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Electronics and Mechanics of Single Molecule Circuits

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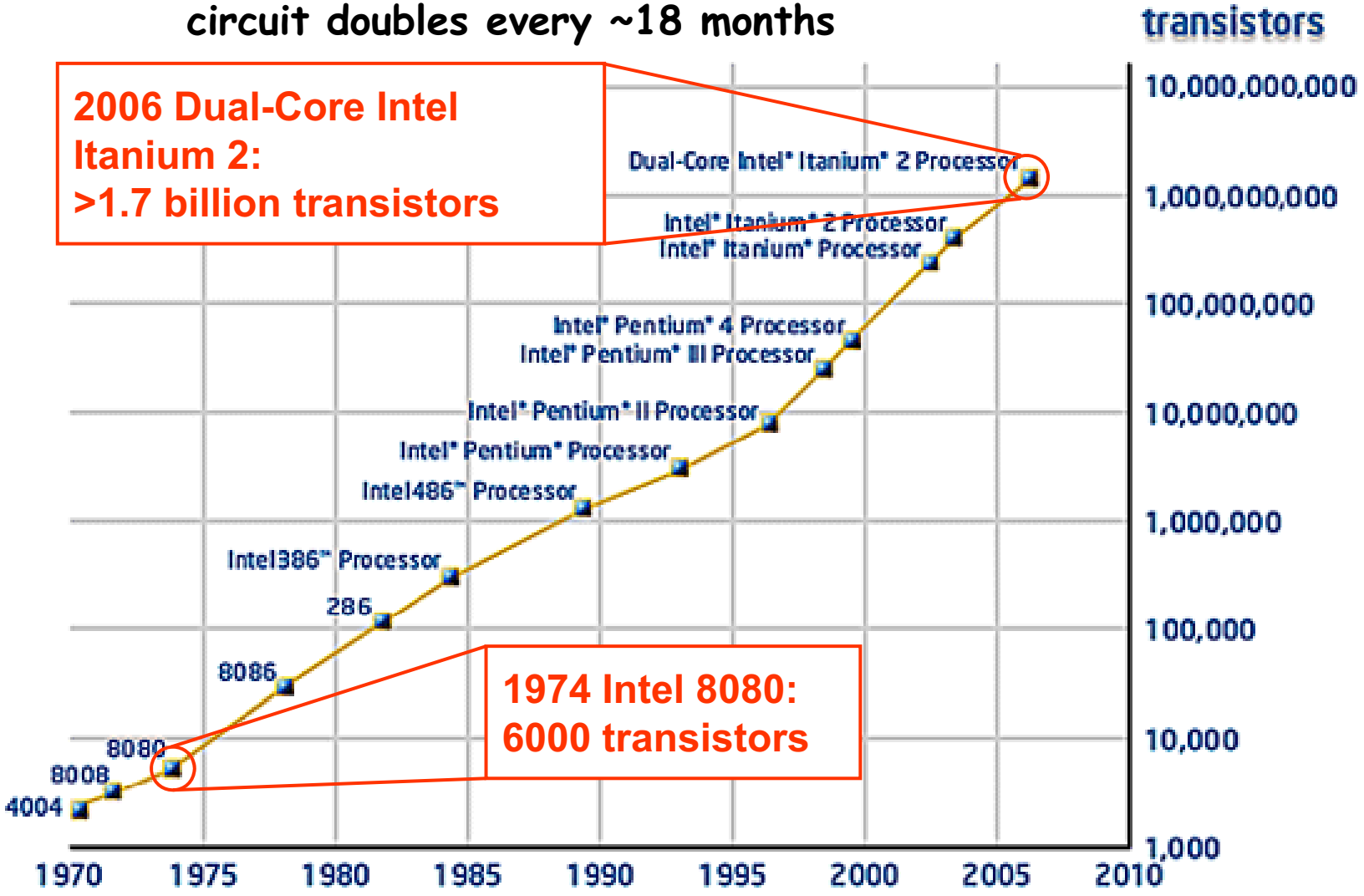
May. 26, 2010. ICTP, Italy

The Future of Electronics

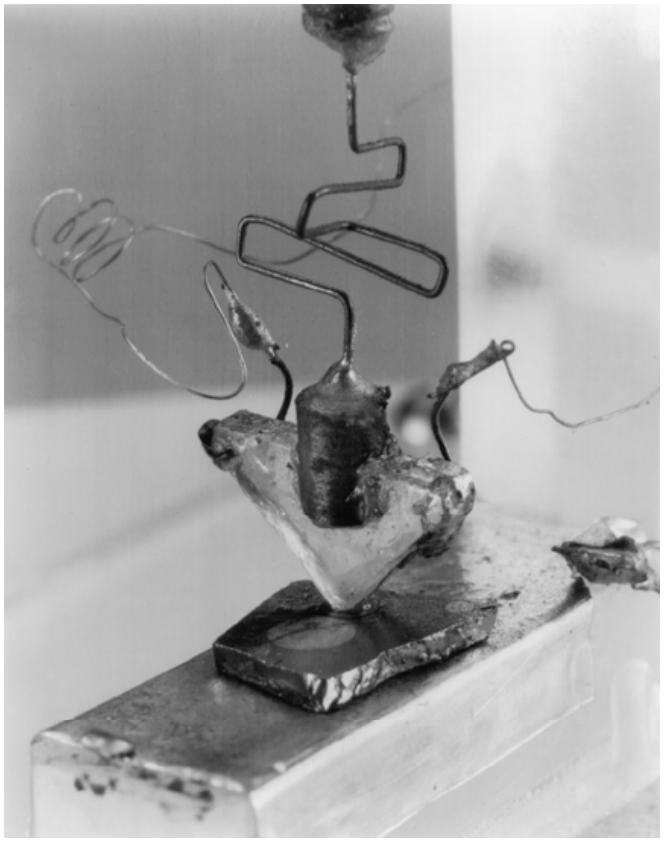
Moore's Law: the number of transistors on an integrated circuit doubles every ~18 months



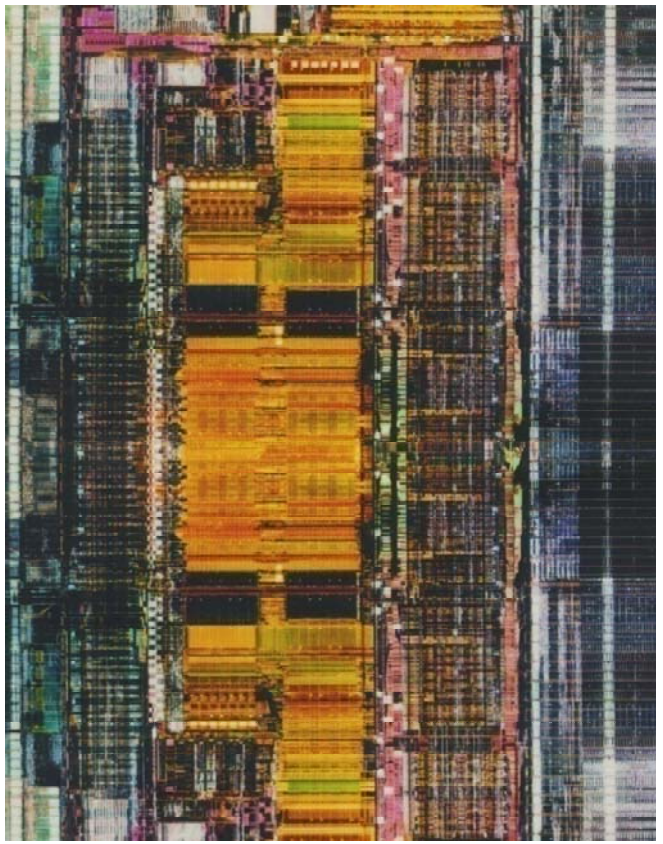
From http://www.intel.com/technology/mooreslaw/index.htm

Changes in the Transistor: From 1947-2008

Bell Labs, 1947 -
Brattain, Bardeen, Shockley
Measured ~0.5" high



Intel: 2006
Itanium-2 chip with
220 million transistors



Molecules as Components of Circuits

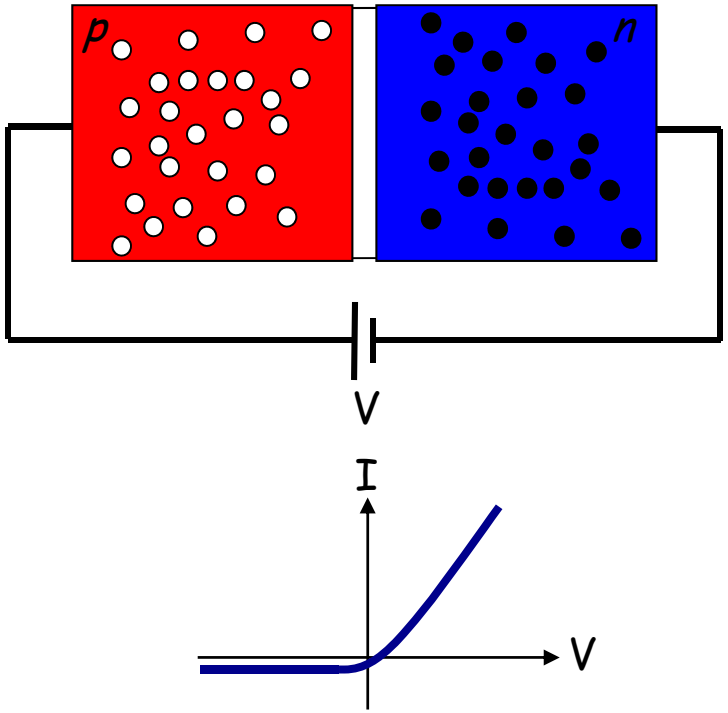
MOLECULAR RECTIFIERS

Arieh AVIRAM
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598, USA

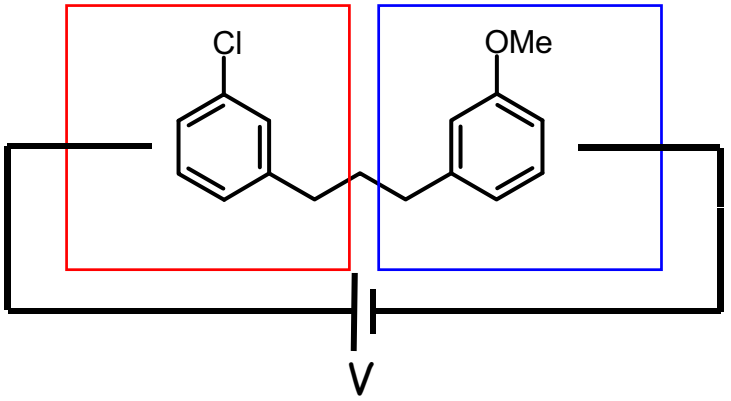
and

Mark A. RATNER*
Department of Chemistry, New York University, New York, New York 10003, USA

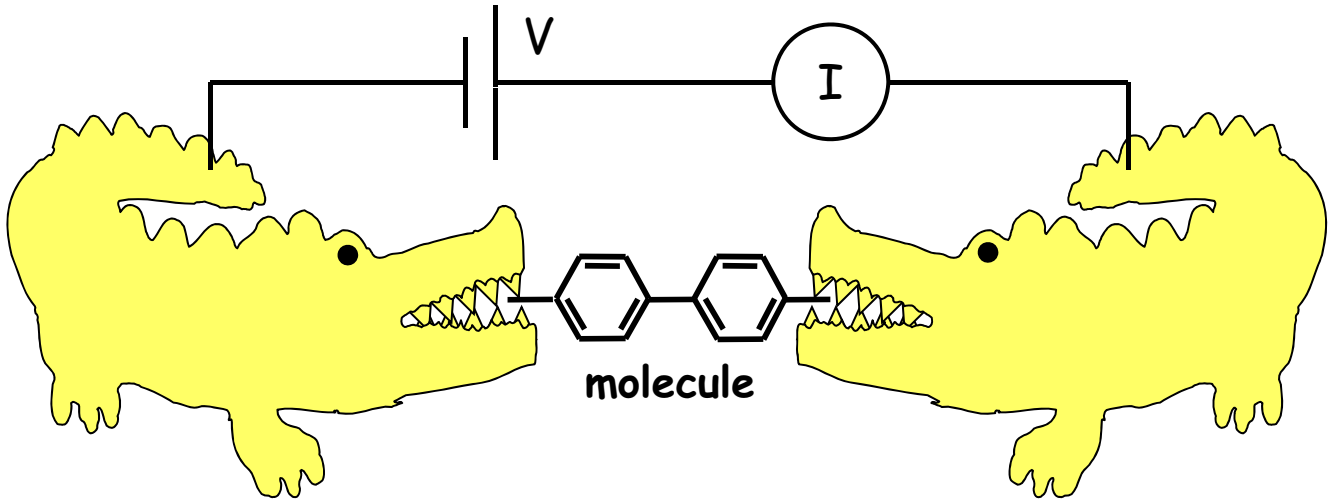
Received 10 June 1974



"The construction of a very simple electronic device, a rectifier. based on the use of a single organic molecule is discussed."

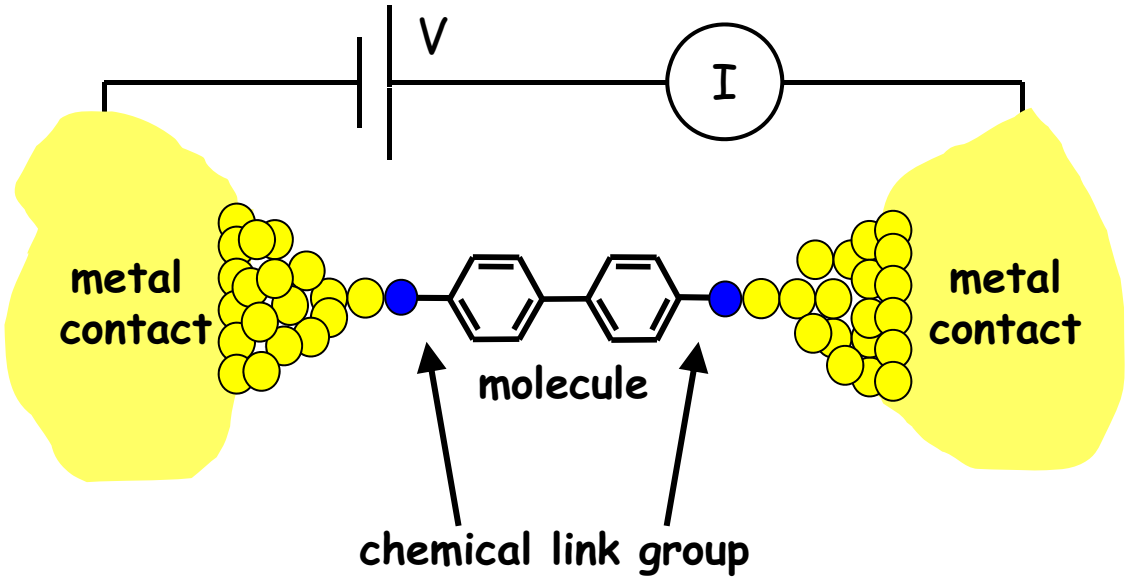


Anatomy of a Single Molecule Device



So What are these Alligators?

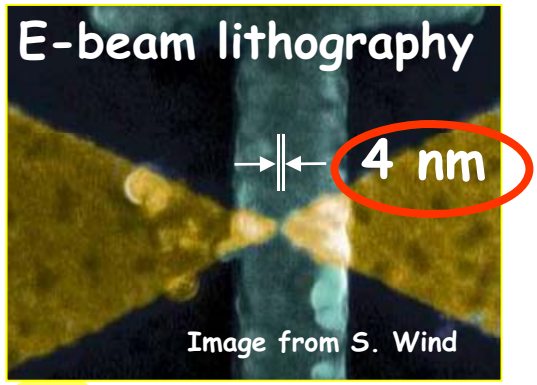
Anatomy of a Single Molecule Device

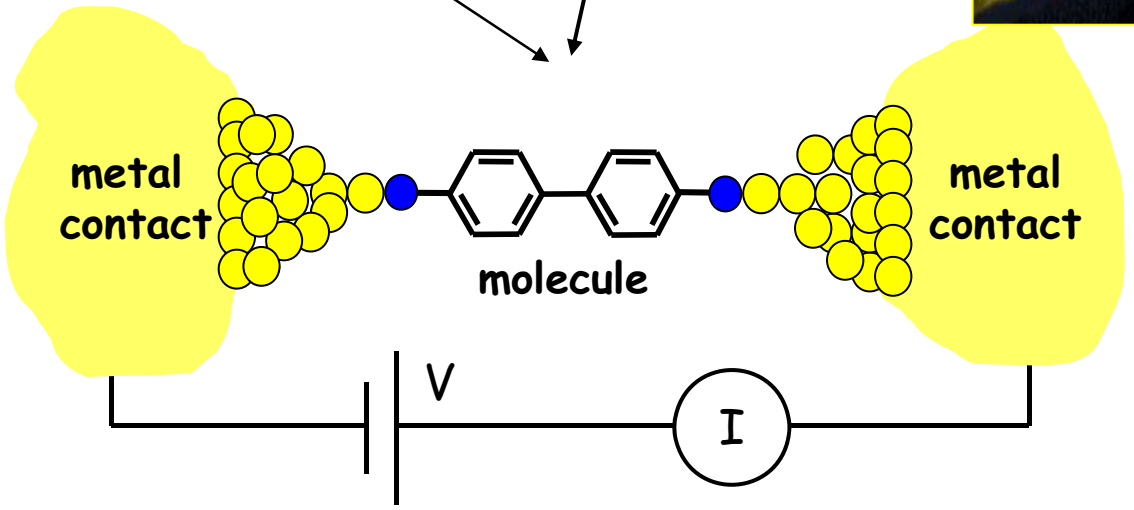


Where is the Experimental Challenge?

A biphenyl is ~ 7 Å

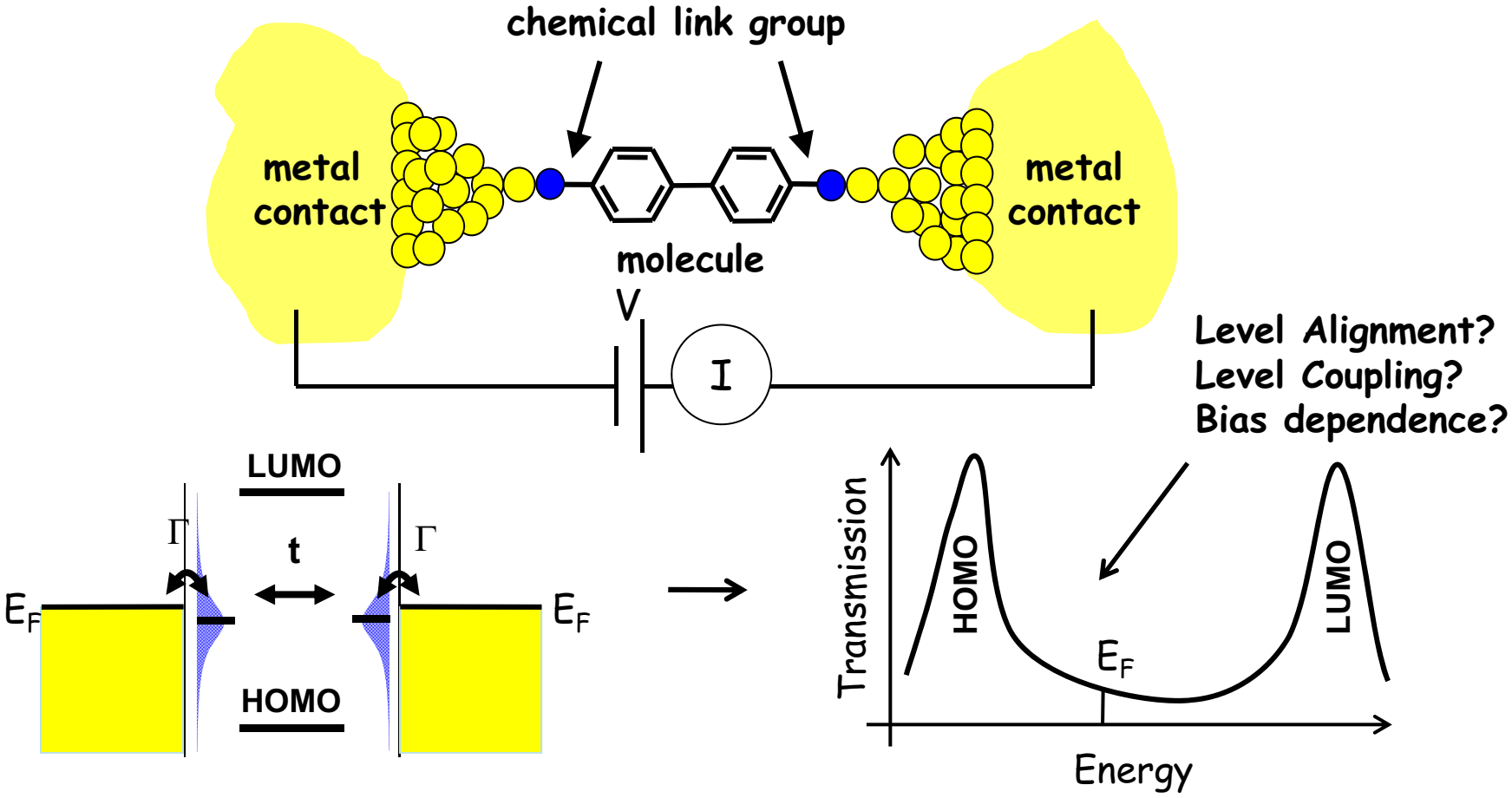
The gap is →





Key Experimental Issues:
- **Reproducibility**
- **Single Molecule Signature**

Anatomy of a Single Molecule Device



- How can we create such single molecule devices and measure transport?
- What are key parameters that control transport?
- How can we get transport functionality from chemistry?

