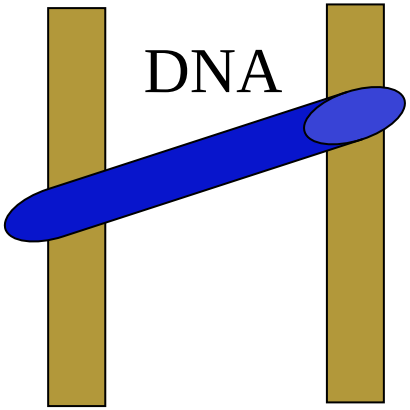
Conclusions

Single Molecule Conductance



Break junctions

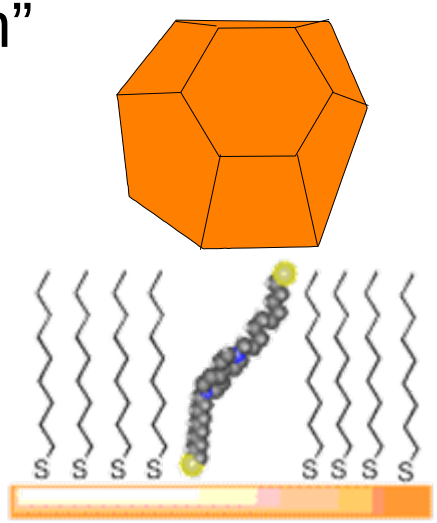
Nano-fabricated contacts



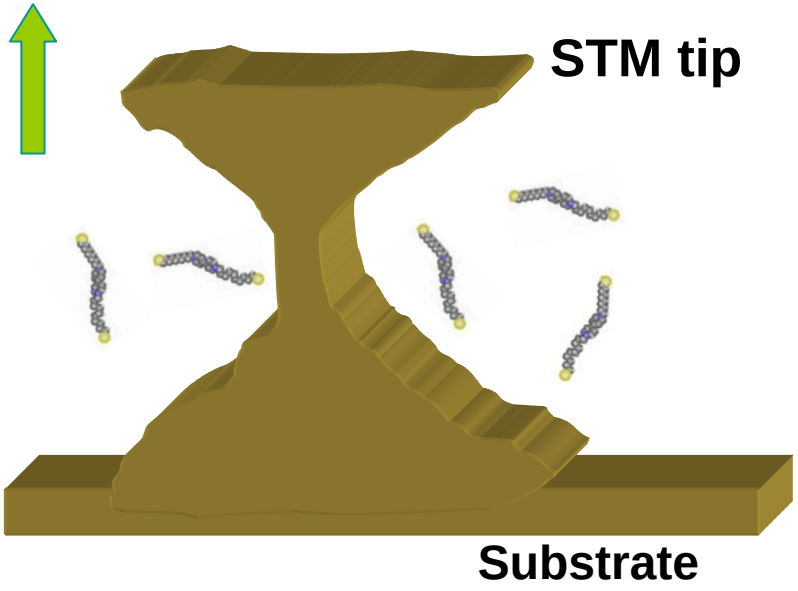
Dekker et al., Nature 2000
8 nm gap

"Matrix Isolation"

Conducting AFM



Cui and Lindsay
Science, 2001

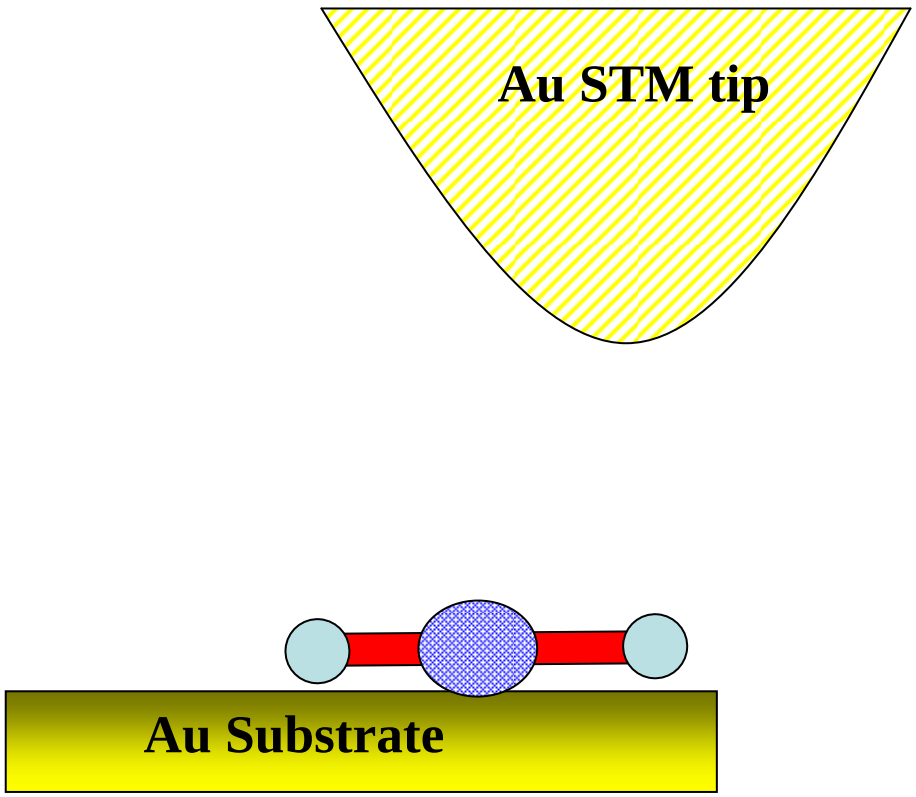


Tao et al., Science 2003

I(s) Method

- Contact between tip and surface avoided
- Current recorded as molecule stretched in junction

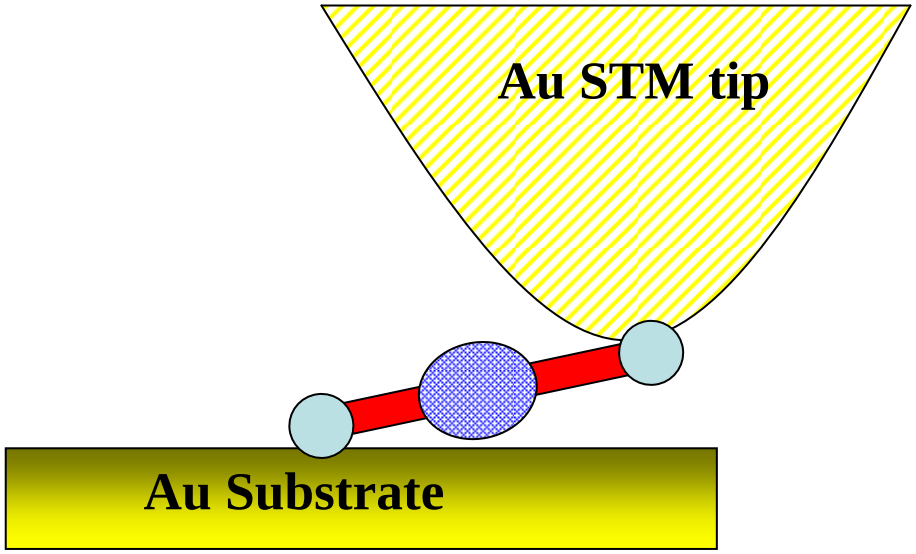
1. Tip approaches



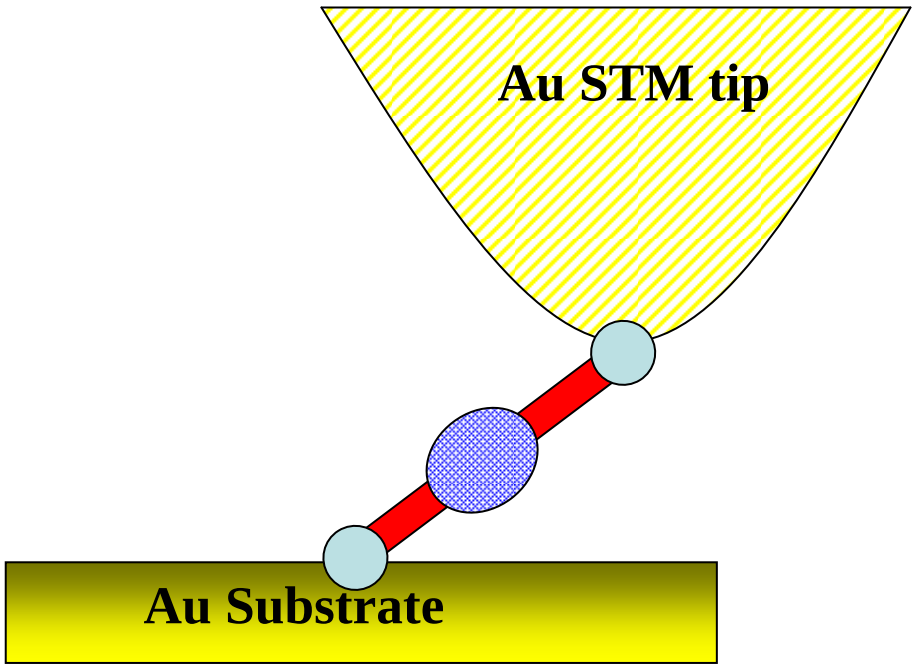
Haiss *et al., J. Am. Chem. Soc*., 2003 **125** 15295