Some Major Accomplishments

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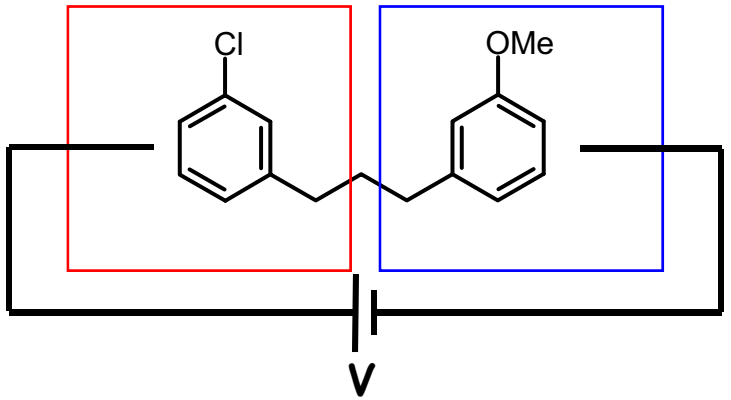
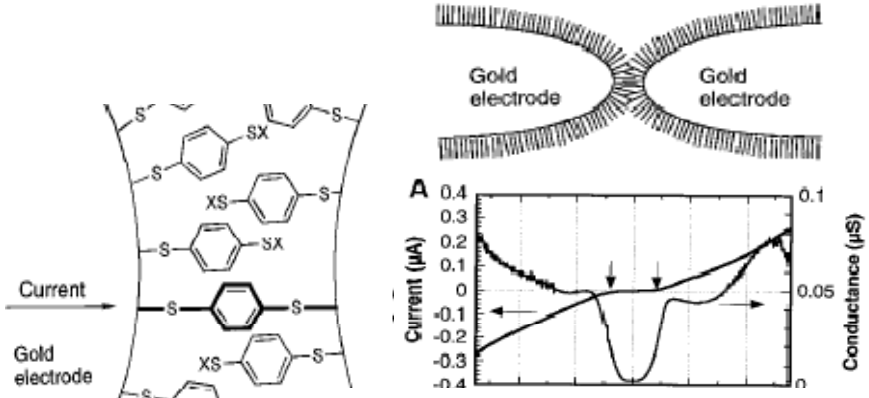


1974

1997

First demonstration of a molecular junction?



Reed & Tour Science 1997

1999

2001

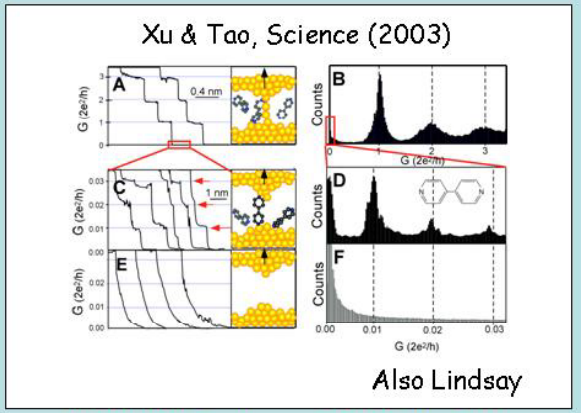
2002

2002

2002

Point-contact in solution

Xu & Tao, Science (2003)



Also Lindsay

Method that allows statistical study

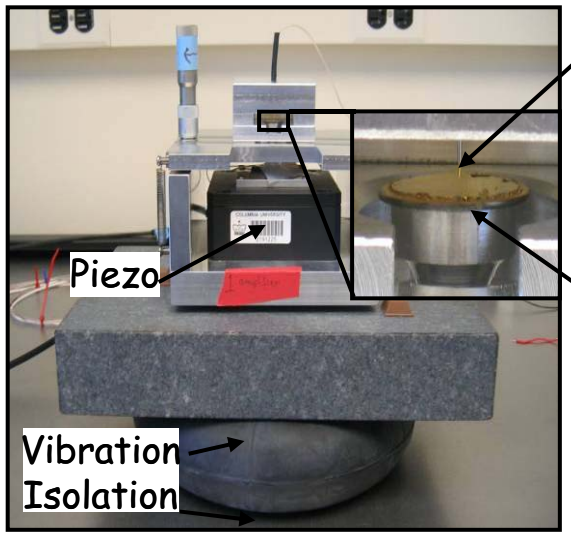
2003

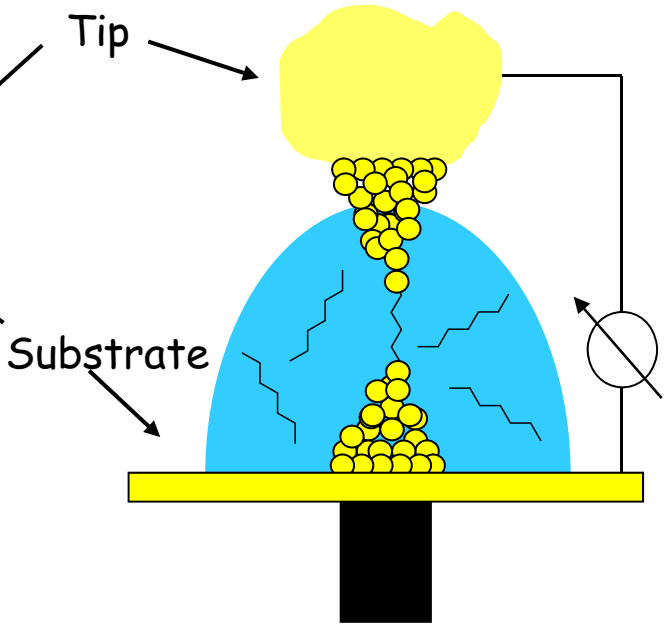
Outline

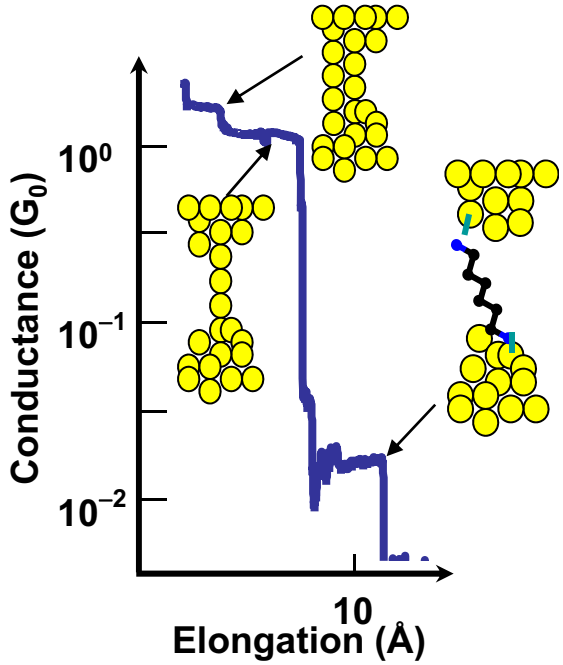
1. Experimental Method
2. Structure-Conductance Relations
3. Conductance and Mechanics
4. Switching in Pyridines

Experimental Method

STM based mechanically controlled break junction





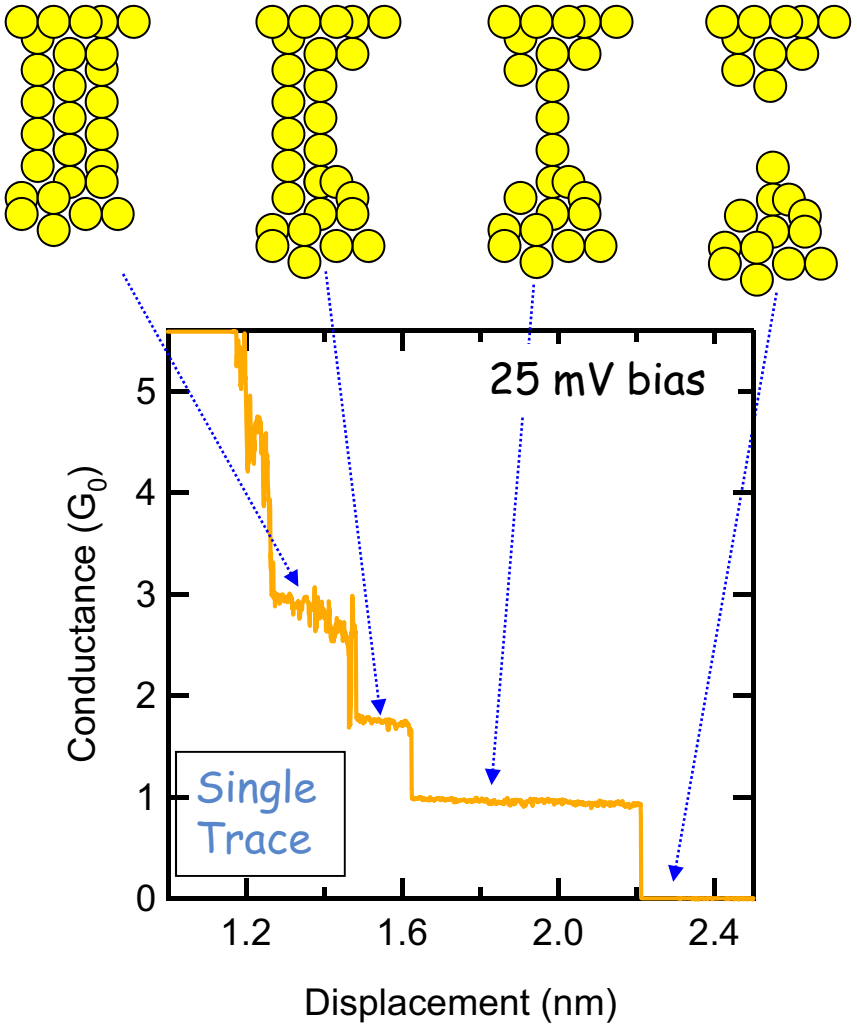


Key Points:
- Good vibration and acoustic isolation
- Low voltage noise for piezo
- Clean substrate & high purity solvents

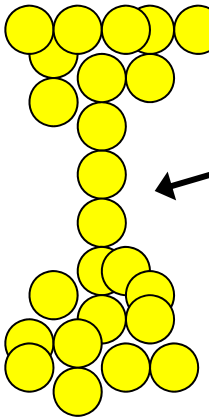
Advantages:
- Statistics
- Same platform for different molecules
- Variable Environment

Based on Xu & Tao, Science 2003

Breaking A Gold Contact

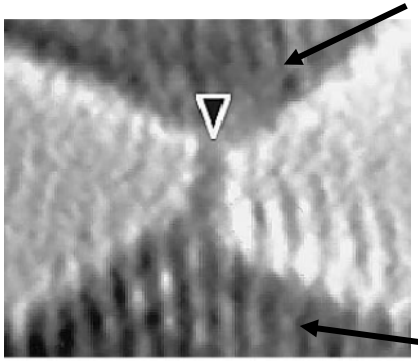


Landauer formalism:
$G = G_0 \times \Sigma t_i$ where
$G_o = 2e^2/h$



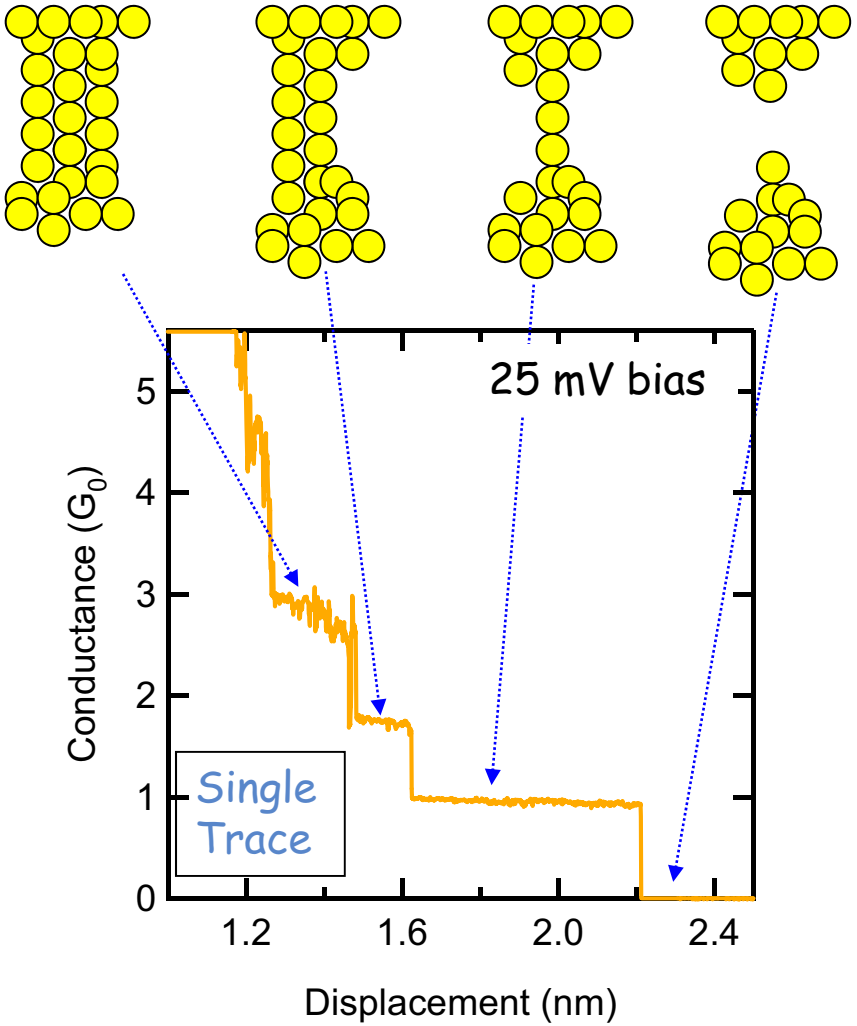
Au single atom chain has only 1 channel → Au 6s

At E_F transmission probability is ~ 1



From H. Ohnishi et al. Nature (1998)

Some Numbers



A single atom contact has:

$G_o = 2e^2/h = 77.5\ \mu S$
$R_0 = 1/G_0 = 12.9\ k\Omega$
At 25 mV:

$$I = 1.9\ \mu A$$

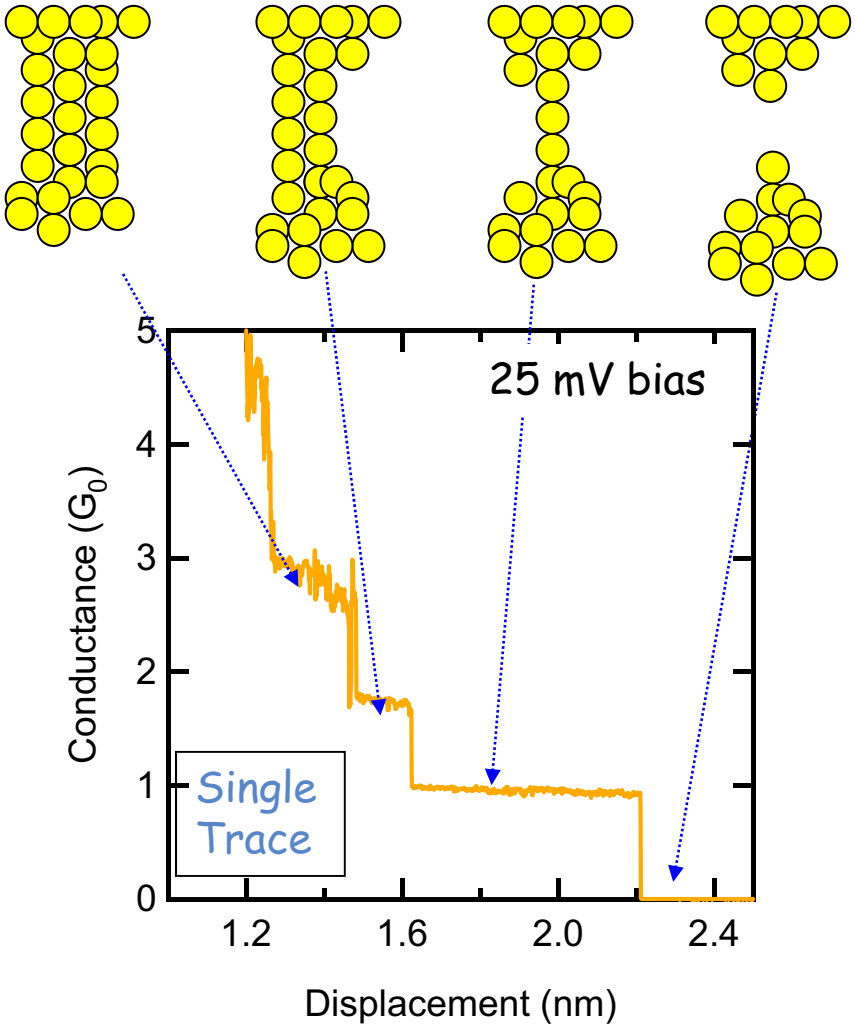
The current density through the single atom is :

$$J = 2.7 \times 10^{13}\ A/m^2$$

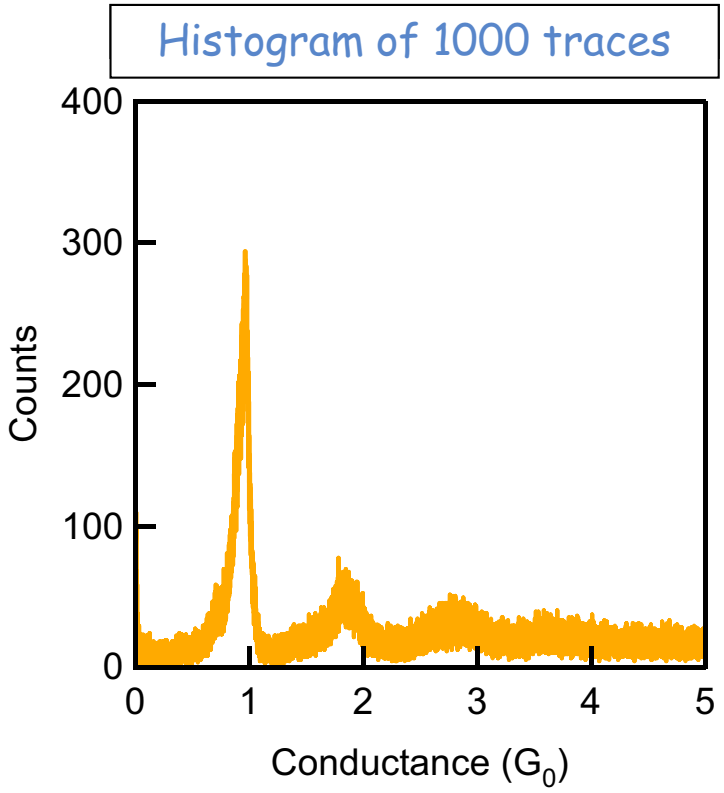
Number of electrons per second:

$$1.2 \times 10^{13}\ \bar{e}/\text{second}$$

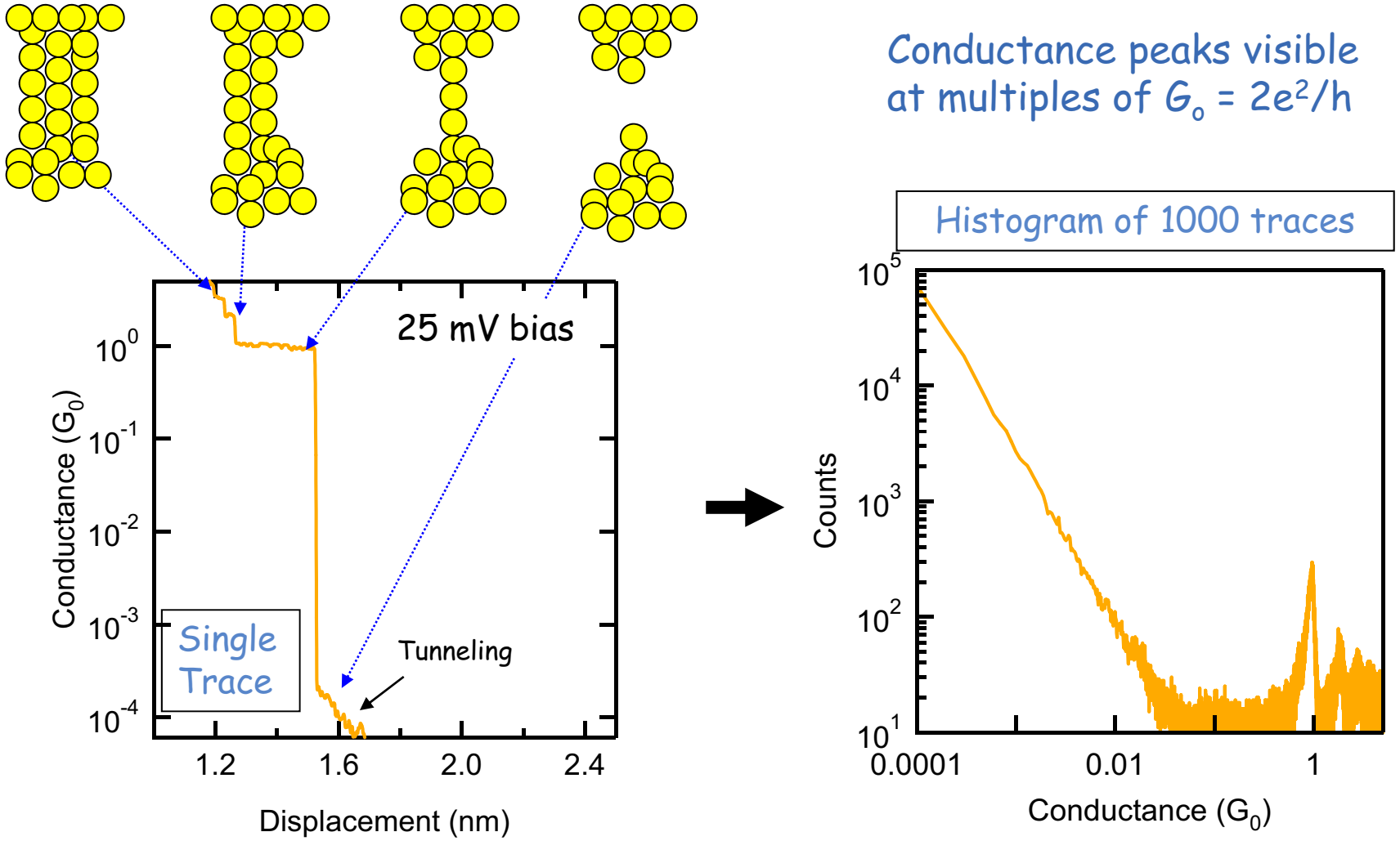
Data Analysis



Conductance peaks visible at multiples of $G_0 = 2e^2/h$



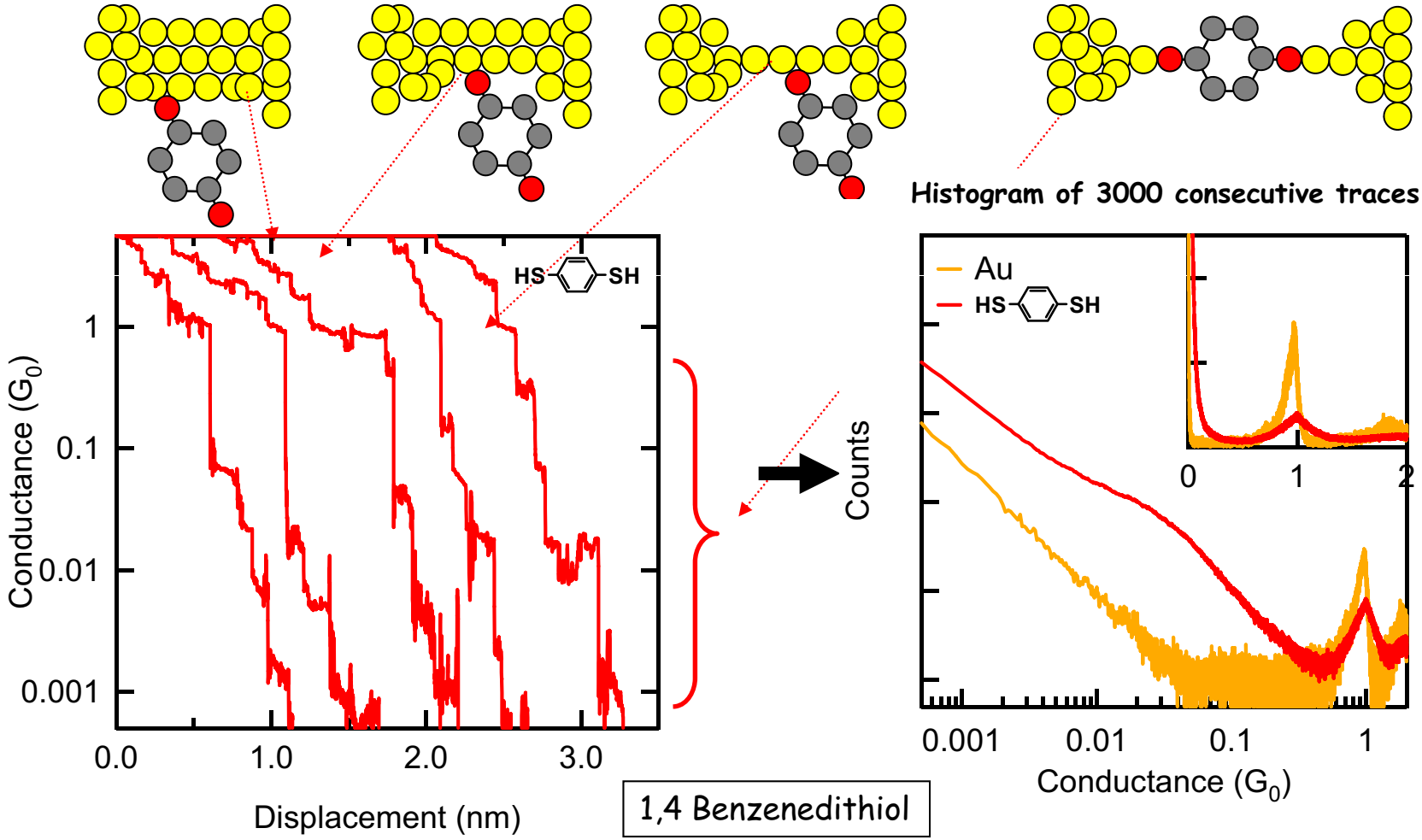
Data on a Log Scale



NOTE: These are linear binned histograms shown on a log-log scale

Adding Thiolated Molecules

(Ulrich et al, J. Phys. Chem. B 2006)



Steps visible over large conductance range.

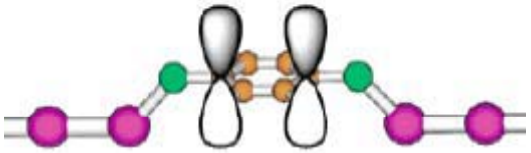
Thiols Links: Not Reproducible

Conductance depends on geometric details

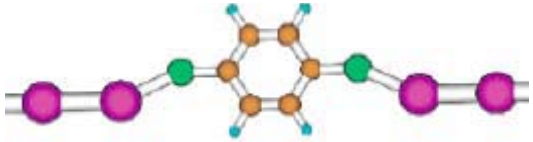
Thiols – bind to hollow, bridge, and atop site
Each configuration has different conductance

→ **Look for alternate links**

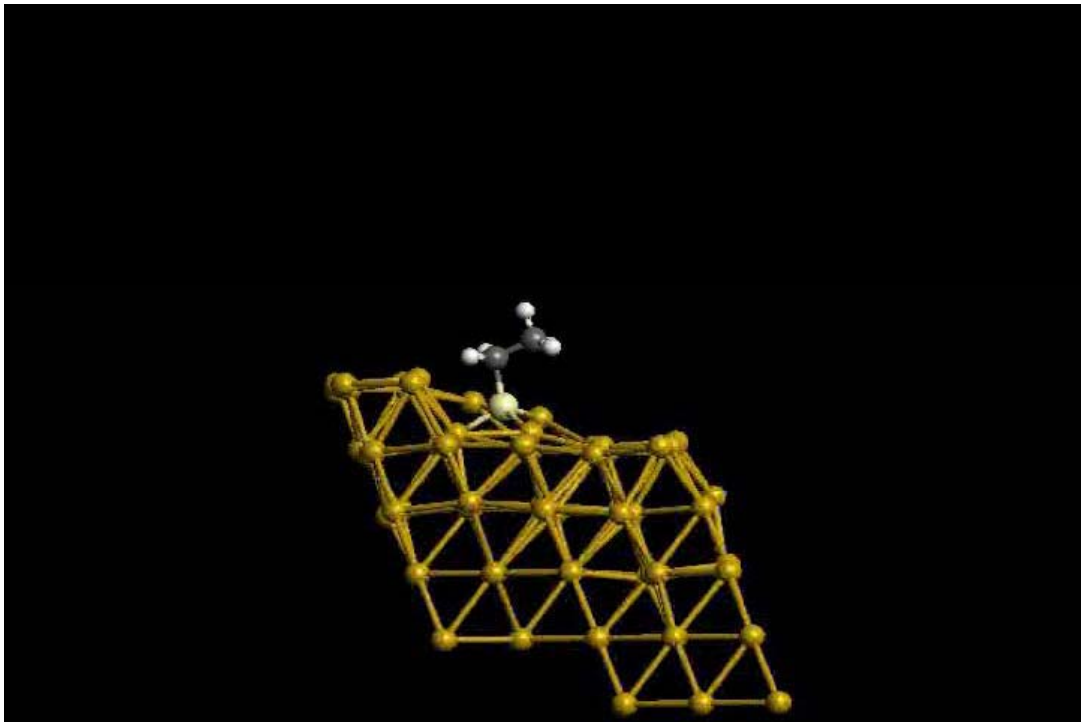
$G = 7 \times 10^{-5}\ G_0$



$G = 2 \times 10^{-8}\ G_0$



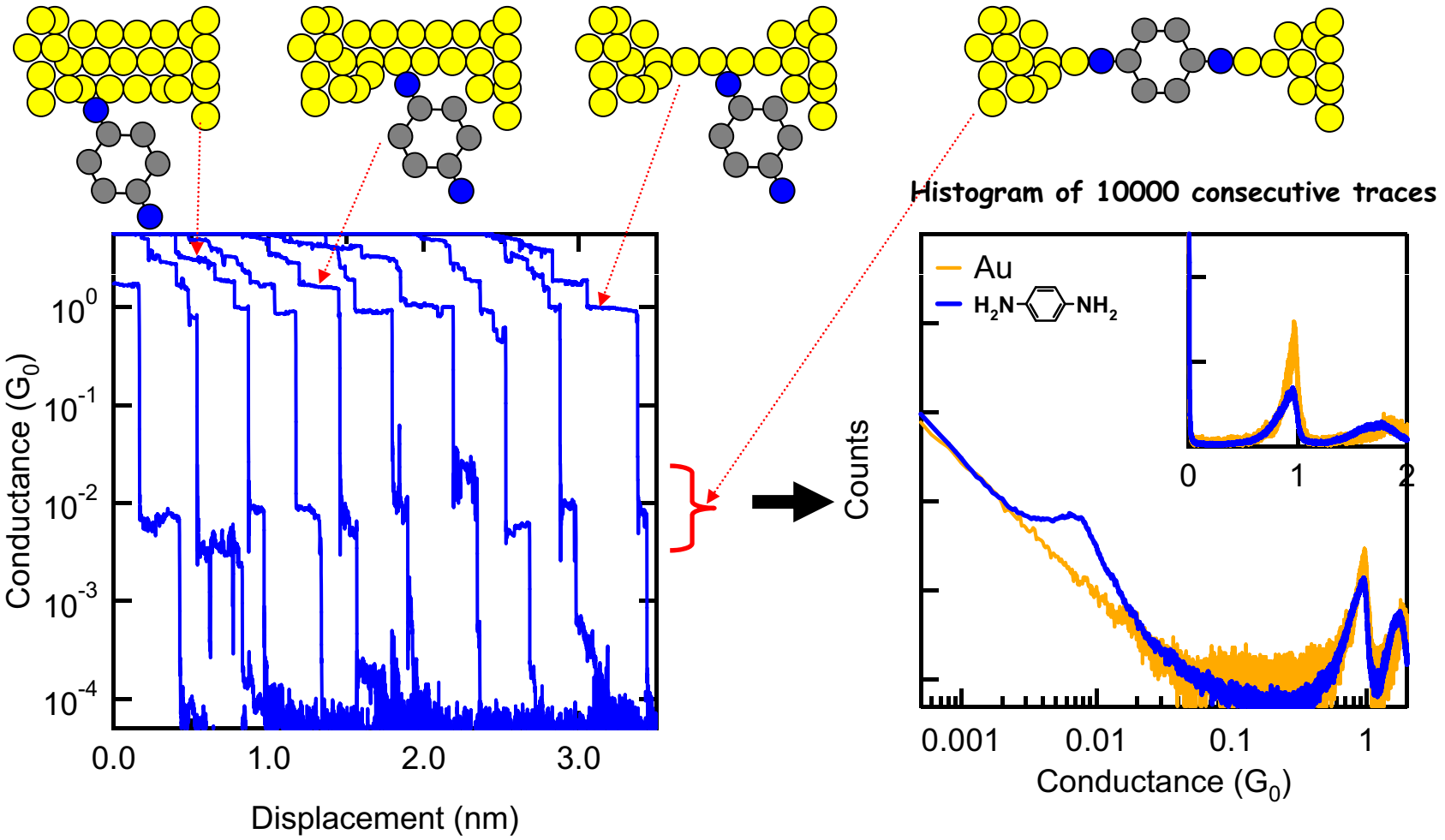
(H. Basch, Ratner et al., Nanoletters 2005)



(D. Kruger, H. Fuchs, Parrinello et al, PRL 2002)

Amines (NH_2): An Ideal Link

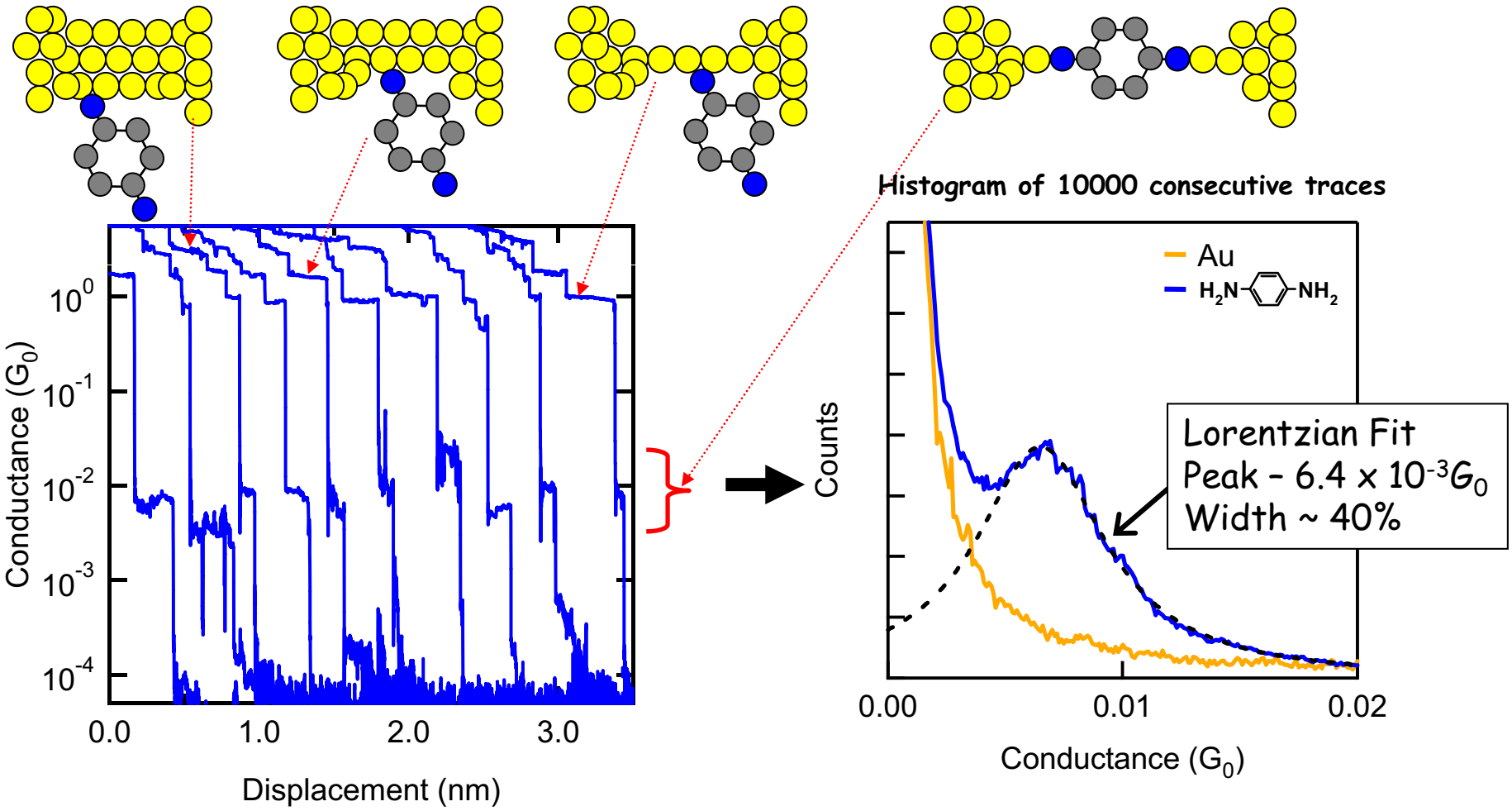
(L. Venkataraman et al, Nano Letters 2006)



With 1,4 Benzenediamine, steps are limited over a narrow conductance range.

Amines (NH_2): An Ideal Link

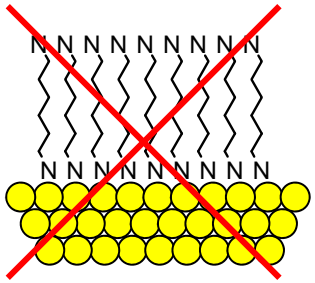
(L. Venkataraman et al, Nano Letters 2006)



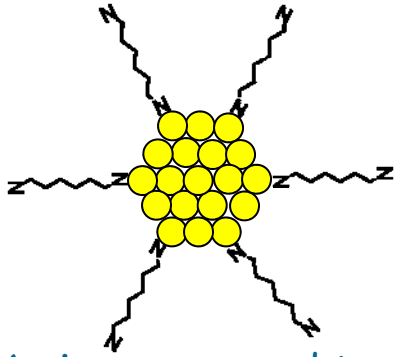
With 1,4 Benzenediamine, steps are limited over a narrow conductance range.

Why Do Amines Work?

Amine's bind preferentially to under-coordinated Au



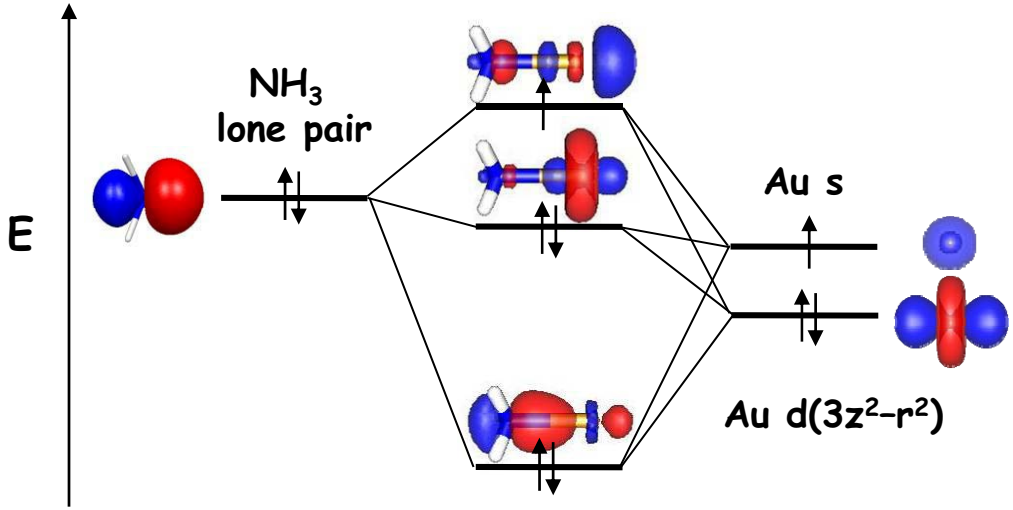
Amines do not form stable SAM's on Au(111)



Amines are used to passivate Au nano-particles.