Single molecules

1. Tip approaches
2. Free thiol group binds with tip

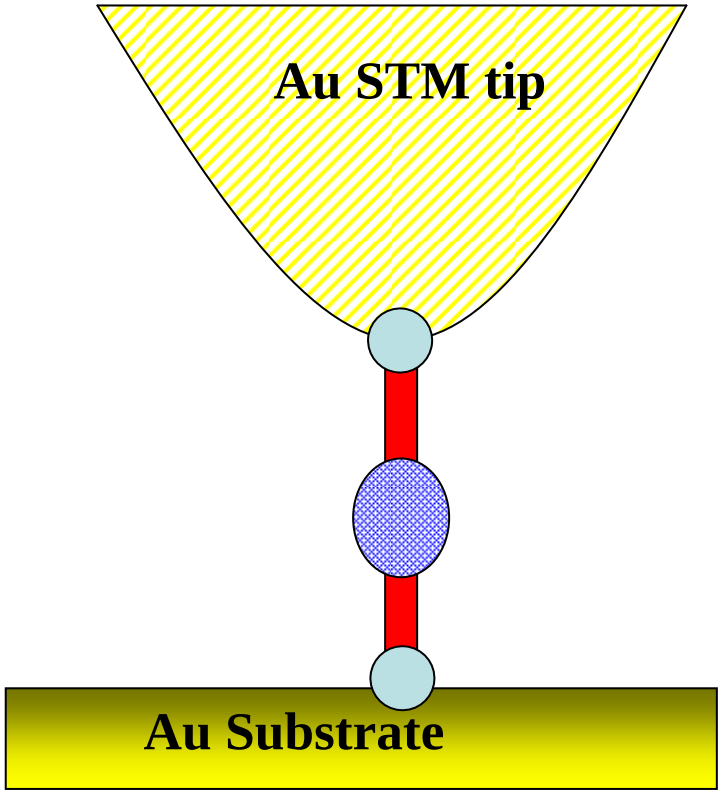


Single molecules



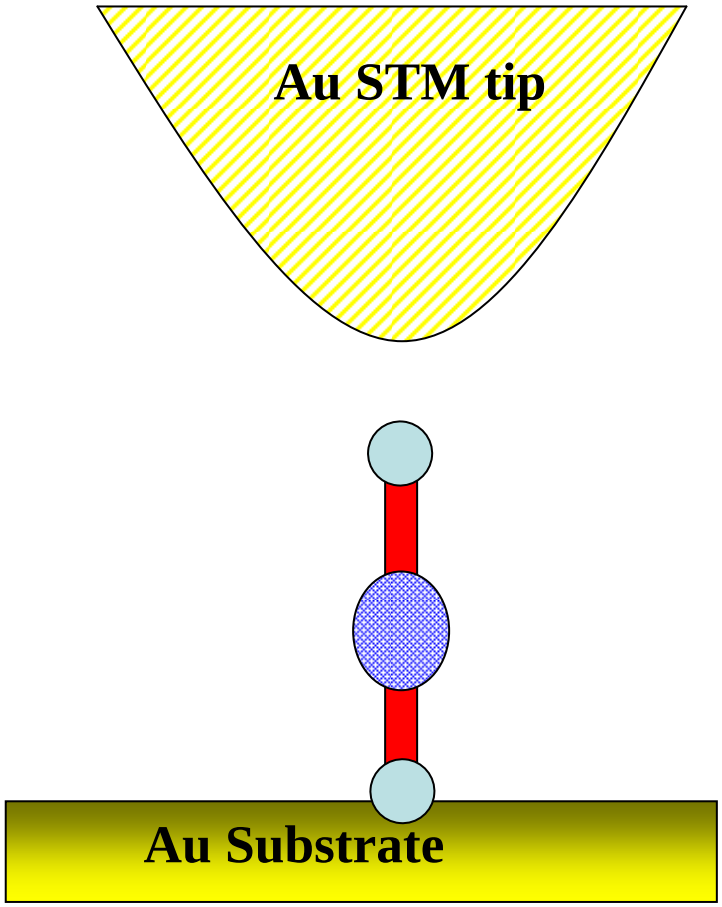
1. Tip approaches
2. Free thiol group binds with tip
3. Tip retracts, conduction through single molecule

Single molecules



1. Tip approaches
2. Free thiol group binds with tip
3. Tip retracts, conduction through single molecule
4. Molecule is standing upright

Single molecules



1. Tip approaches
2. Free thiol group binds with tip
3. Tip retracts, conduction through single molecule
4. Molecule is standing upright
5. Molecule is ripped off

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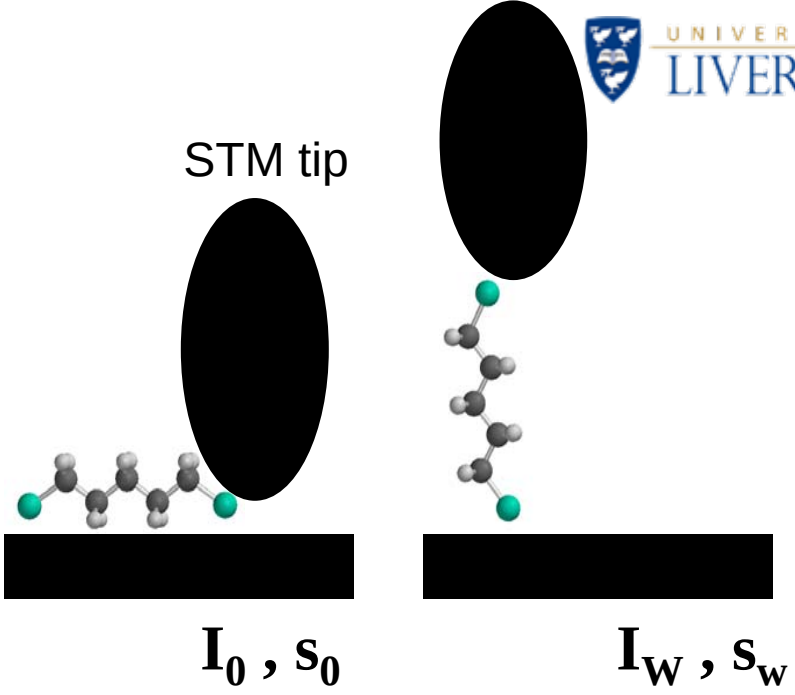
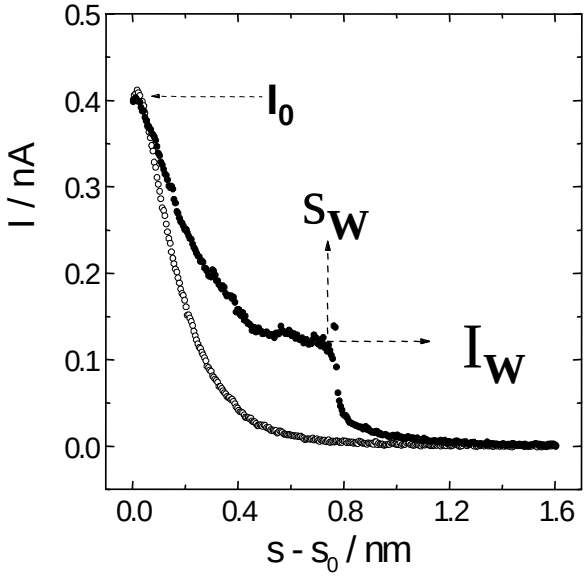
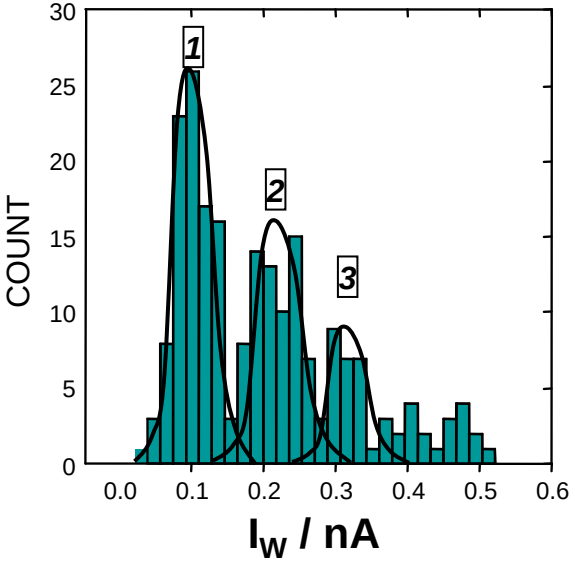
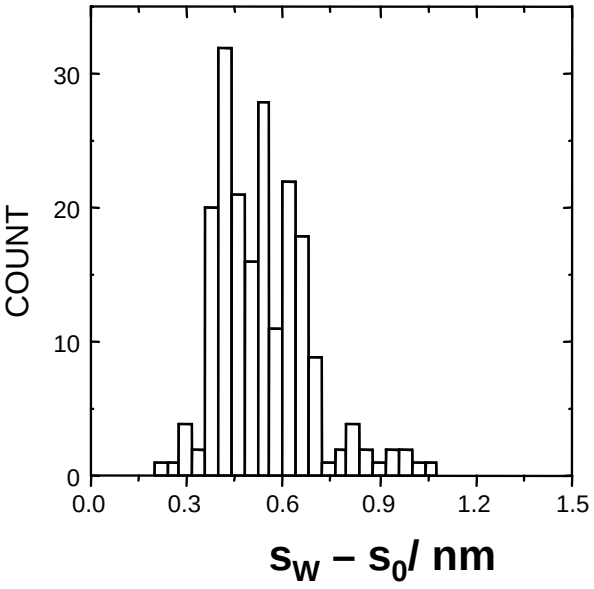
Measurement of single molecule conductance using I(s) method - **alkanedithiols**