Details in:

1. Quek et al Nano Letters 2007
2. Li & Kosov, PRB 2007
3. Kamenetska et al, PRL 2009



Binding Energy ~ 0.7 eV
Au-N Bond length ~2.3 Å
(DFT in GGA approximation)

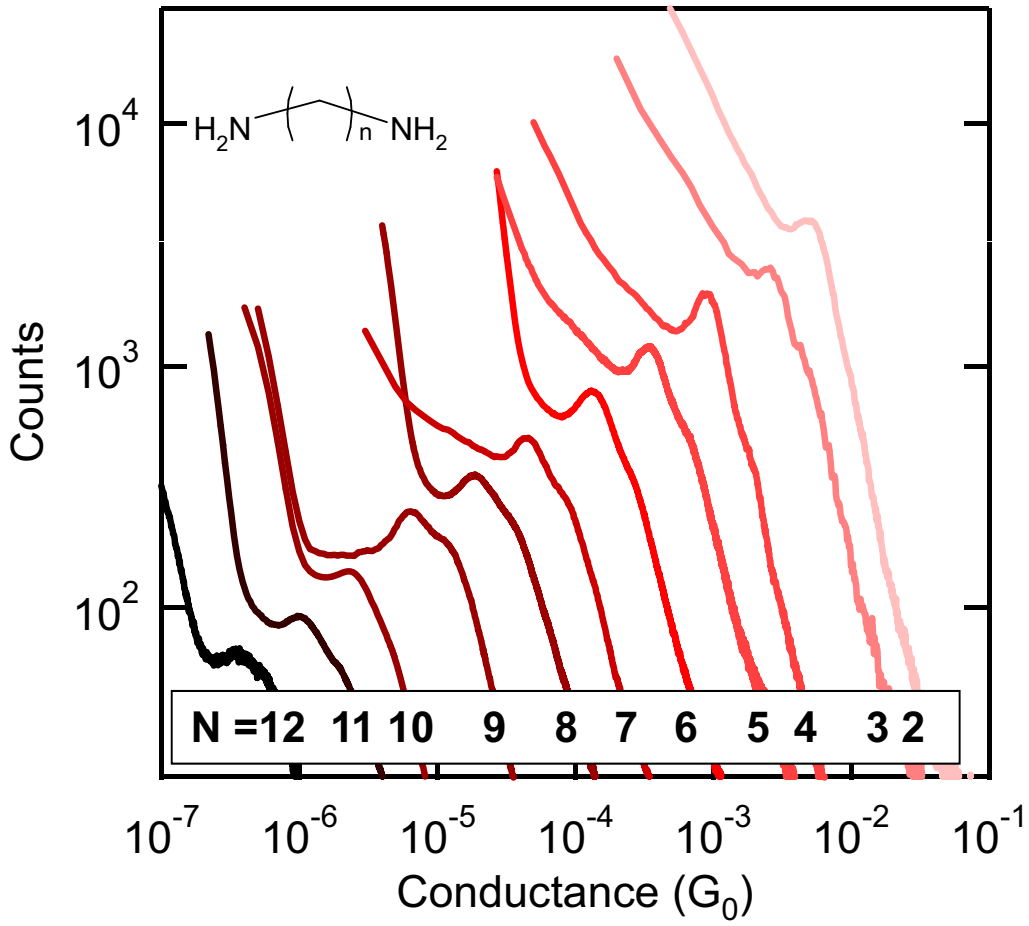
Donor – acceptor is formed between N-lone pair and Au

Outline

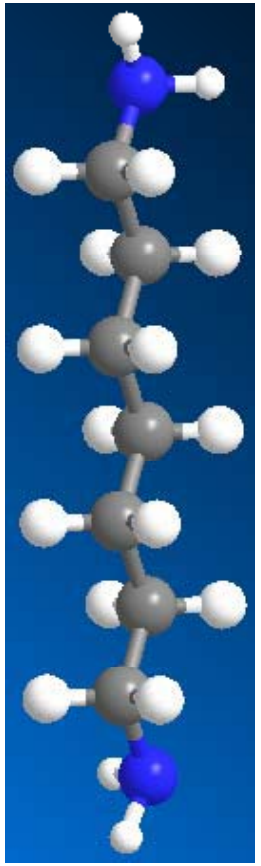
1. Experimental Method
2. Structure-Conductance Relations
3. Conductance and Mechanics
4. Switching in Pyridines

Conductance of Alkanes

(L.Venkataraman et al, Nano Letters 2006,
M. Hybertsen et al, J. Phys. Cond. Matter 2008)

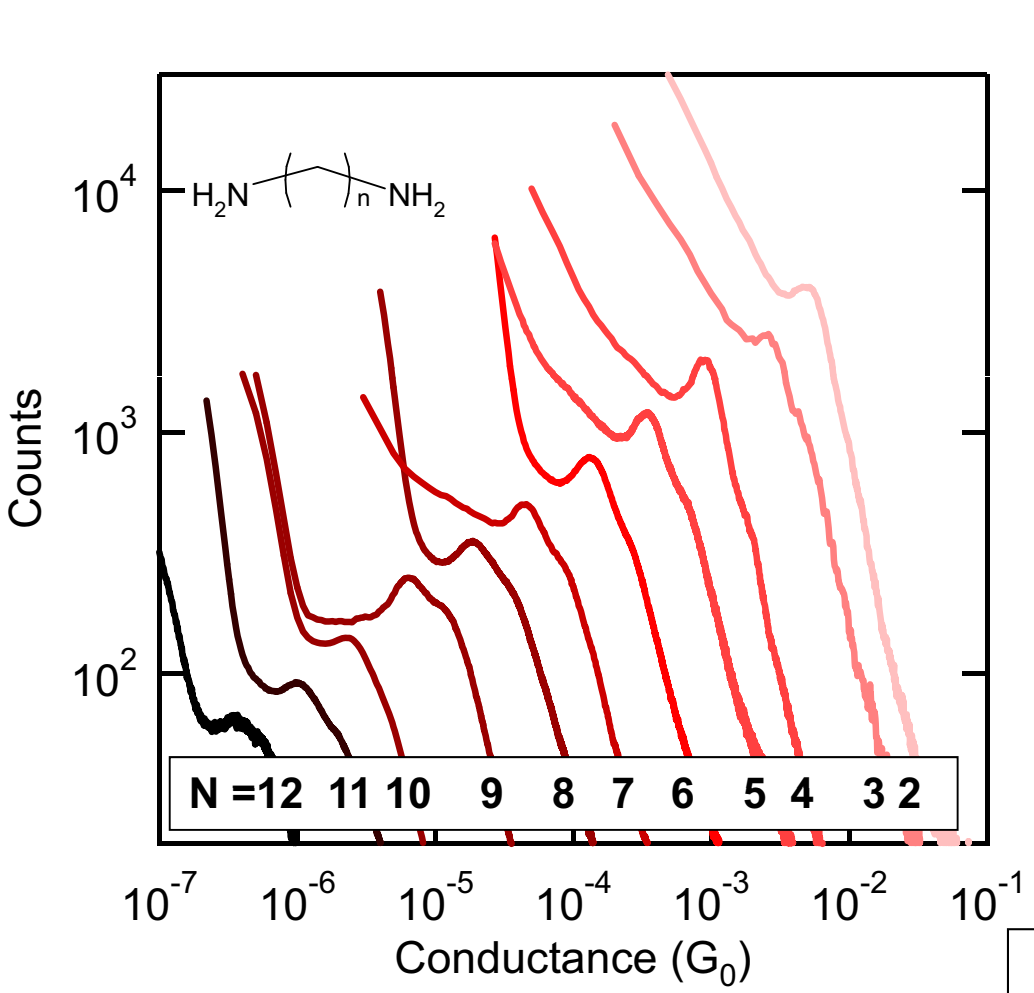


Data offset vertically for clarity

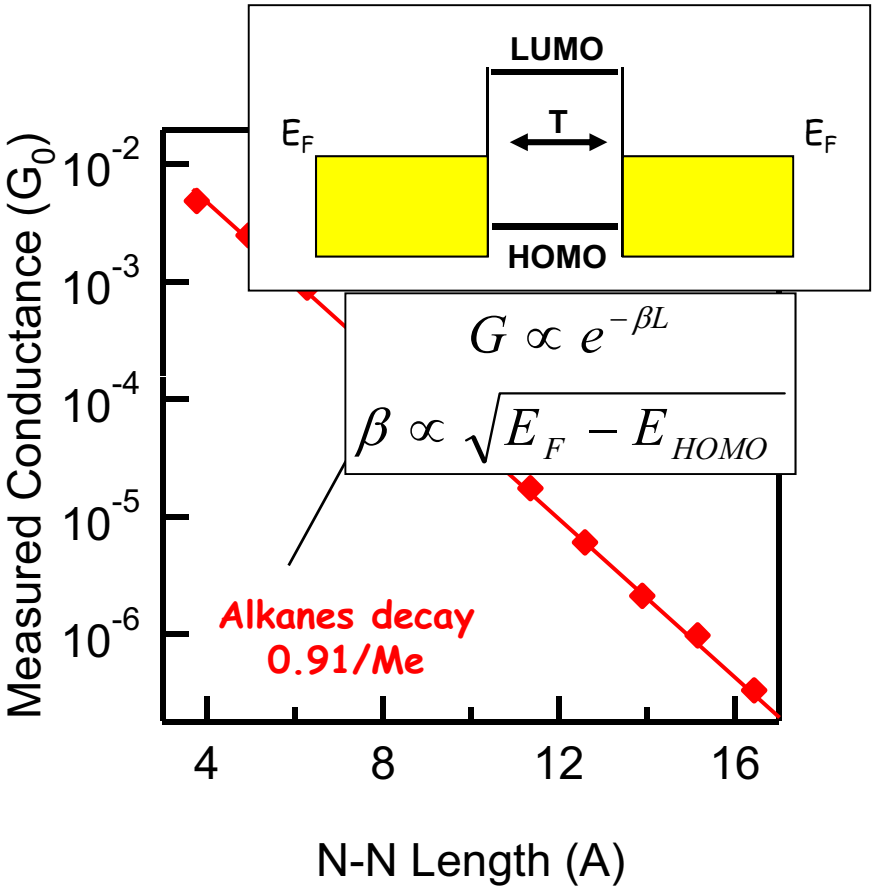


Alkane with 7 Carbon atoms and Amine groups on the two ends

Conductance vs Length



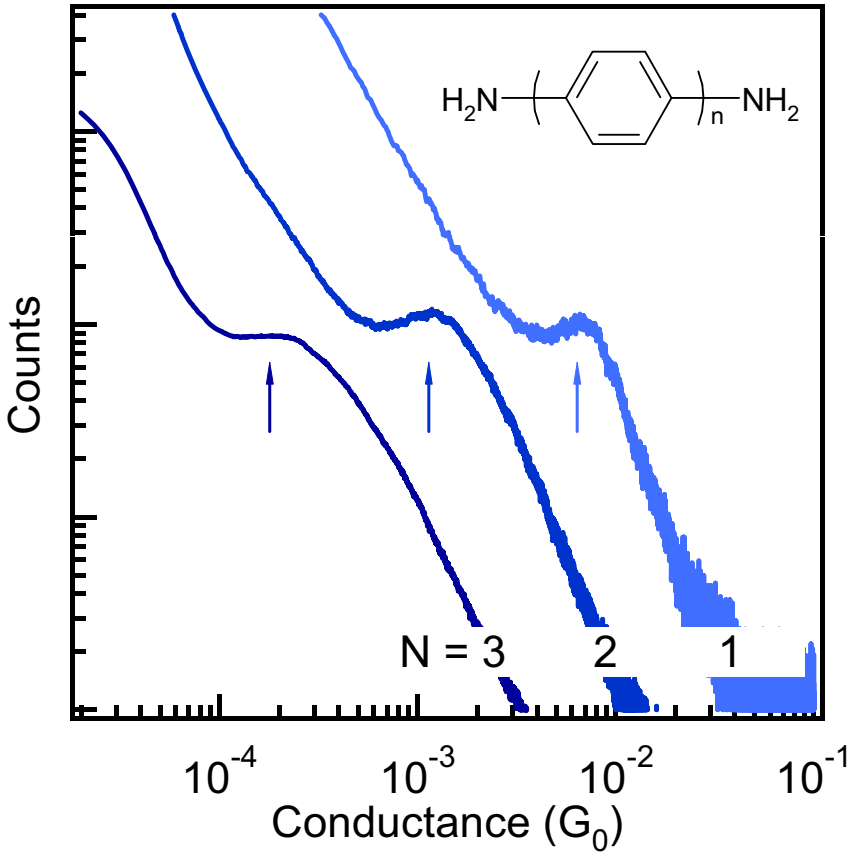
Data offset vertically for clarity



Direct evidence for non-resonant tunneling

(L.Venkataraman et al, Nano Letters 2006,
M. Hybertsen et al, J. Phys. Cond. Matter 2008)

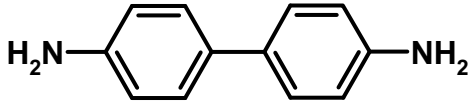
Conductance of Polyphenyls



Data offset vertically for clarity

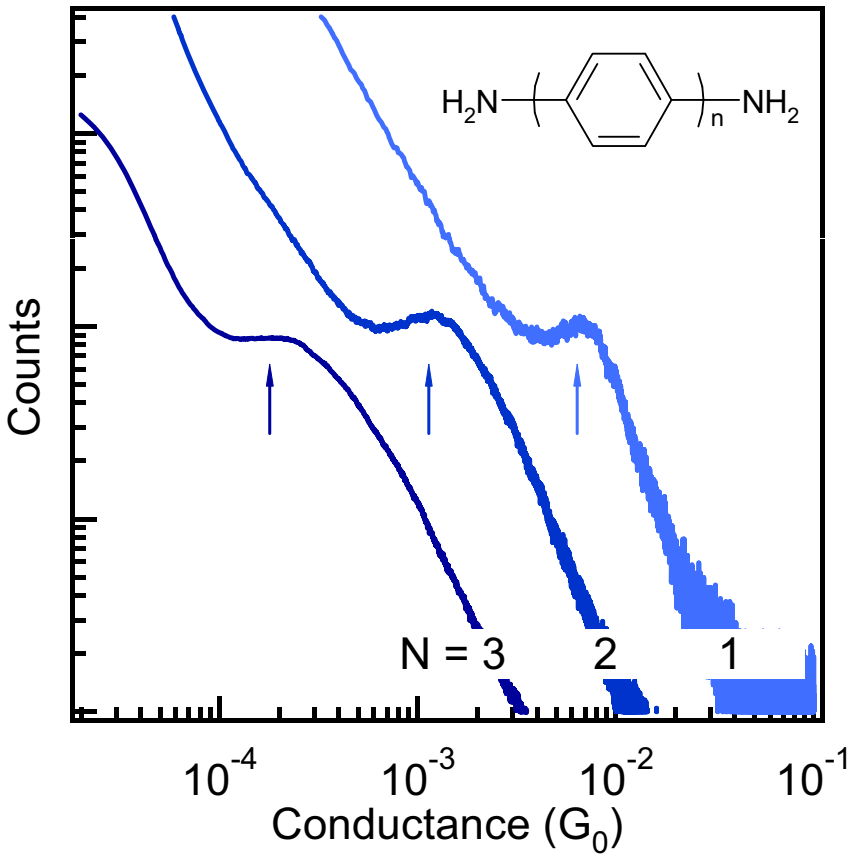
N: Phenyl Chains Attempted

1 

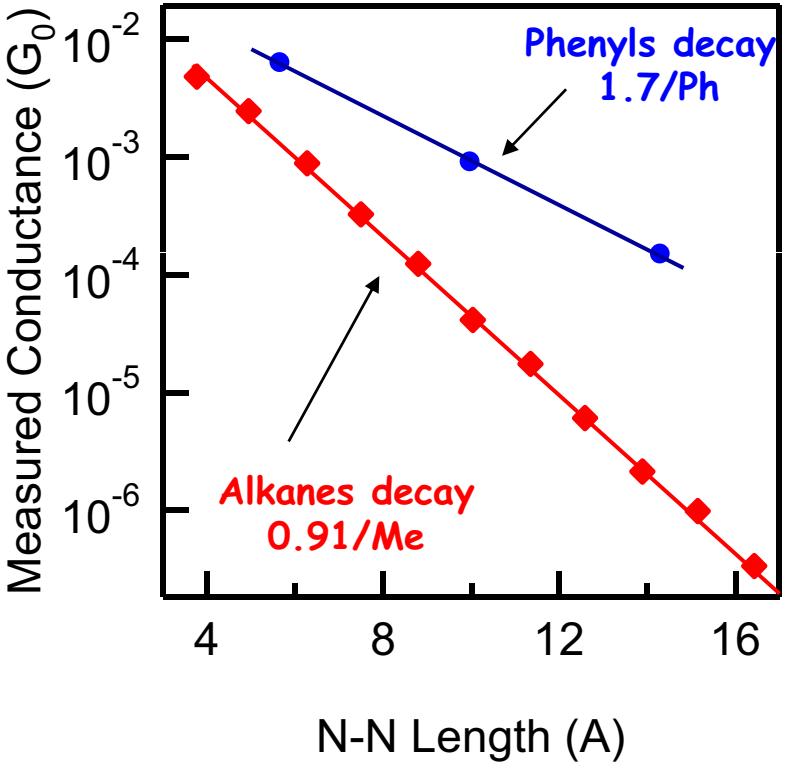
2 

3 

Conductance vs Length



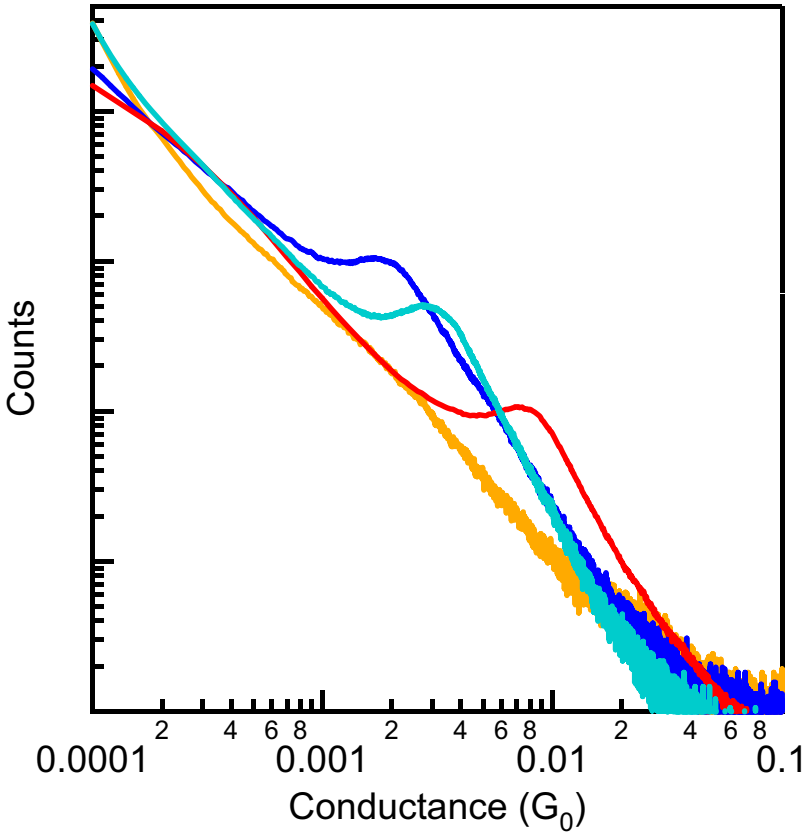
Data offset vertically for clarity



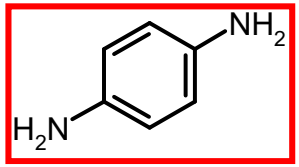
- Conjugated better than saturated
- We are measuring single molecule conductance.

Conductance of Acenes

(J. Quinn, F. Foss, M. Hybertsen, L. Venkataraman, R. Breslow, JACS Comm. 2007)

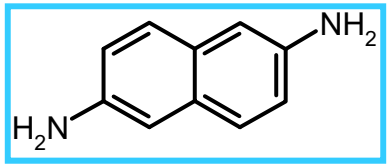


HOMO-LUMO Gap



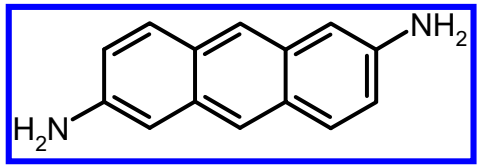
→ 10.3 eV

1,4 diaminobenzene



→ ~ 8.3 eV

2,6 diaminonaphthalene

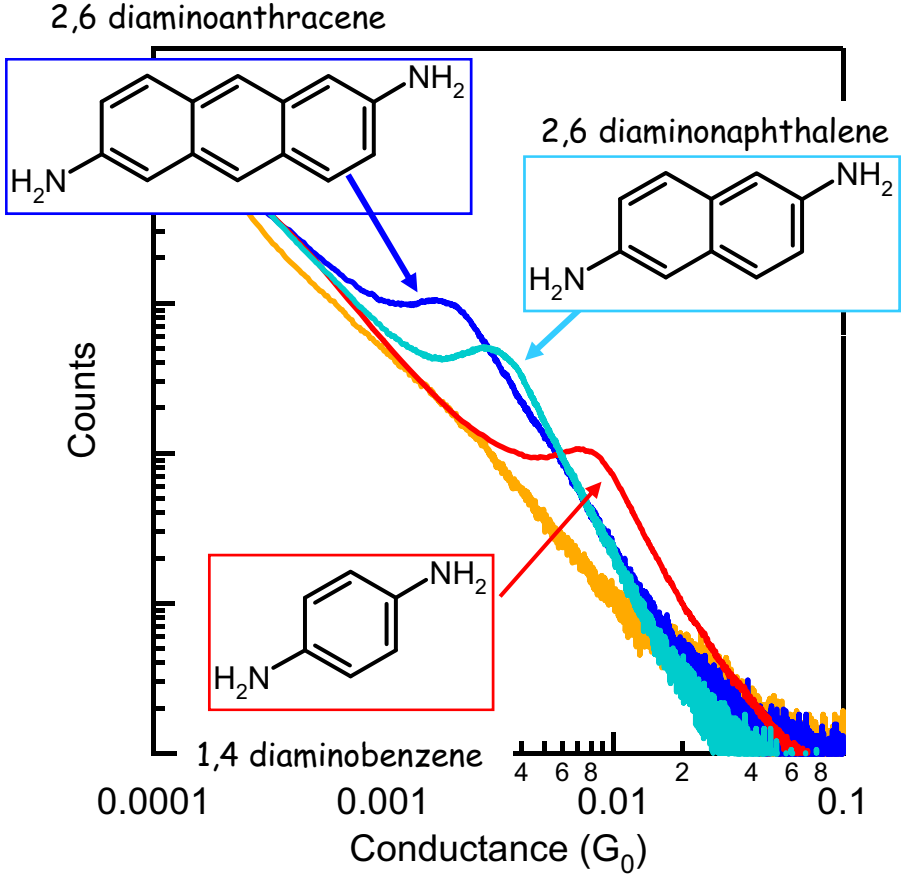


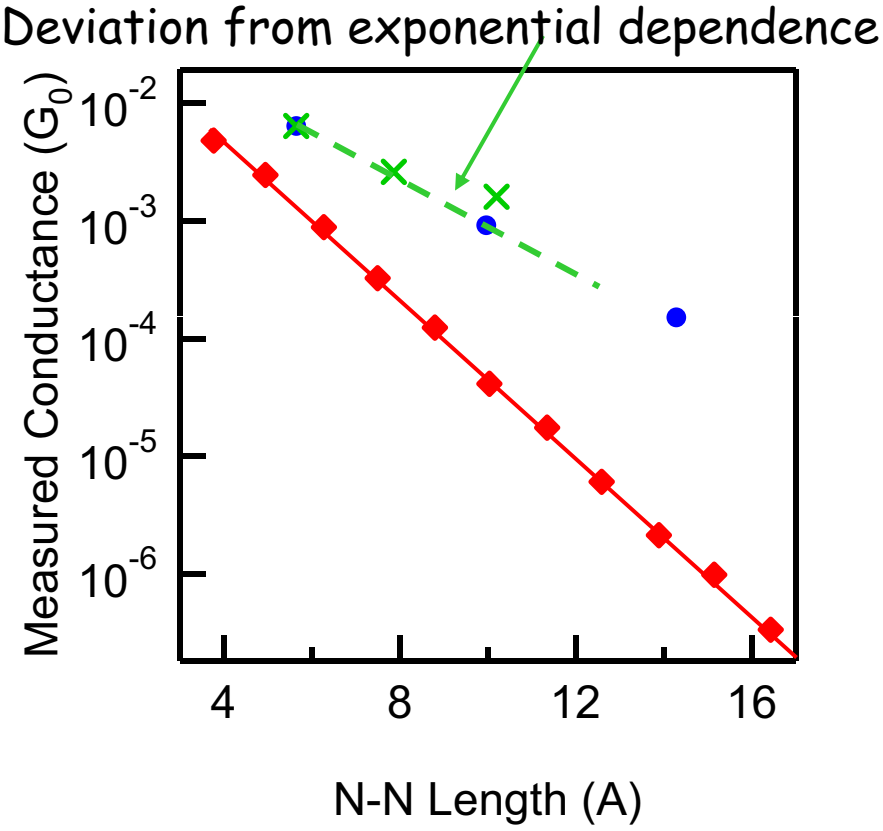
→ ~ 6.9 eV

2,6 diaminoanthracene

Conductance vs Length

(J. Quinn, F. Foss, M. Hybertsen, L. Venkataraman, R. Breslow, JACS Comm. 2007)

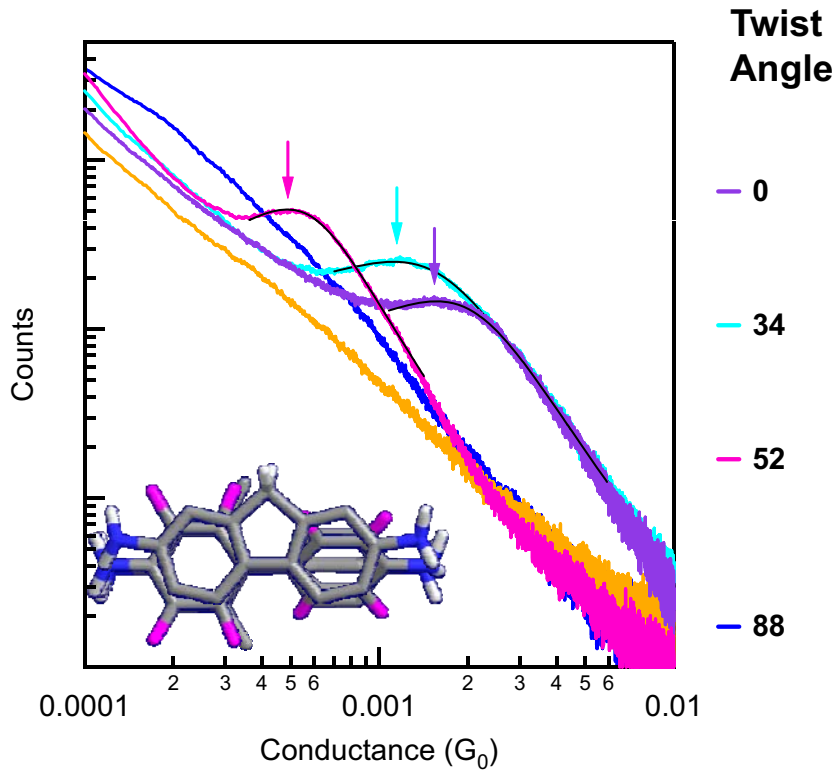


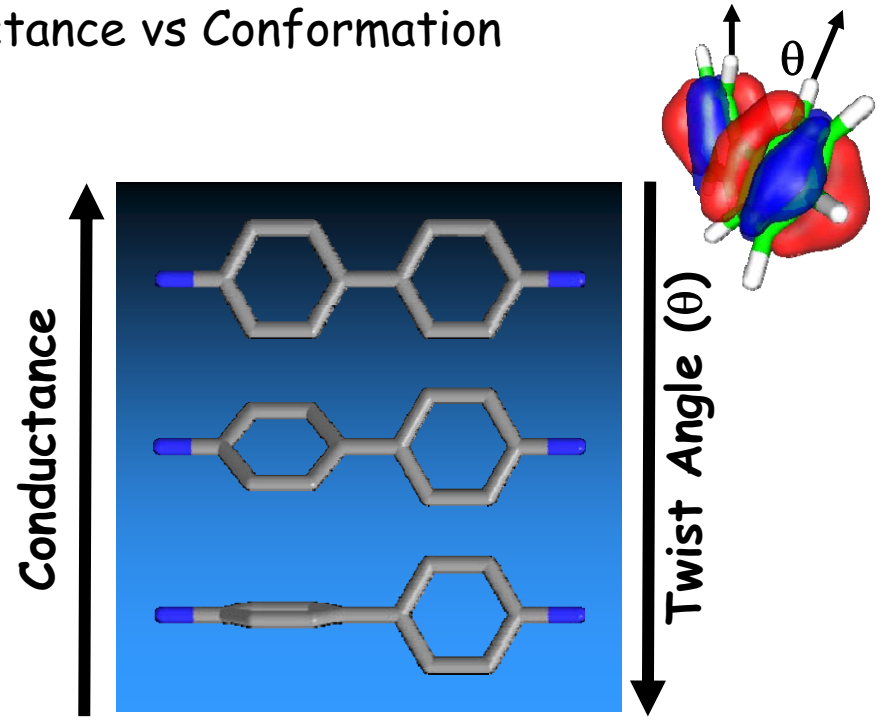


What Can We Learn With Amine Links?

(L. Venkataraman, J. Klare, M. Hybertsen, C. Nuckolls, M. Steigerwald, Nature 2006)

A Study of Biphenyls: Conductance vs Conformation



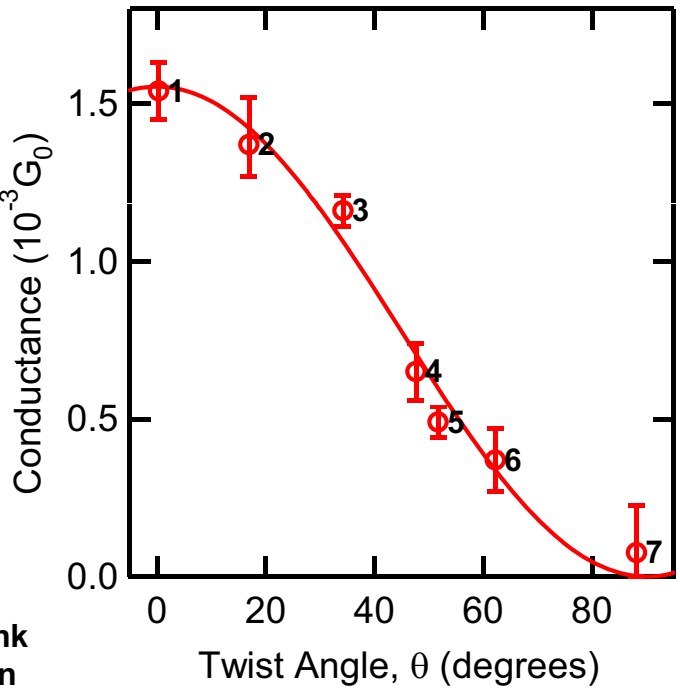


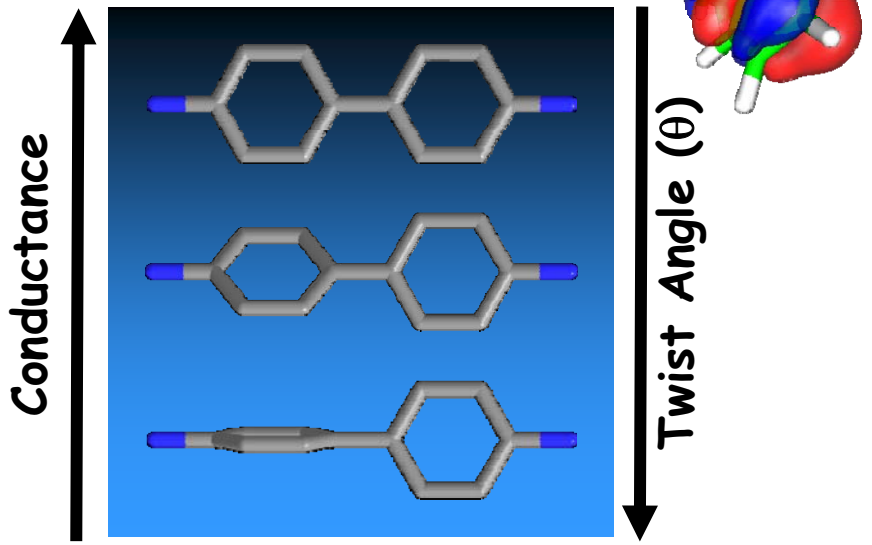
Twist Angle are from calculations

What Can We Learn With Amine Links?

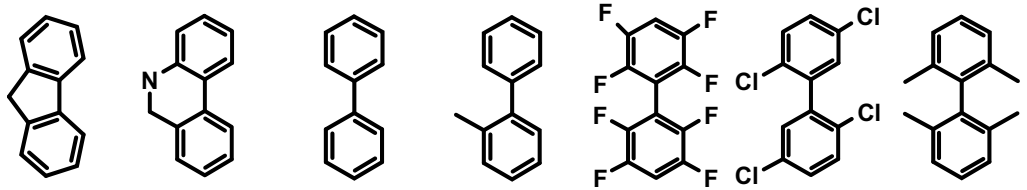
(L. Venkataraman, J. Klare, M. Hybertsen, C. Nuckolls, M. Steigerwald, Nature 2006)

A Study of Biphenyls: Conductance vs Conformation





Amine Link not shown

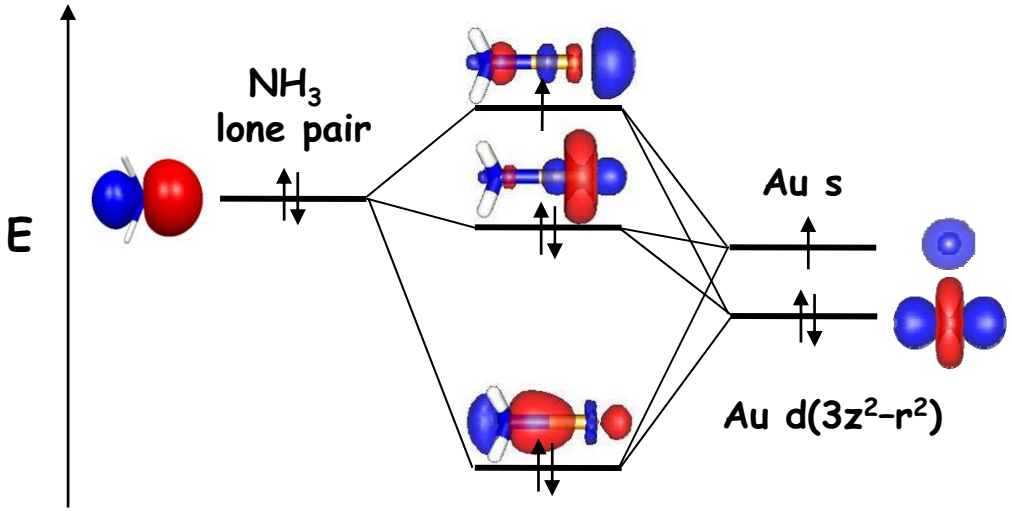


1 2 3 4 5 6 7

Cosine square dependence measured

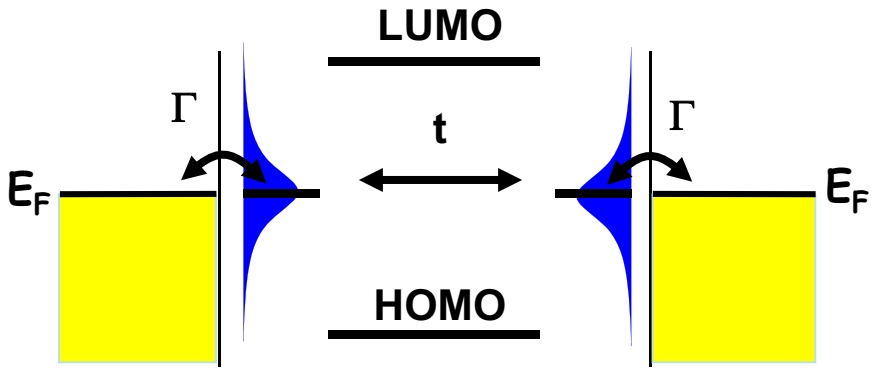
Conductance from Tunnel Coupling

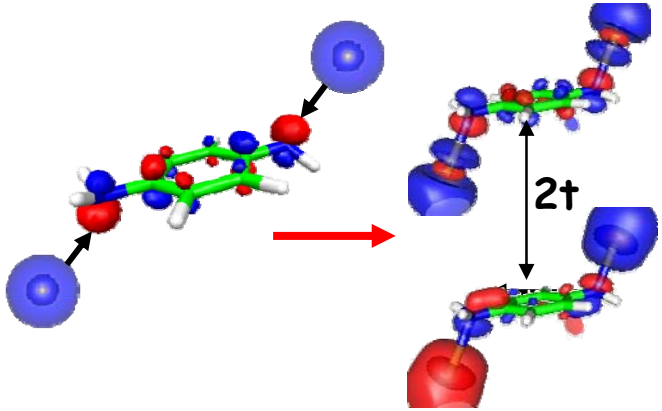
Amine's bind preferentially to under-coordinated Au



Binding Energy ~ 0.5-0.7 eV
Au-N Bond length ~2.3 Å
(DFT in GGA approximation)

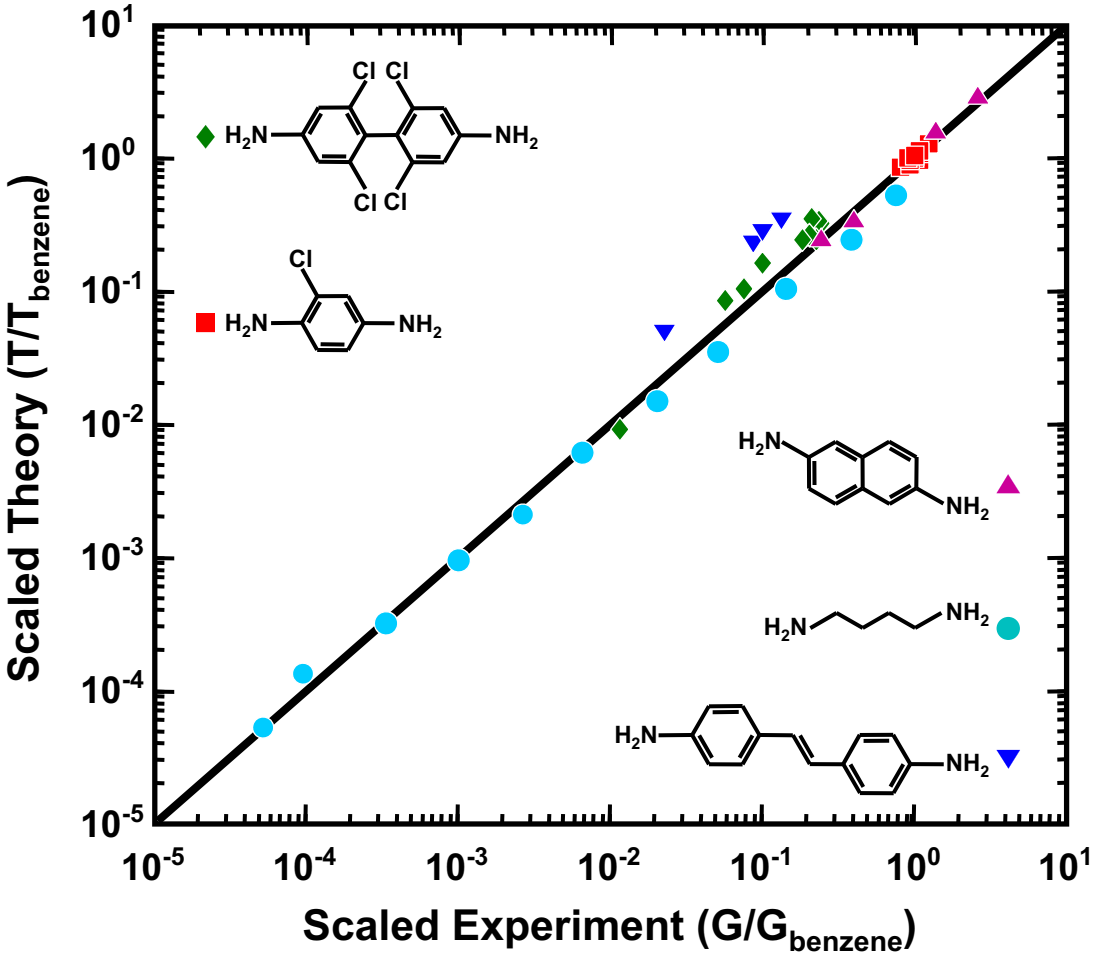
Donor – acceptor bond is formed between N-lone pair and Au