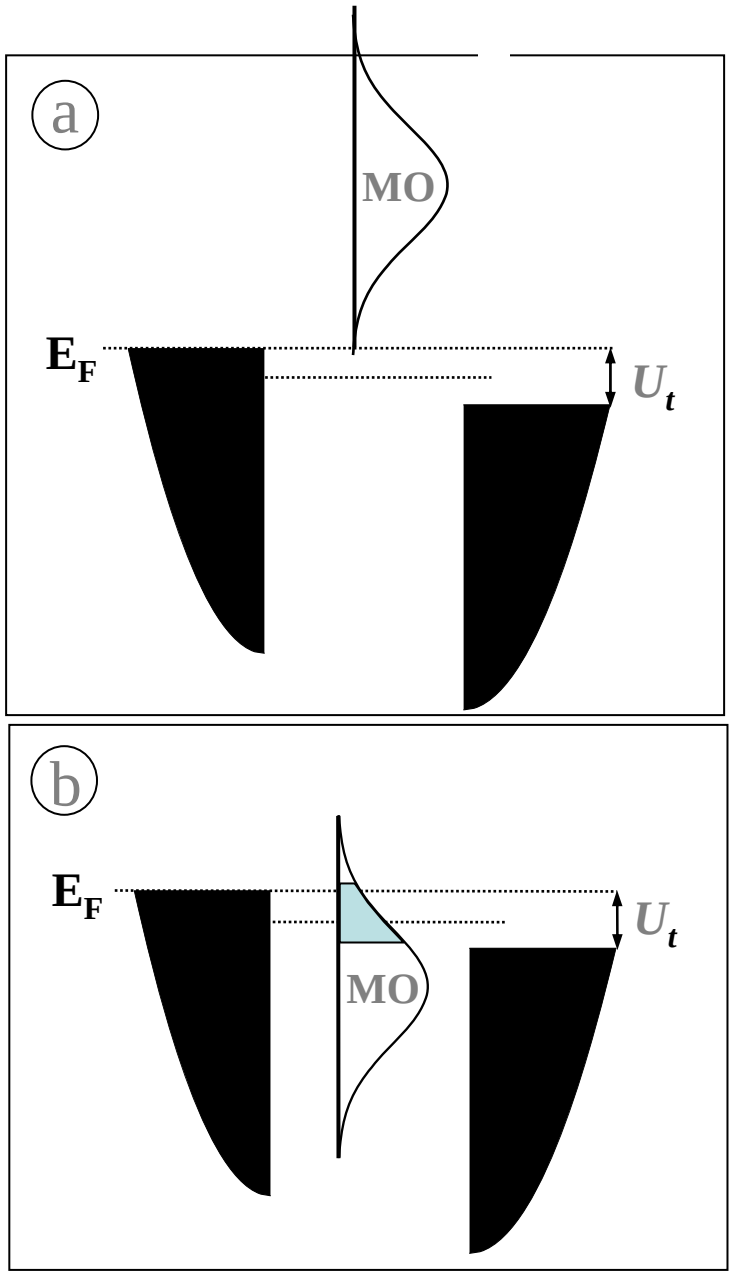
Nonanedithiol, $HS(CH_2)_9SH$







Functional molecular wires



Build in functionality that has an orbital closer to Au Fermi level.

Should increase conductance.

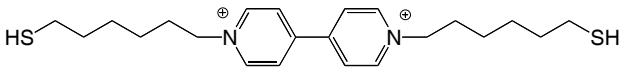
Hopping or tunneling?

'Tune' conductance *via*

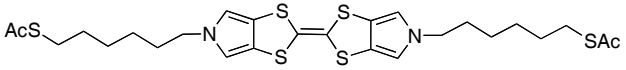
-synthetic chemistry (substituents) Leary *et al.*, *Chem. Comm.* 2007 3939.