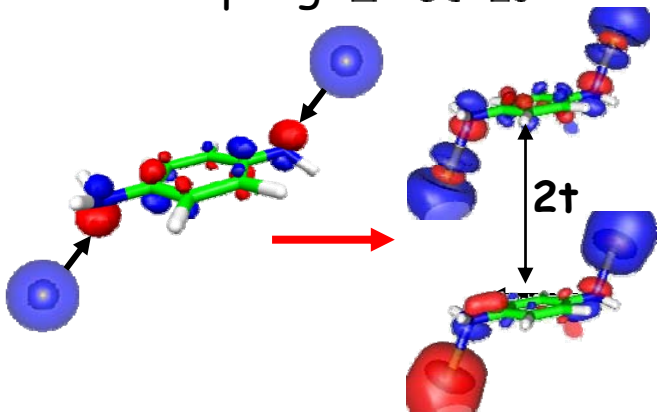


Structure-Conductance Relation

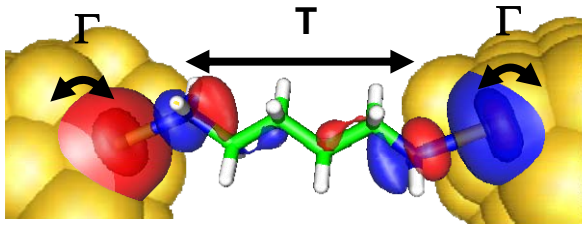
Calculated tunnel coupling vs measured conductance



Use an Au_1 cluster to obtain tunnel coupling $T \propto 4t^2$



Trends show that G is roughly the same for all molecules



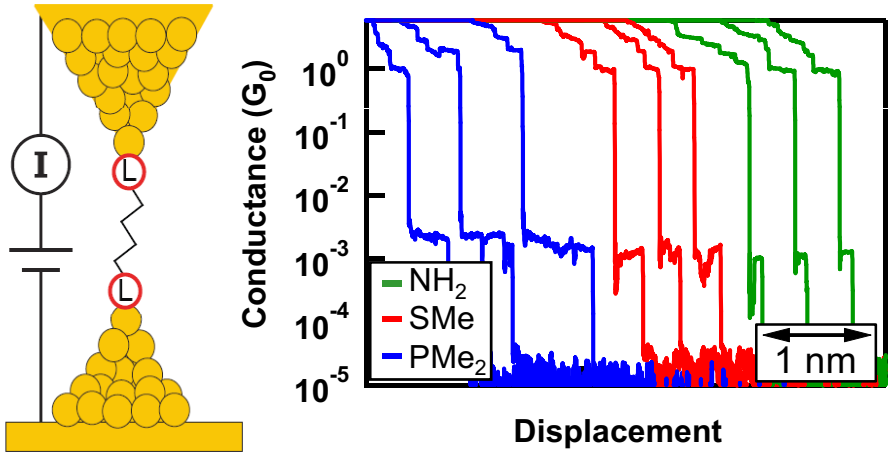
41 molecules shown here

M. Hybertsen et al, J. Phys. Cond. Matter 2008

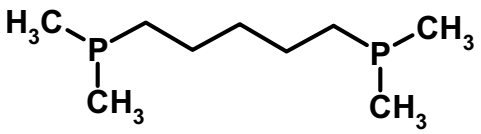
Are Amines Special?

(Park, et al, JACS Comm 2007)

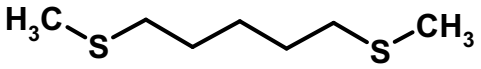
Conductance Measurements for Alkanes with different Ligands



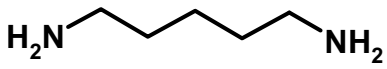
Phosphine ($P-(CH_3)_2$)



Methyl Sulfide ($S-CH_3$)



Amine (NH_2)

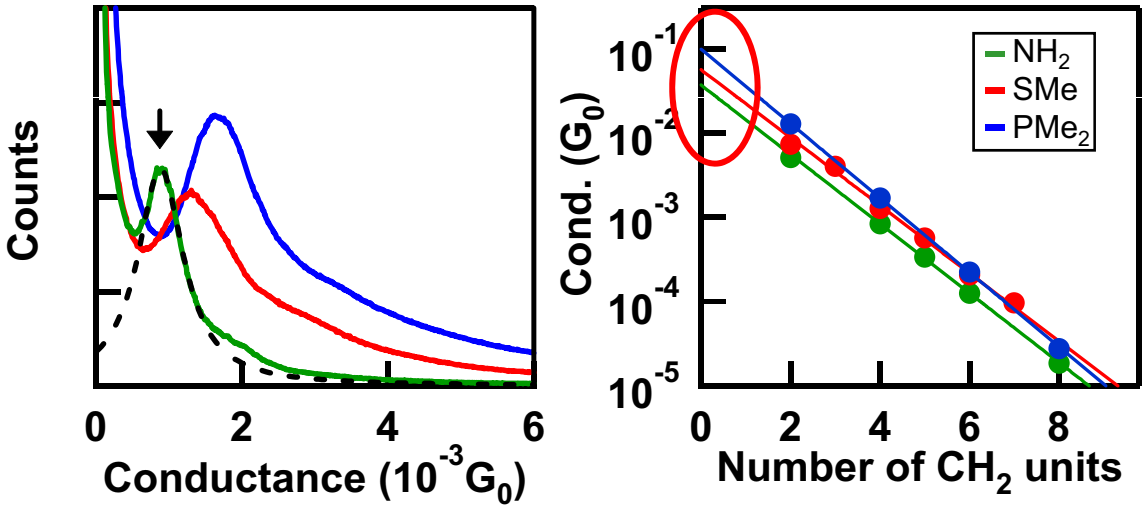


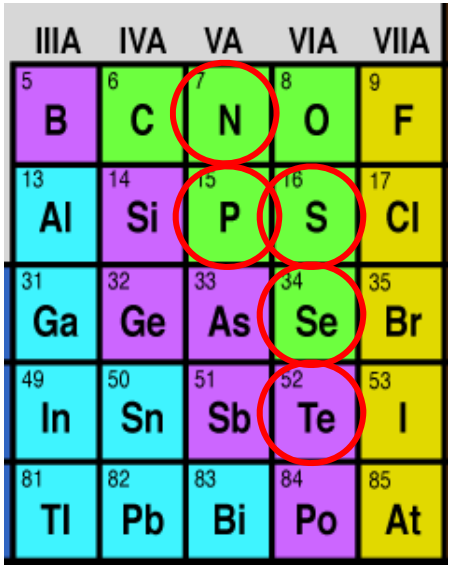
Donor – acceptor bonding can be generalized to a range of link groups

Testing Alternate Link Chemistries

(Park, et al, JACS Comm 2007)

Conductance Measurements for Alkanes with different Ligands



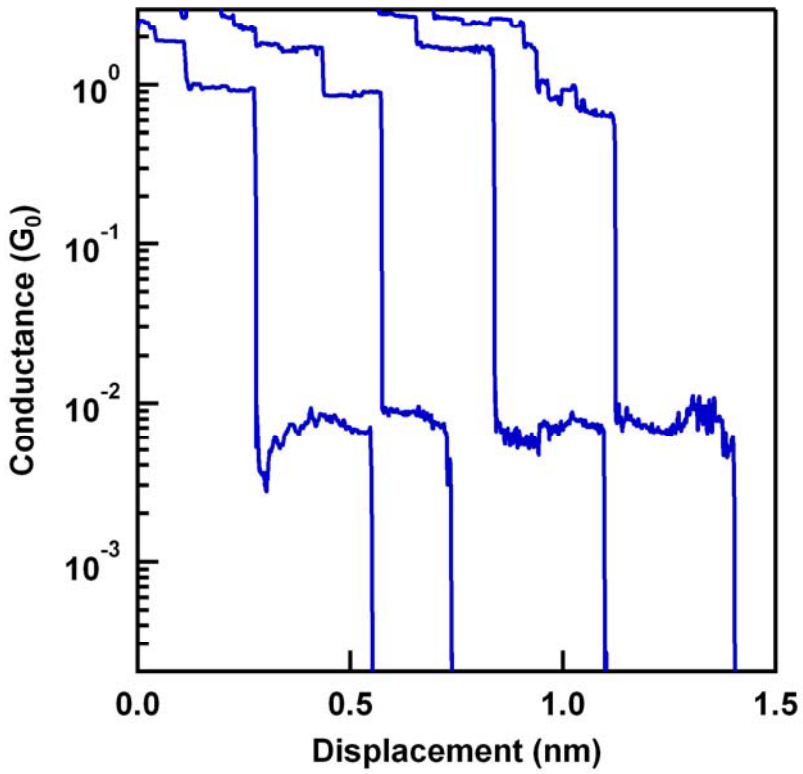


Donor – acceptor bonding can be generalized to a range of link groups

Outline

1. Experimental Method
2. Structure-Conductance Relations
3. Conductance and Mechanics
4. Switching in Pyridines

What Else Can We Learn?



We have focused on the conductance histogram peak position – but we can get more information:

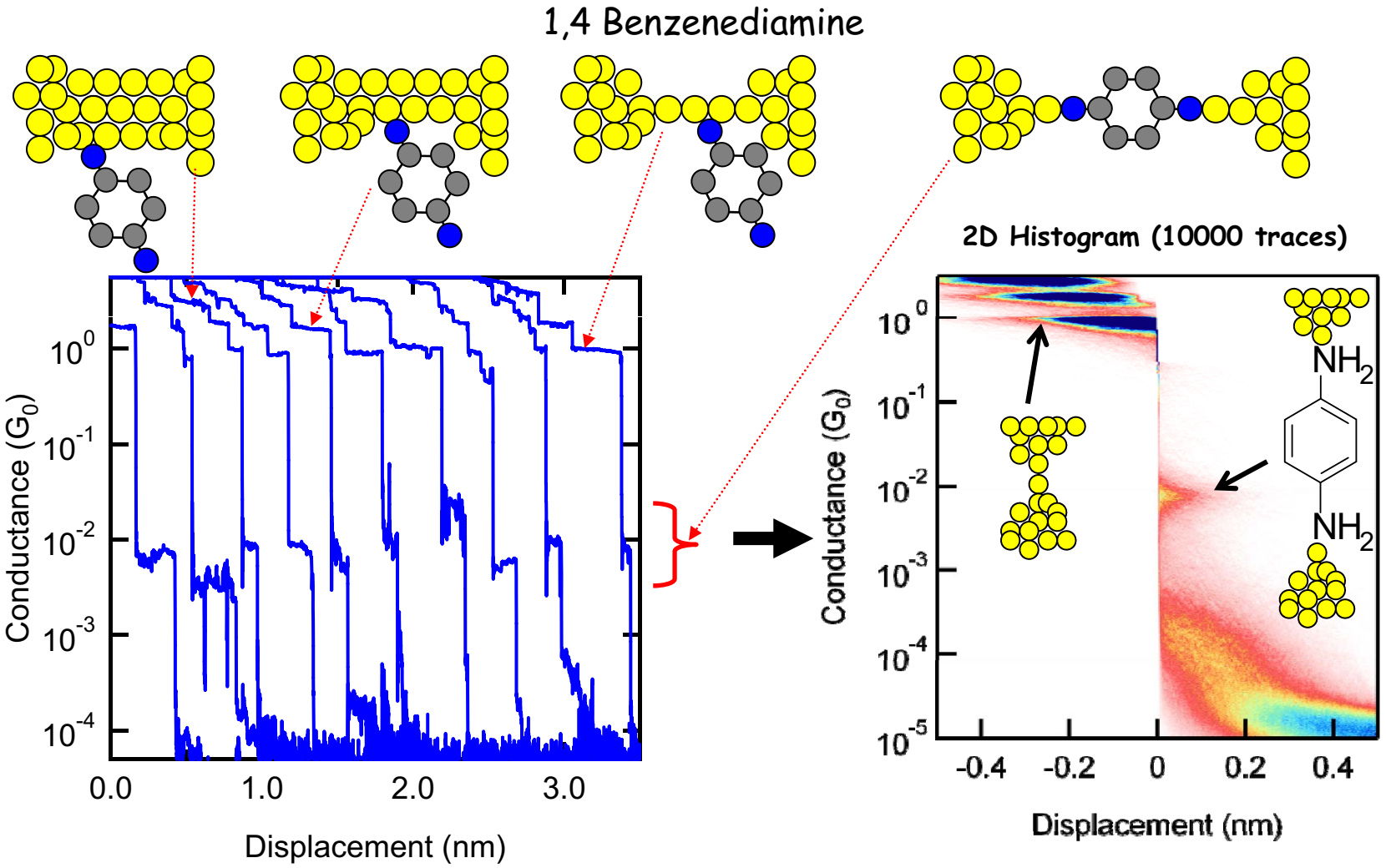
- Conductance step length
- Probability of seeing a step
- Electrode separation in a junction

And with slight modifications to the instrument:

- Current-voltage measurements
- Temperature dependent measurements
- Bond breaking forces

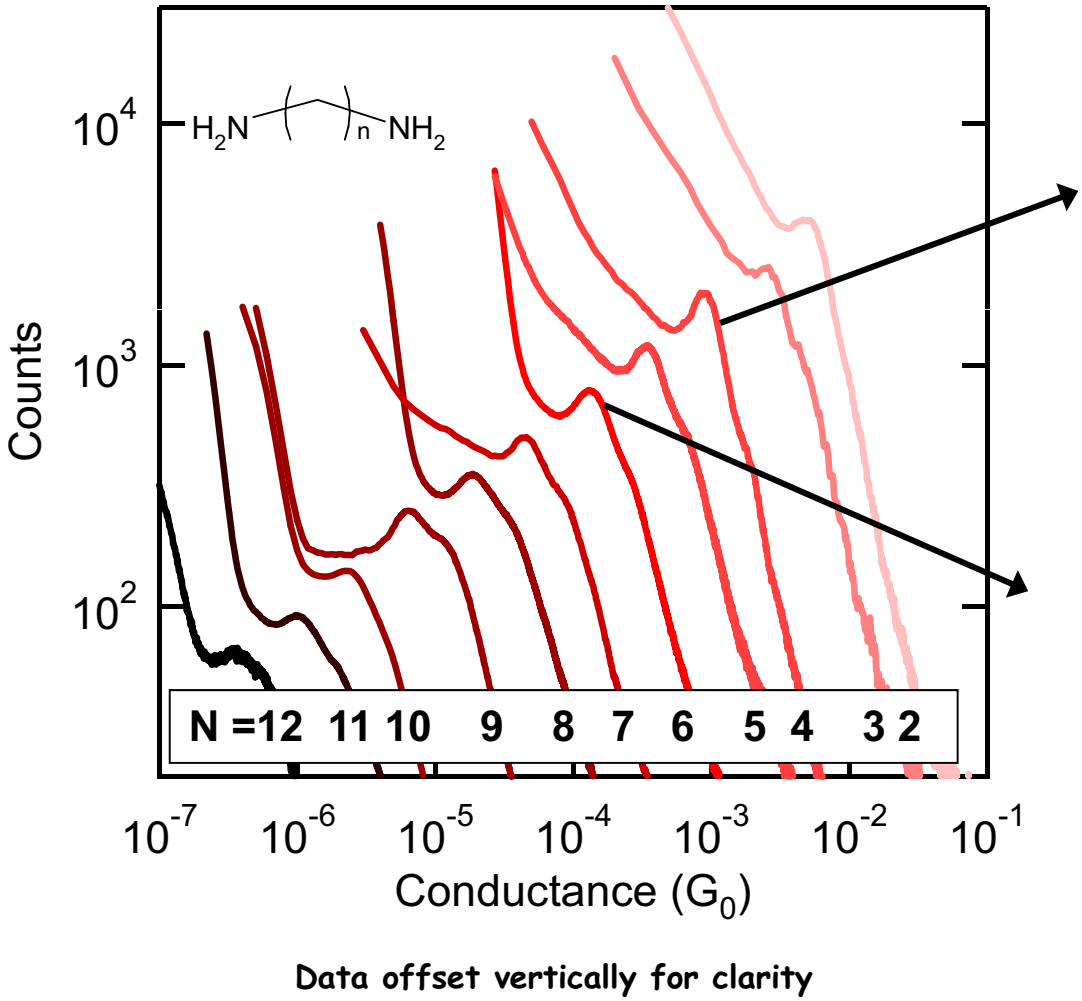
…

Conductance & Displacement

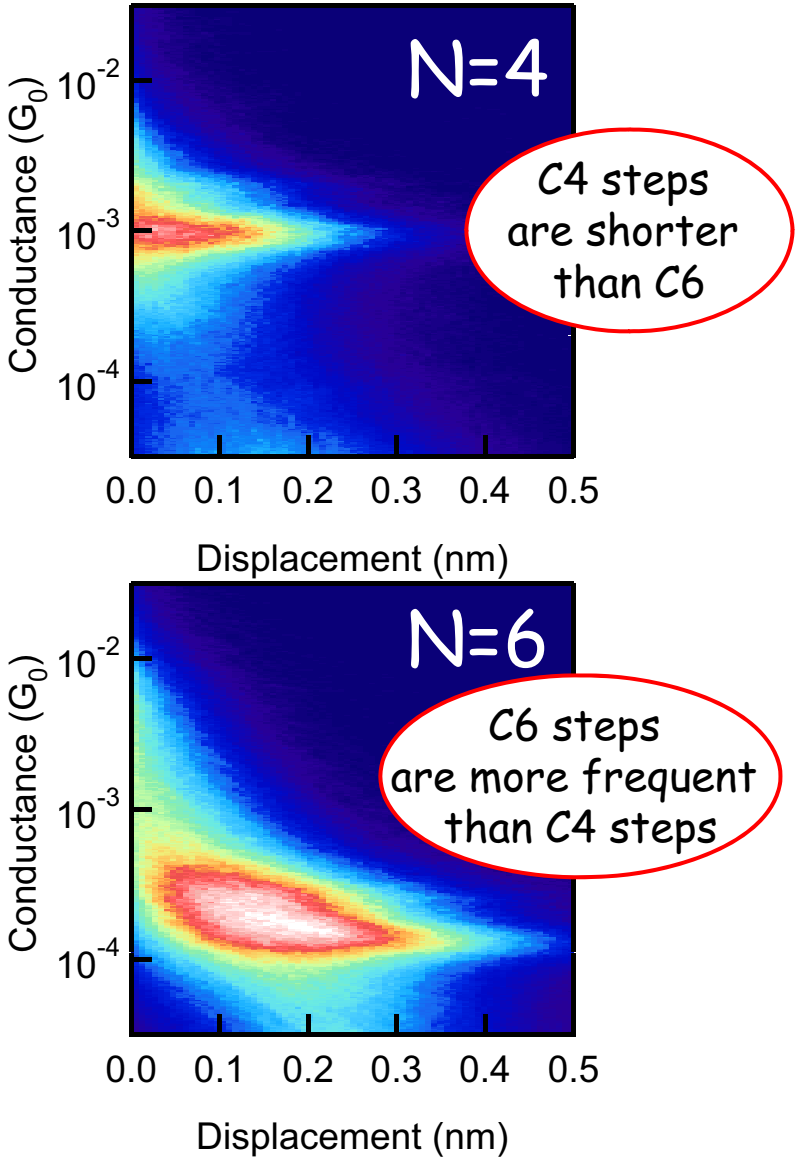


2D Histograms for Alkanediamines

(Kamenetska, Koentopp, Hybertsen, L.V. PRL 2009)



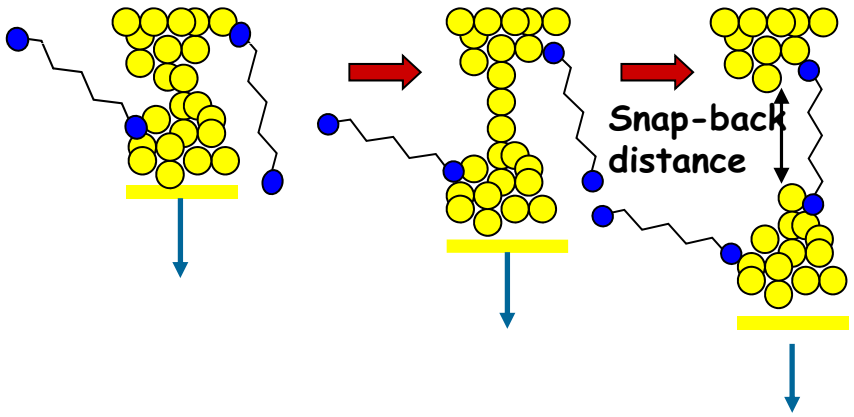
Data offset vertically for clarity

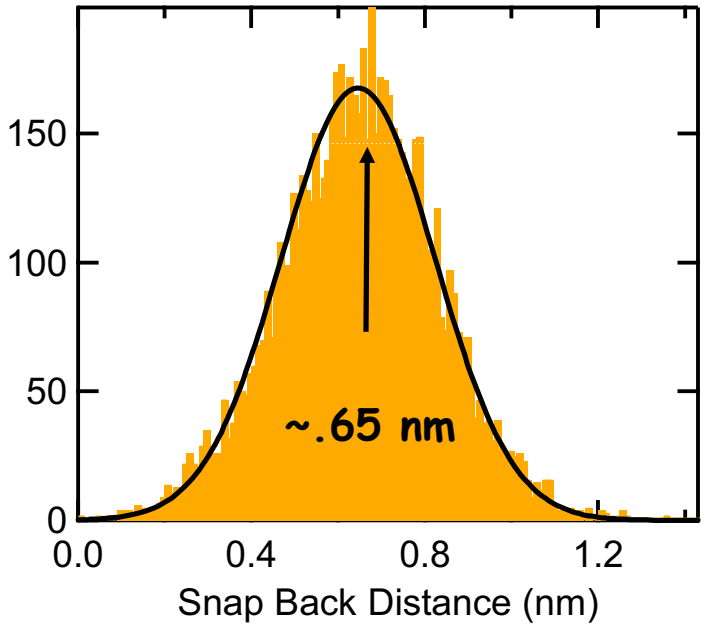


Mechanics of Junction Formation

Data shows:

1. Junctions with longer molecules can sustain greater elongation
2. Junctions with longer molecules form more frequently





Hypothesis: Junctions form only when molecules are long enough to bridge the gap between the electrodes. For short molecules, this happens less frequently. For molecules longer than ~ 1nm, junctions from in 90% of the measurements.