-redox state (experiments under potential control in electroly te)

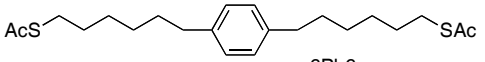
‘Double tunneling barriers’



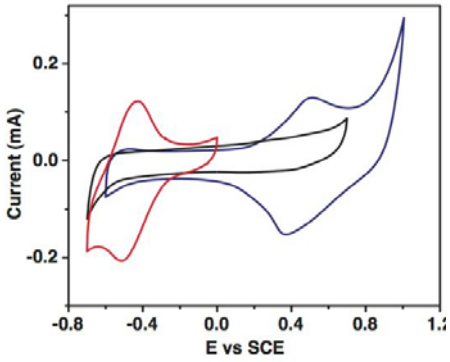
Viologen - 6V6

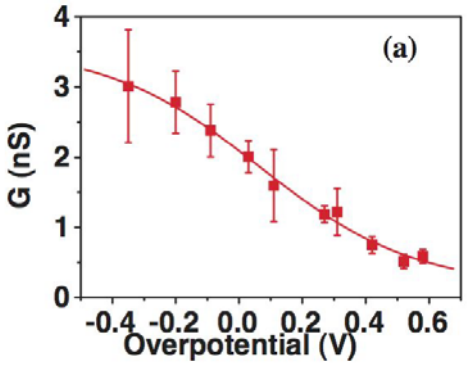


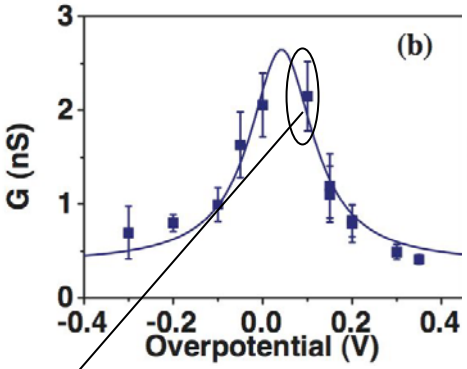
6PTTF6

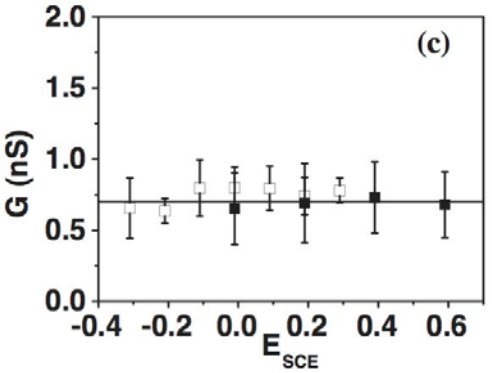


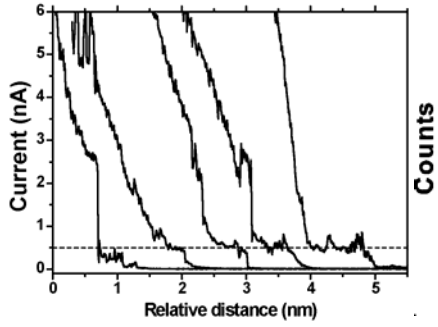
6Ph6

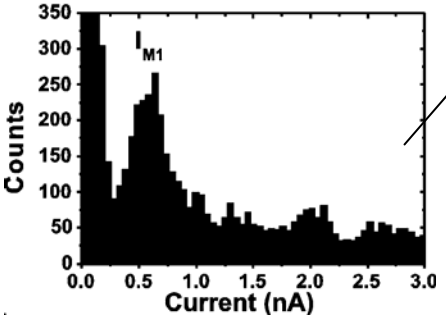












As redox orbital (HOMO of TTF; LUMO of viologen) approaches E_F of Au, conductance increases by *ca* 6–fold for both systems.

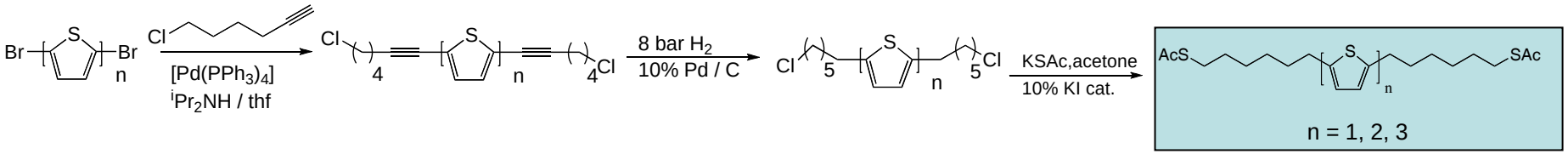
Viologen ‘rigidifies’ on reduction whereas TTF is rigid in both redox states; may explain difference in current-overpotential relation.

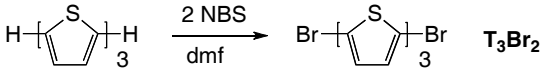
Viologens: *J. Am. Chem. Soc.* 2003, **125,** 15294. *Langmuir* 2004, **20,** 7694. *J. Phys. Chem. B*. 2007, **111,** 6703.
Pyrrolo-TTF: *J. Am. Chem. Soc*. 2008, **130,** 12204.

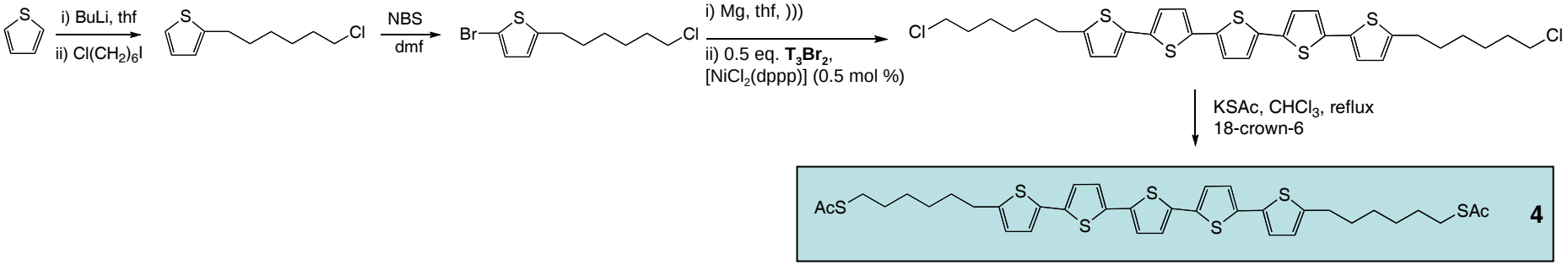
Viologens also looked at by Li, Wandlowski *et al.*, *Faraday Disc*. 2006 **131** 121; *Nanotech*. 2007 **18** 044018.