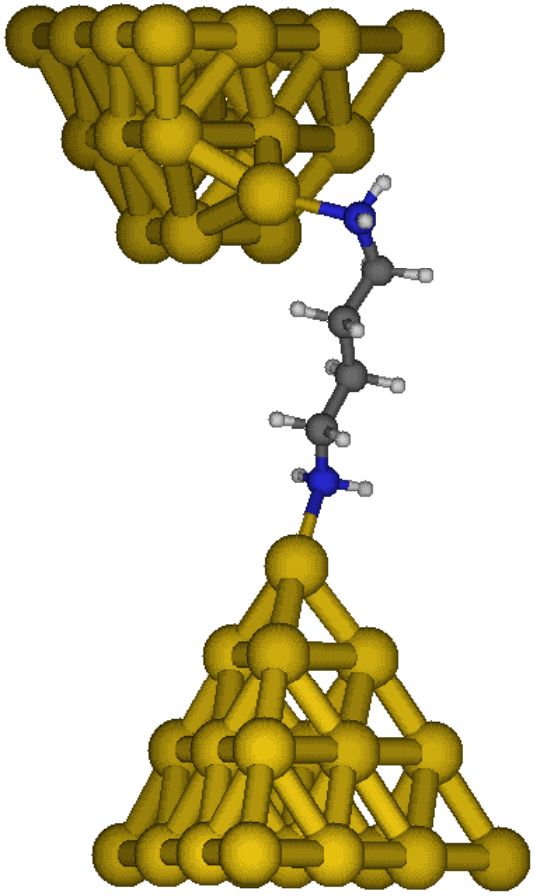
Junction Elongation Simulations

(Kamenetska, Koentopp, Hybertsen, L.V. PRL 2009)

DFT-based simulations

(Turbomole package)

- 20 atom Au clusters
- Junction was elongated in 0.05 Å steps
- Top layer of Au held fixed
- Total energy, force and transmission was calculated at each step

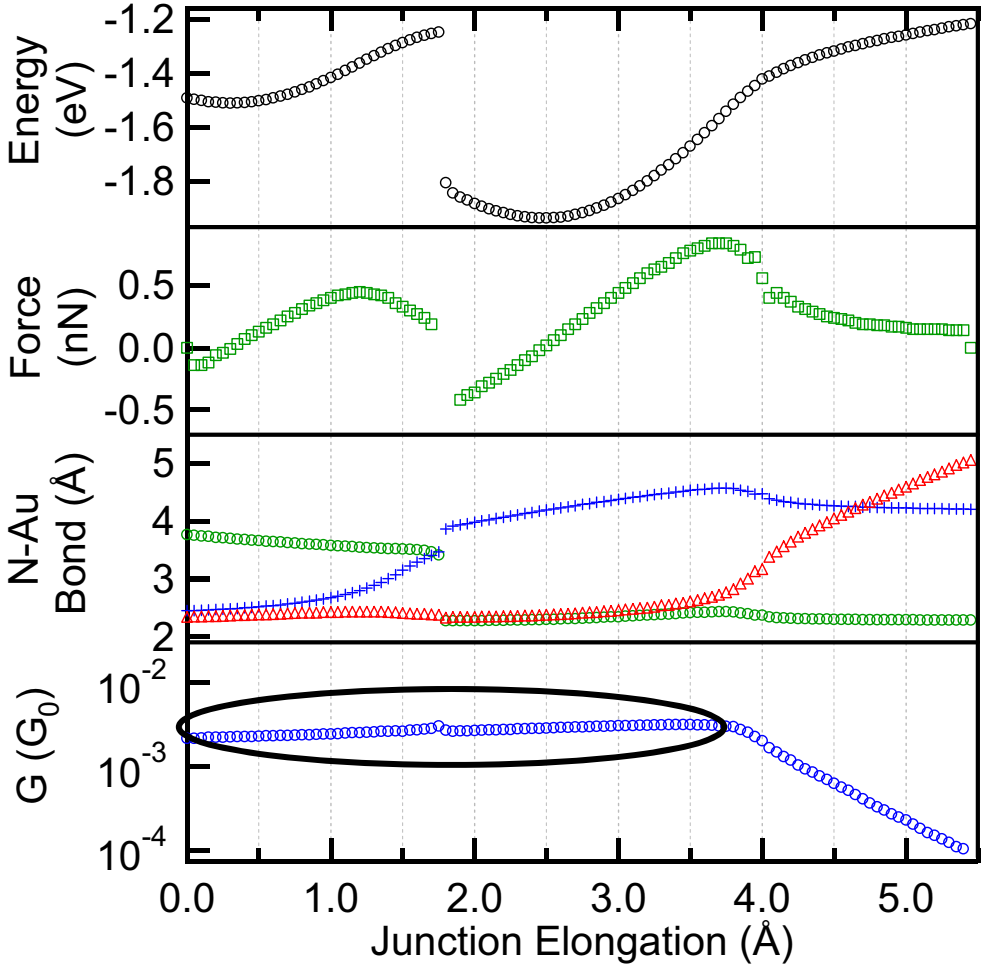


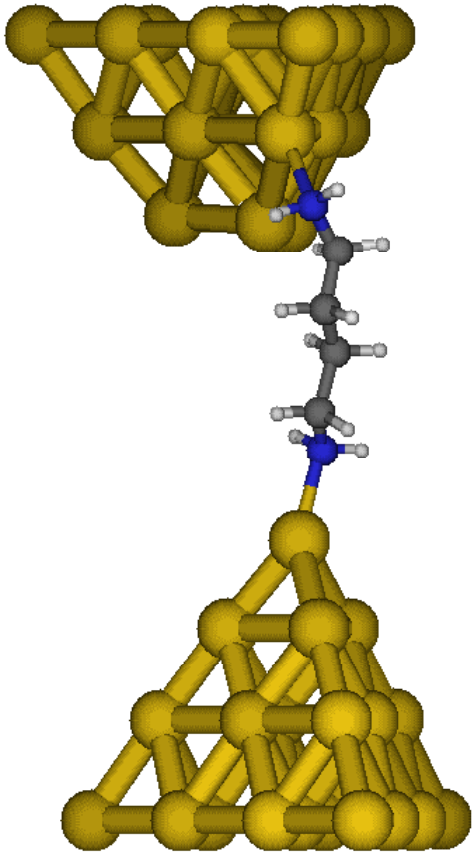
Junction 1: Butanediamine bonded to apex on bottom pyramid and to an adatom on top pyramid

Junction Elongation Simulations

(Kamenetska, Koentopp, Hybertsen, L.V. PRL 2009)

Junction 2: Butanediamine bonded to apex on bottom and to an edge atom on the top





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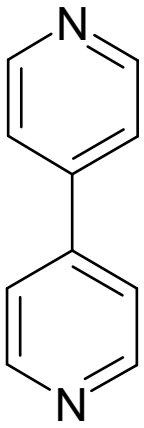
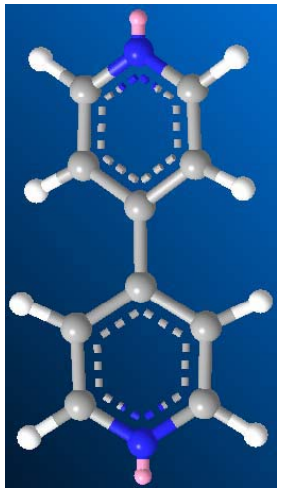
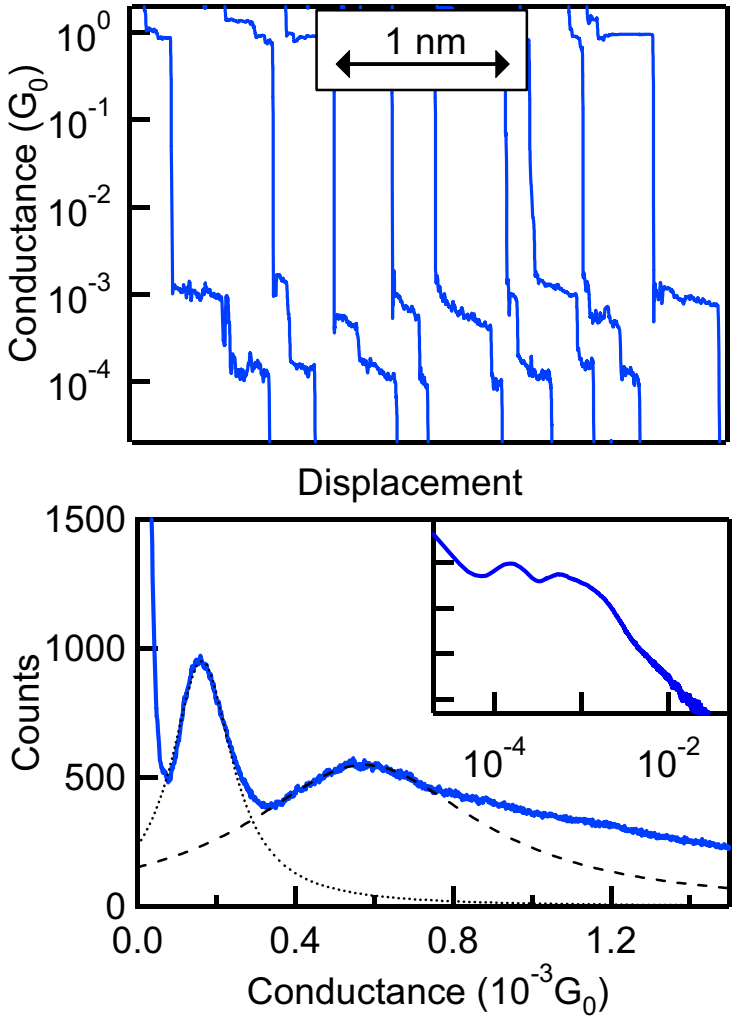
Functionality From a Molecule?

Bipyridine:
A Variation on the Amine



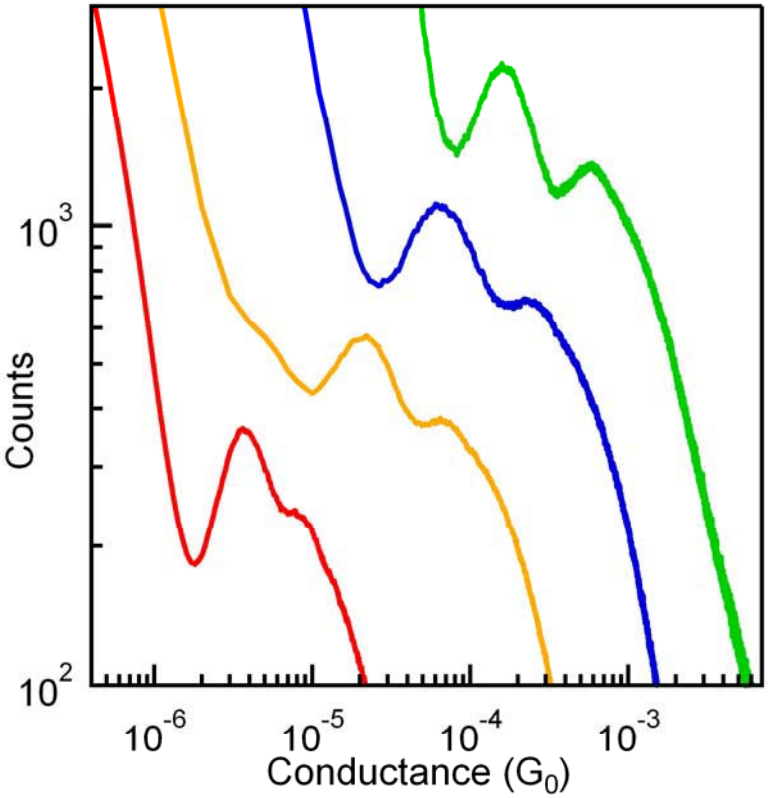


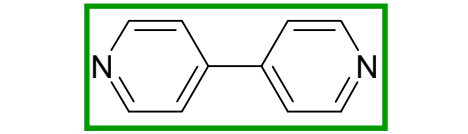
One molecule with two conducting states



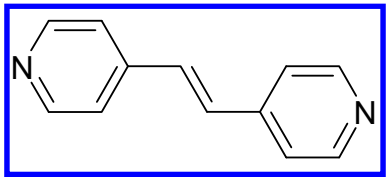
Are The Two Peaks Due To Pyridine Link?

(Kamenetska et al, submitted)

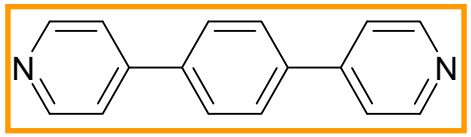




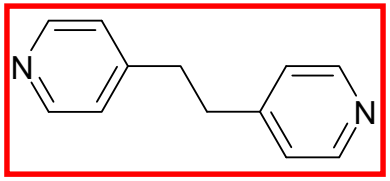
Bipyridine



Pyridine-Ethylene-Pyridine



Terpyridine

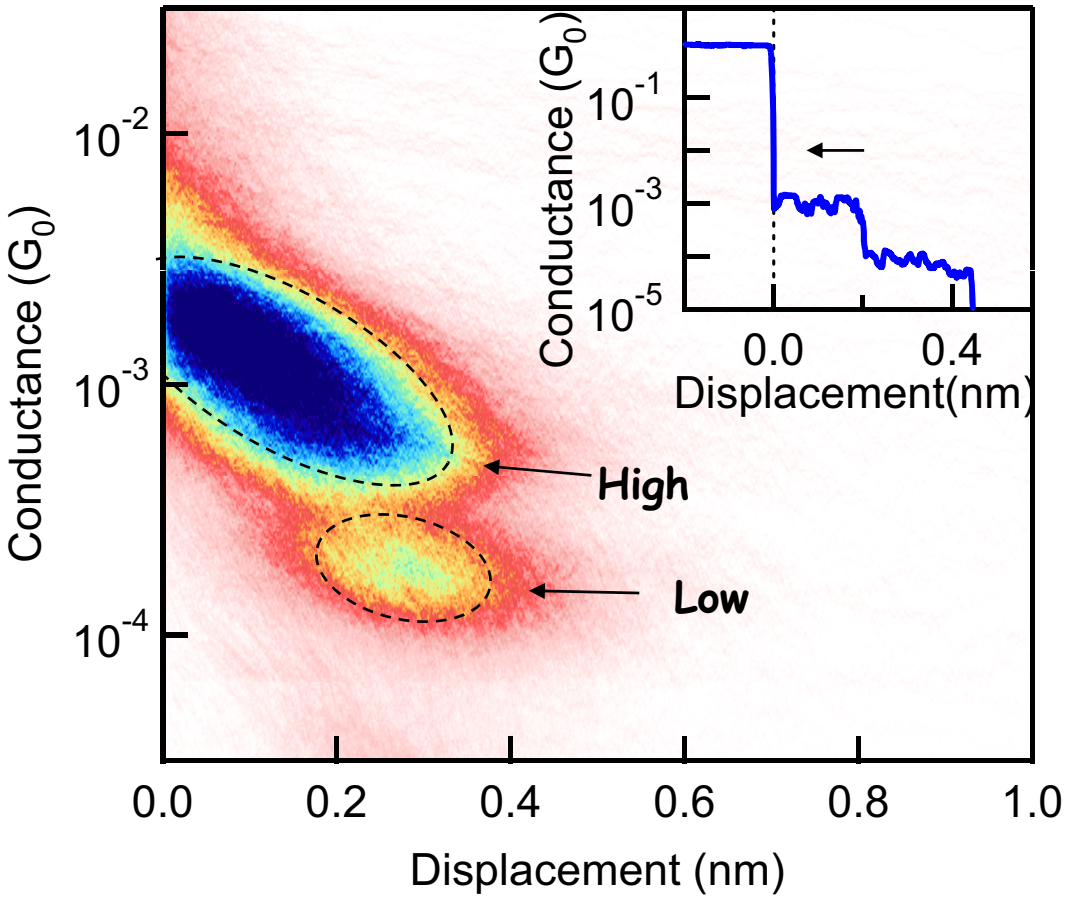


Pyridine-Ethane-Pyridine

Yes, two conducting states are due to the pyridine link.

2D Histograms from Bipyridine Data

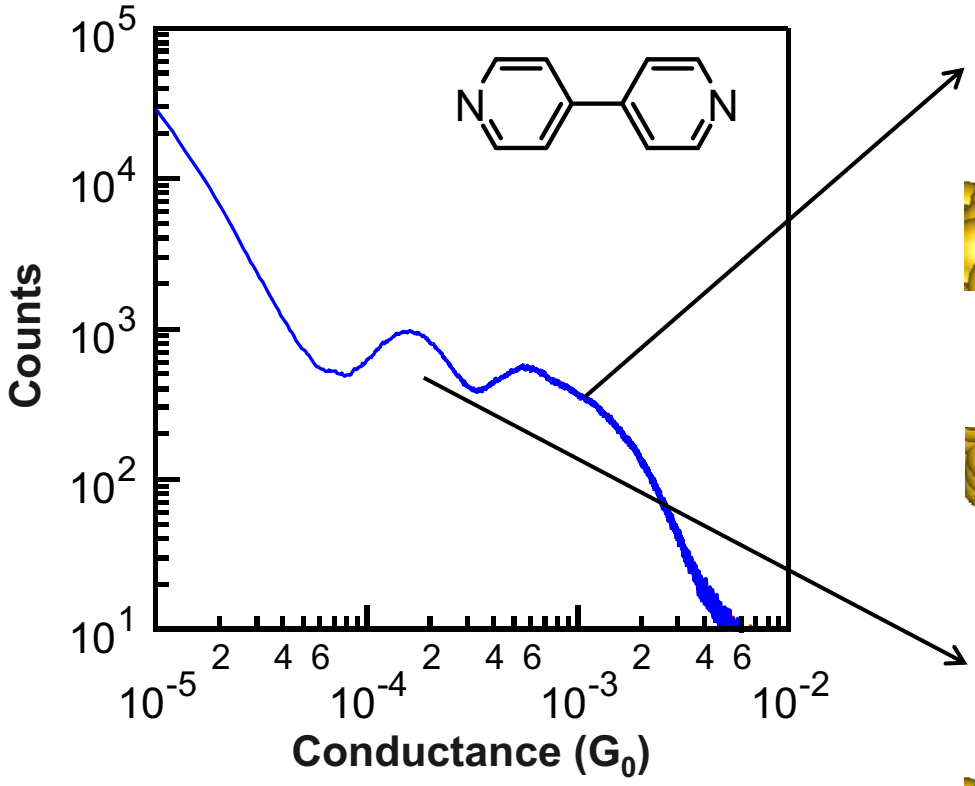
(Quek, Kamenetska et al, Nature Nanotechnology 2009)

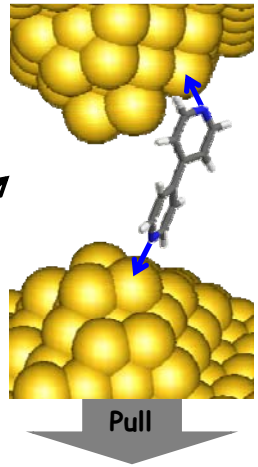


Low conductance follows high conductance on junction elongation

Hypothesis: Two Contact Geometries

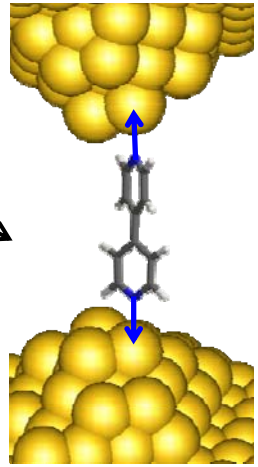
(Quek, Kamenetska et al, Nature Nanotechnology 2009)





Junction forms with C-N-Au angle smaller than 180 degrees.