Oligothiophenes

Syntheses





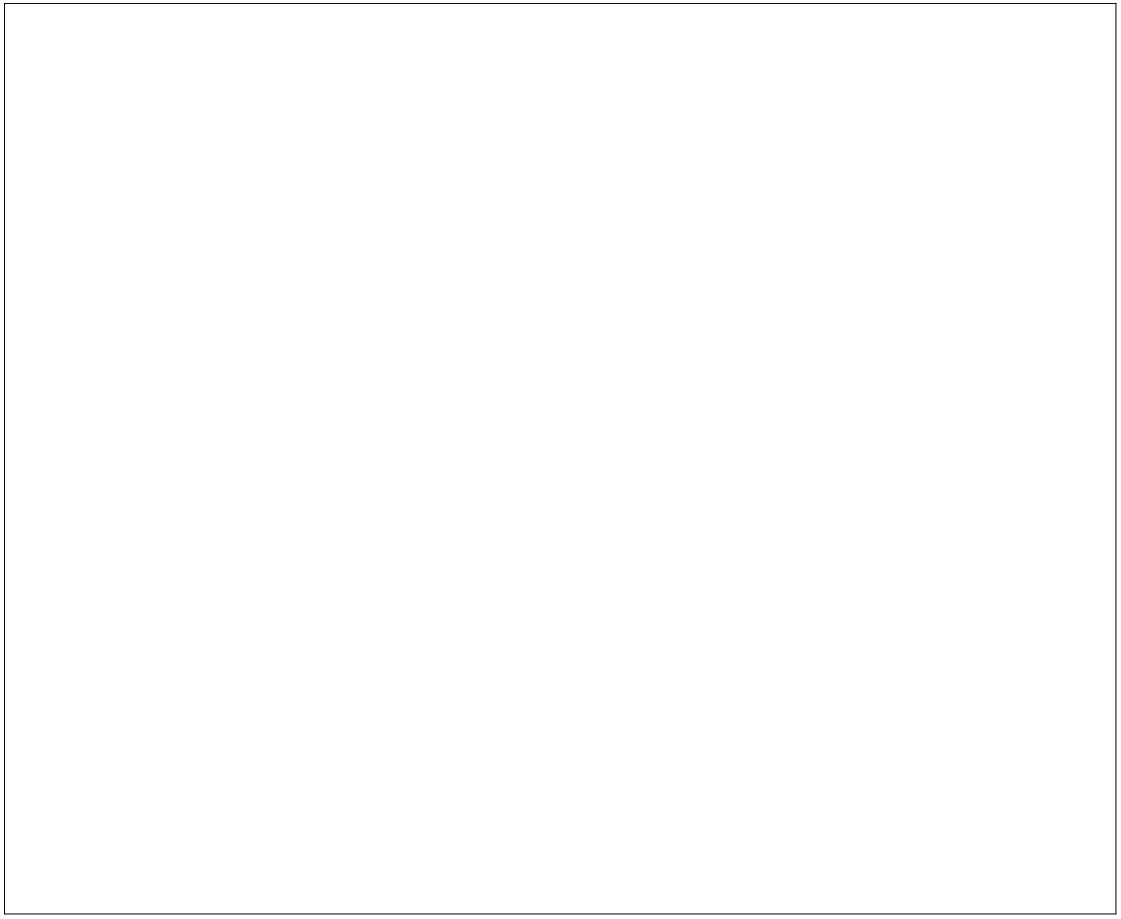


Monolayer formation

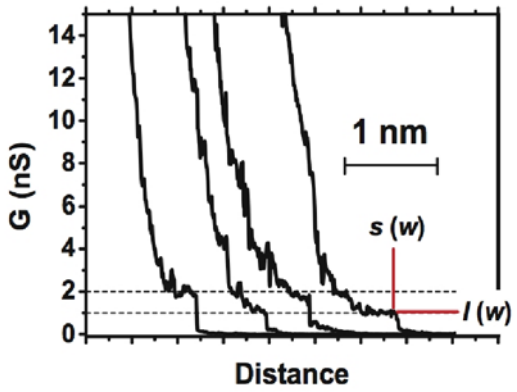
Au-on-glass slides; 10^{-4} M di-thioacetate, 1 minute dip time (5 minutes for XPS).

Oligothiophenes

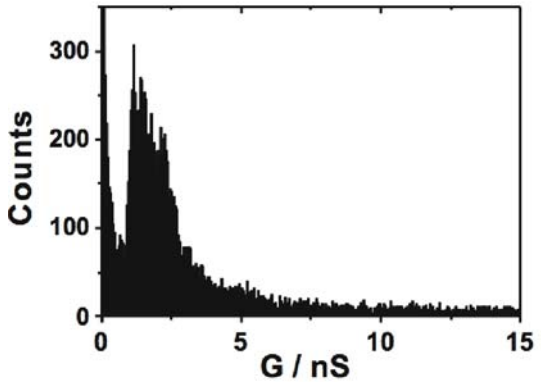
XPS characterisation - representative data



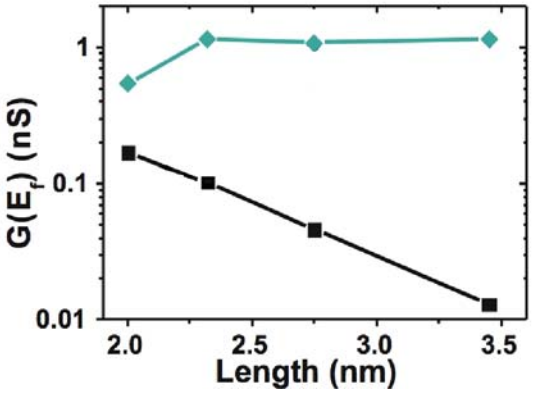
Representative I(s) data



Some I(s) curves for molecule **2**



…and a histogram from 100-150 such curves showing plateaux (molecule **3**).



Measured conductances of **1**–**4** plotted vs. S…S distances.

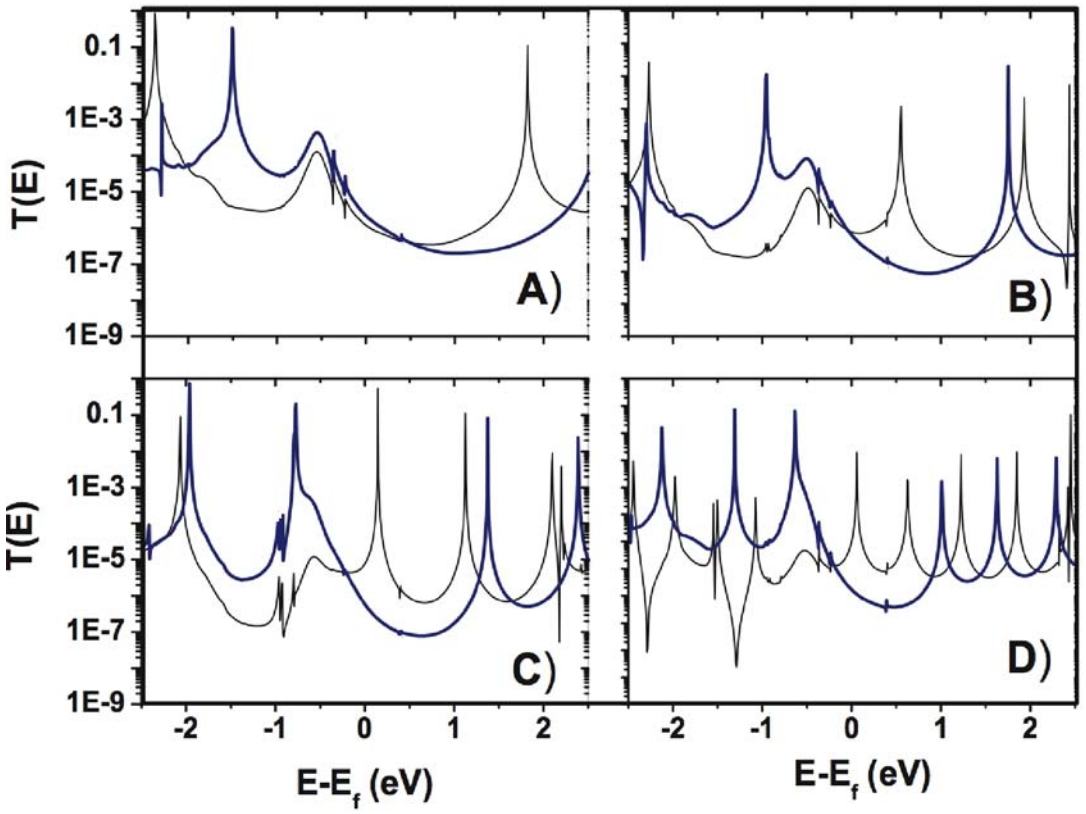
Theory predicts a *decrease in conductance with length*, in spite of the decreasing HOMO-LUMO separation (black line)!

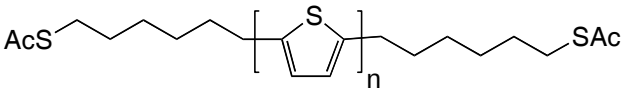
Water

Ab initio non-equilibrium Green's function (SMEAGOL) method*

*Rocha, A. R. *et al*. *Phys. Rev. B*. **73,** 085414 (2006); *Nature Mater.* **4**, 335 (2005).

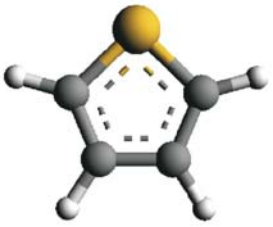
Calculations in presence of 'special' water

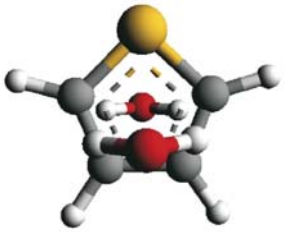




A: n = 1
B: n = 2
C: n = 3
D: n = 5

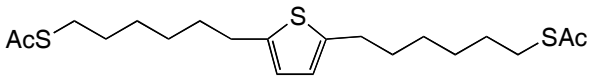
Blue line: *Vacuo*.
Black line: Water present.

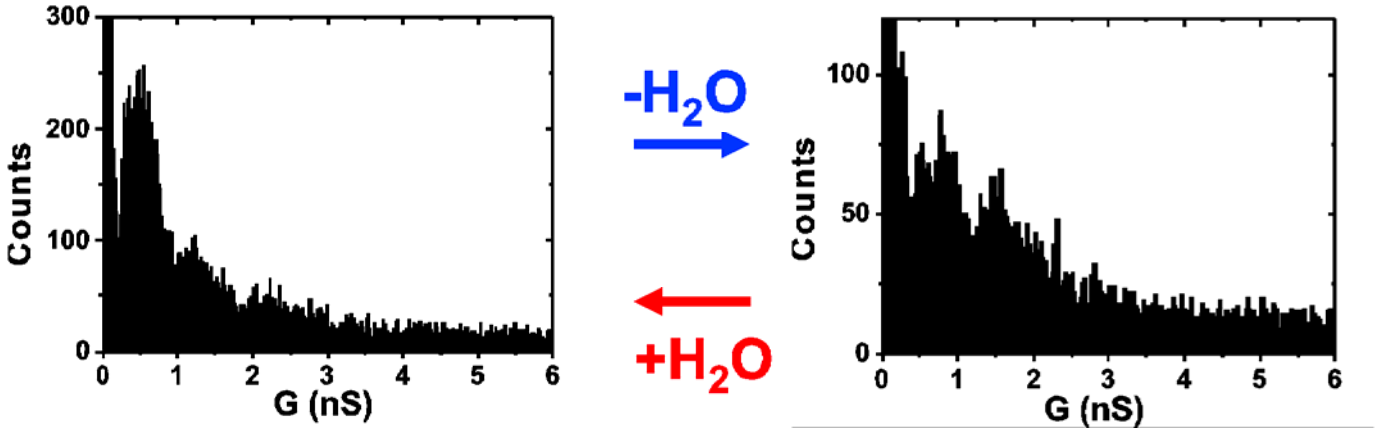




Try experiments 'without water'

* We do not have routine access to high vacuum STM. *





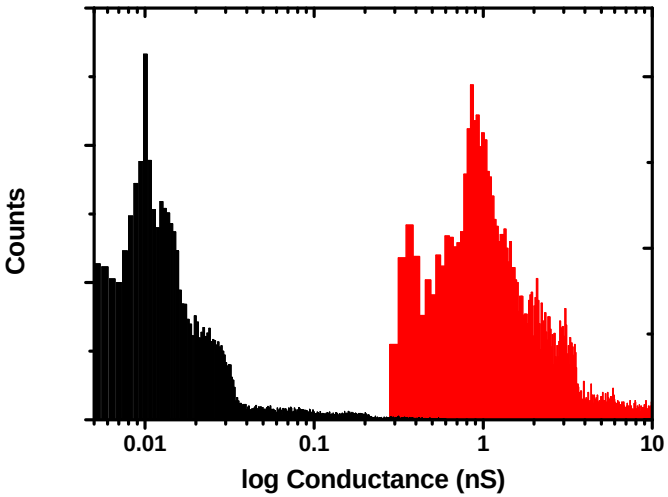
In ambient

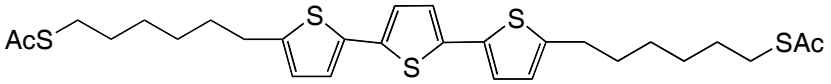
Under argon (24 h purge)

No change for the mono-thiophene derivative.

(Limited experiments with **1** in vacuum also give same conductance).

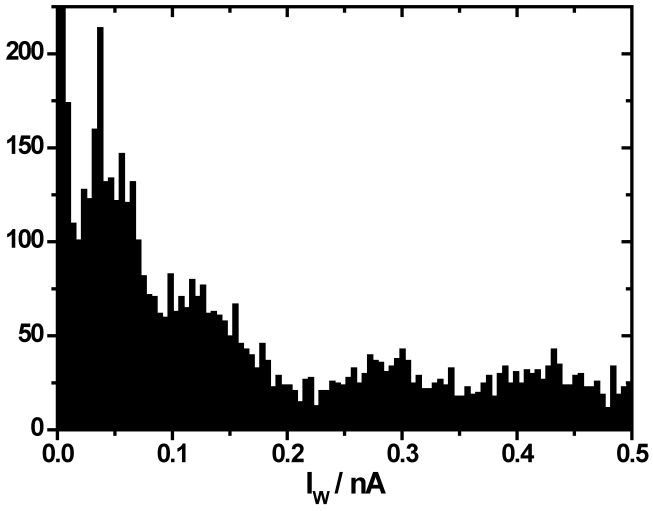
For longer oligothiophenes…





(Black): I(s) experiments recorded under argon after 15 h purging at room temperature.

(Red): I(s) experiments after introducing a beaker of degassed water into the sample chamber, also under argon.

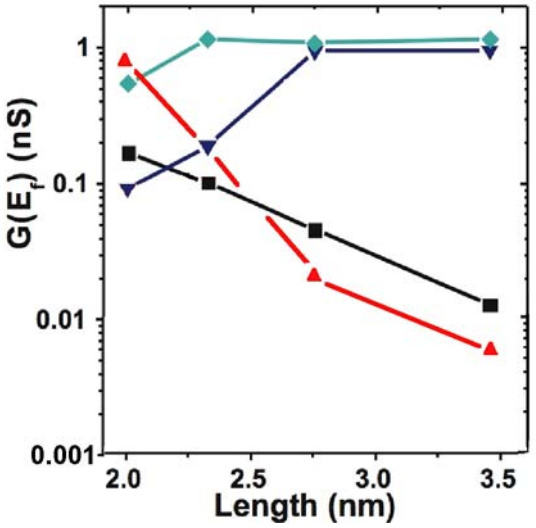


Preliminary data obtained with vacuum STM (Physics, Liverpool).

Conductance *ca*. 0.04 nS at U_{tip} +1.0 V

(I/V behavior highly unusual; reminiscent of NDR)

Summary of theory and experiment



Green-blue: Experimental, ambient.
Black: Theory, in *vacuo*.
Blue: Theory, 'special' + random water.
Red: Experimental, in dry argon*.

*For the pentathiophene molecule, the value is an **upper limit**.

Brief conclusions

Water 'gates' conductance of Au | molecule | Au junctions with these molecules.

For n = 5, this results in a *>200-fold change* in conductance!

Important to bear in mind for potential-dependent studies of redox-active molecules.

Acknowledgements

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