Au is better coupled to the molecular π-system, giving a higher conductance

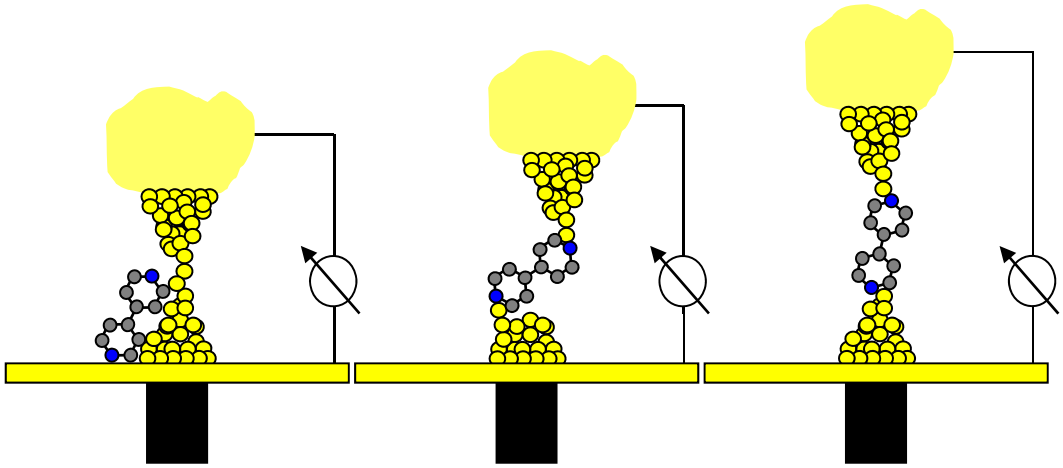


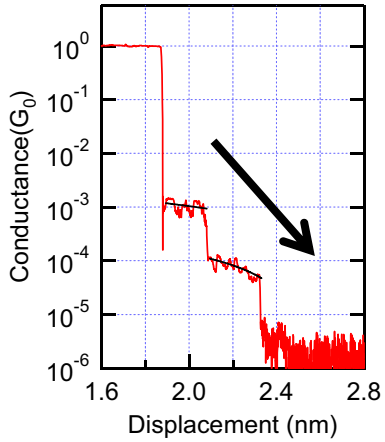
On pulling, molecule becomes vertical in the junction.

Au is not well coupled to the molecular π-system. This results in a lower conductance

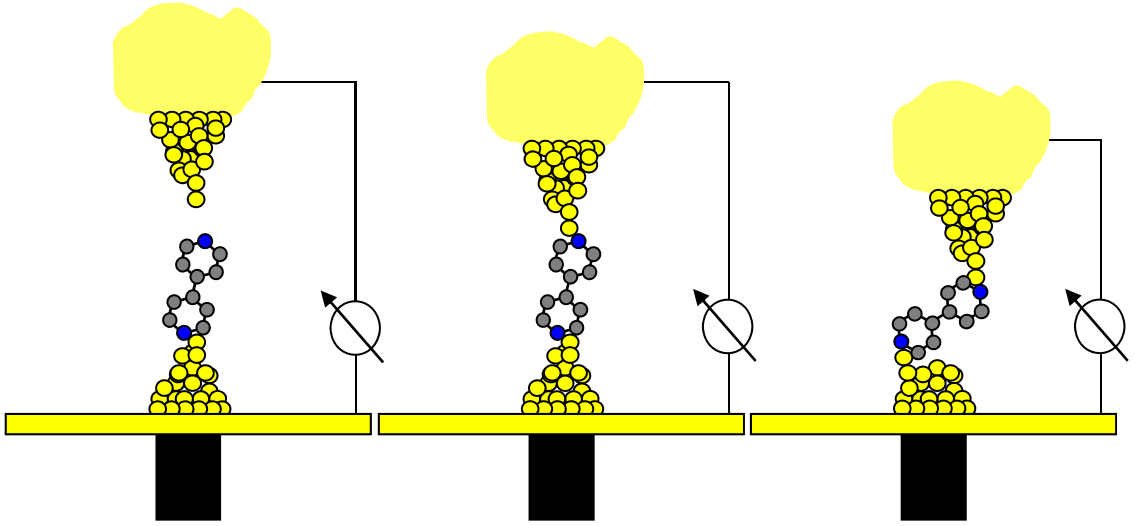
Two Types of Measurements

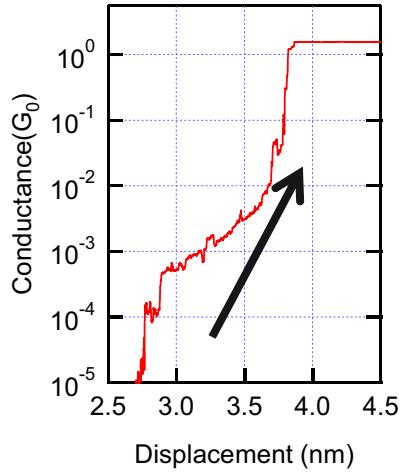
Pulling





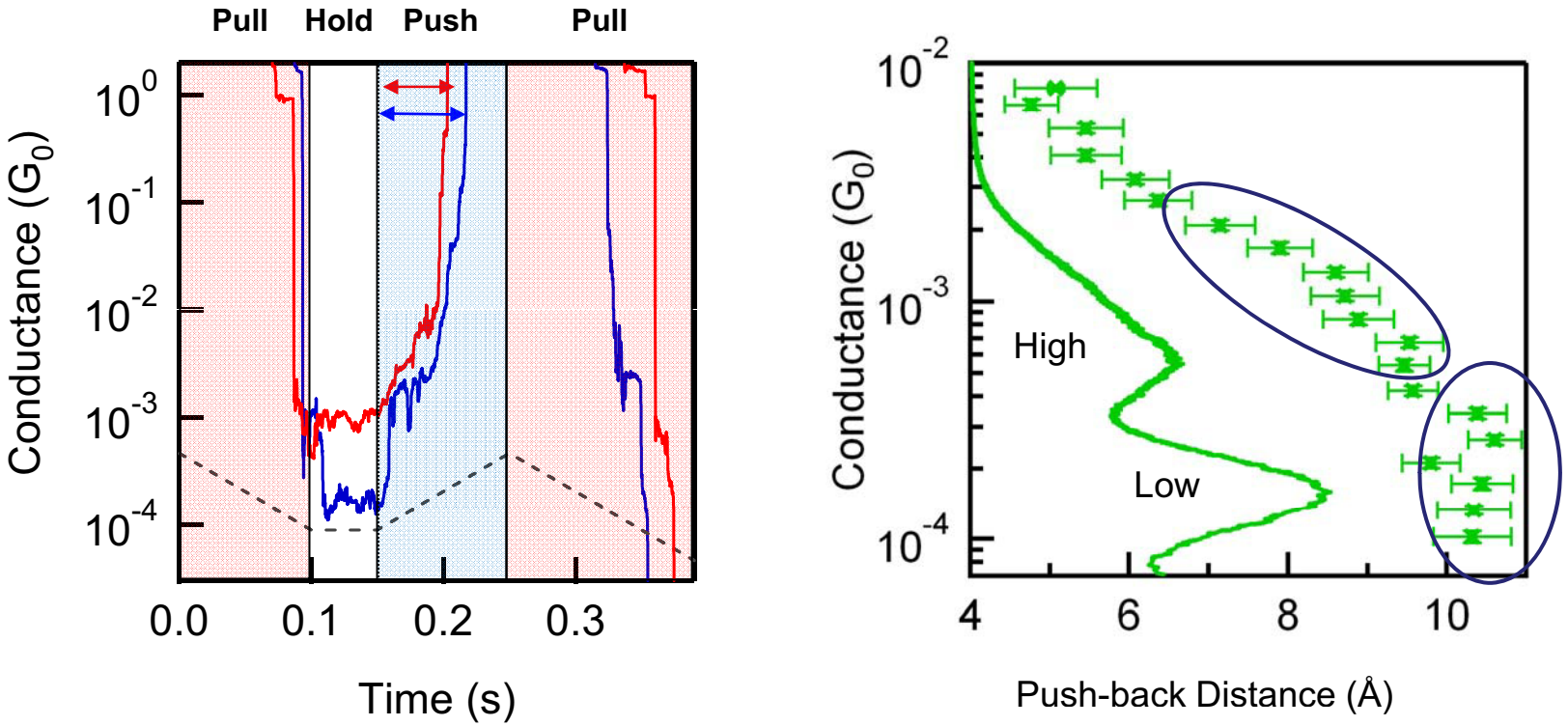
Pushing





Au-Au Separation & Conductance

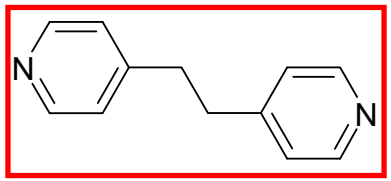
(Quek, Kamenetska et al, Nature Nanotechnology 2009)



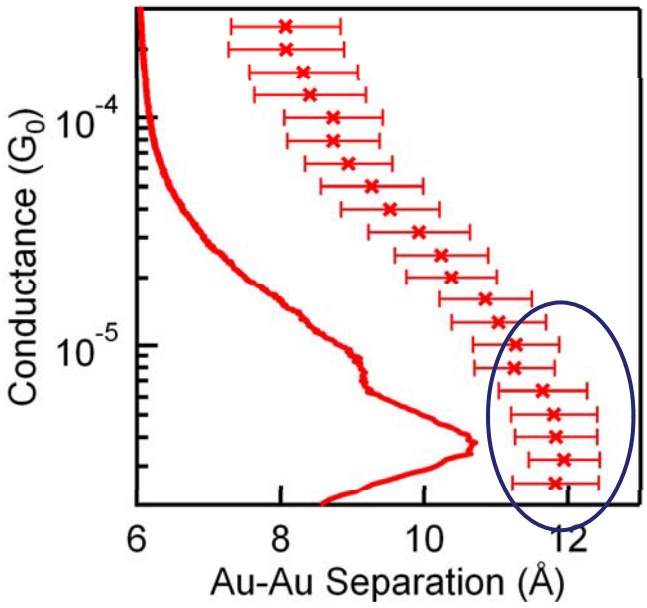
Pull – push – pull a molecular junction. Use the "push-back" distance to correlate Au electrode separation to junction conductance.

Au-Au Separation & Conductance

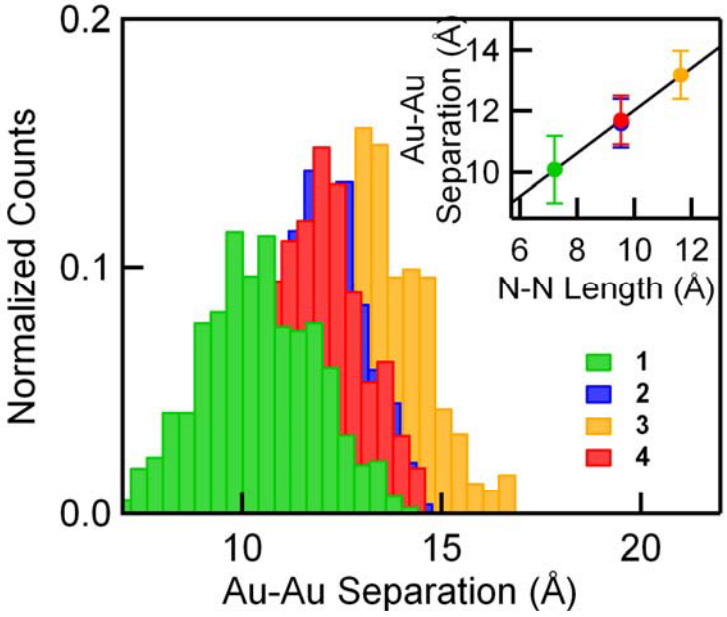
(Kamenetska et al, submitted)



Pyridine-Ethane-Pyridine



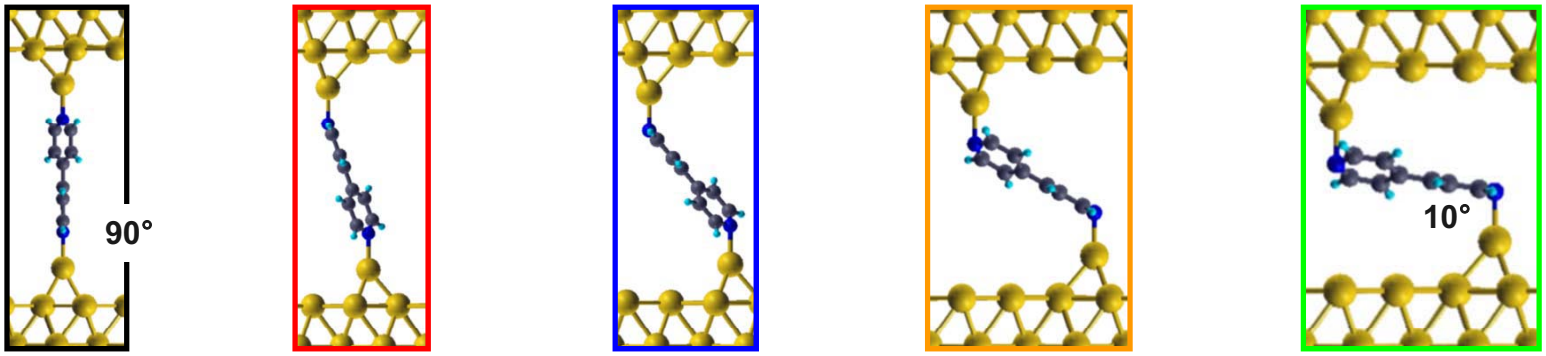
Push-back distance correlates with molecule length for all molecules

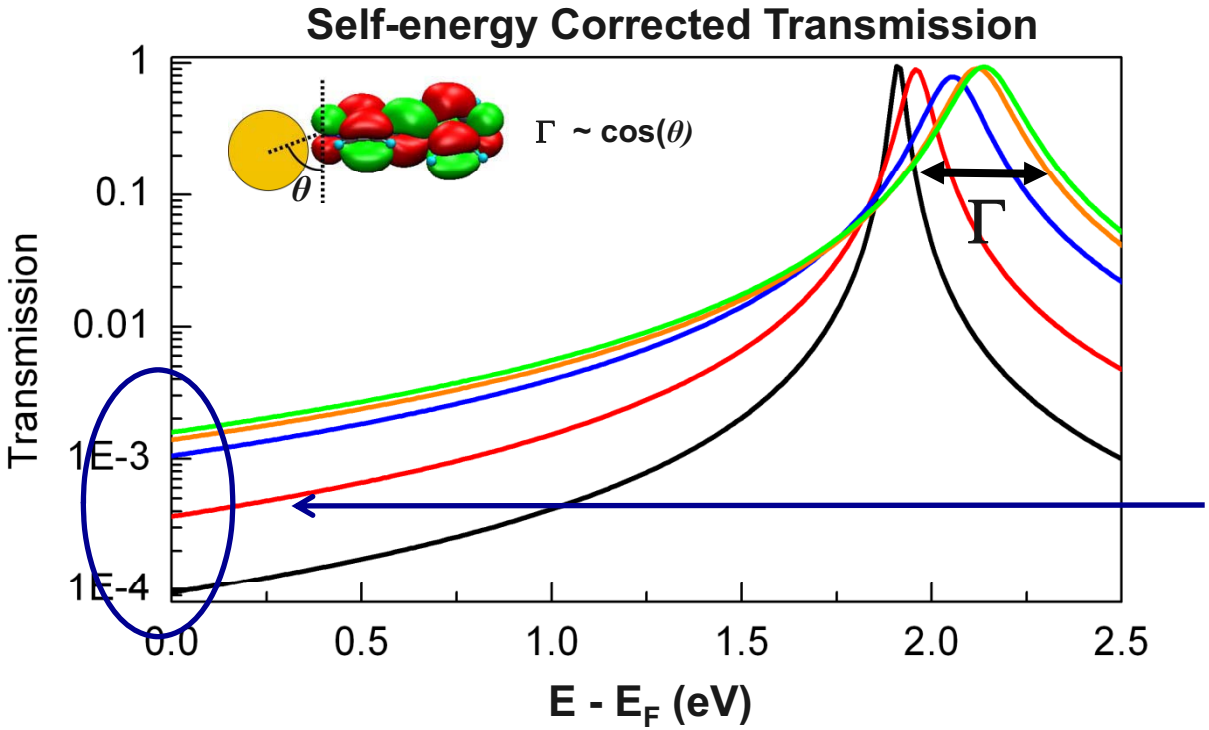


These data agree with the hypothesis: High G-conductance results from tilted geometries, while Low-G junctions have a vertical geometry

BiPy Transmission Sensitive to Geometry

(Quek, Kamenetska et al, Nature Nanotechnology 2009)

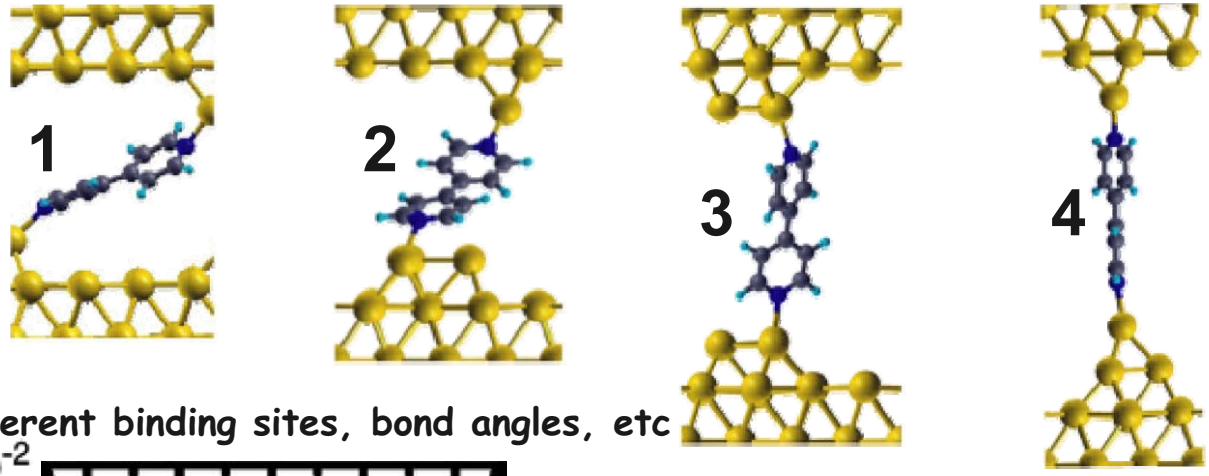




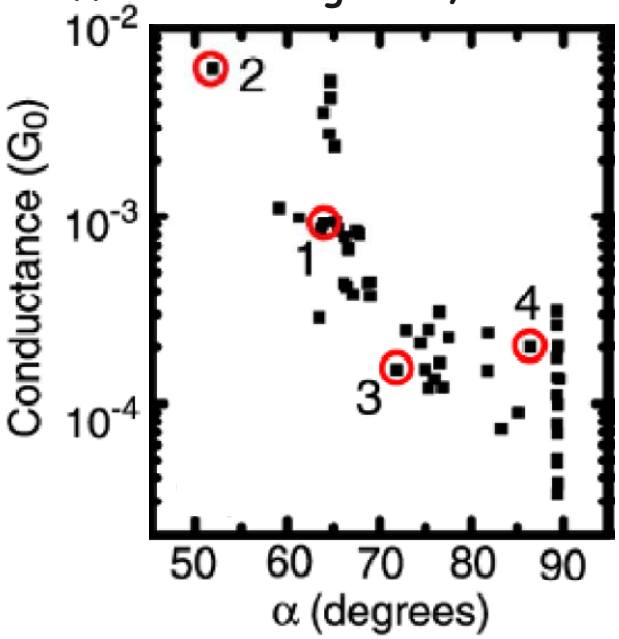
- LUMO dominates $T(E_F)$
- Large correction (~ 1 eV)
- Coupling of pi system to Au enhanced w/ angle (w/ modest binding energy cost)
- Conductance increases by 10x, covers 'Low G' & 'High G' expt'l range

Structure-Conductance: 55 Junctions

(Quek, Kamenetska et al, Nature Nanotechnology 2009)



Different binding sites, bond angles, etc



Experimental Conductance Range

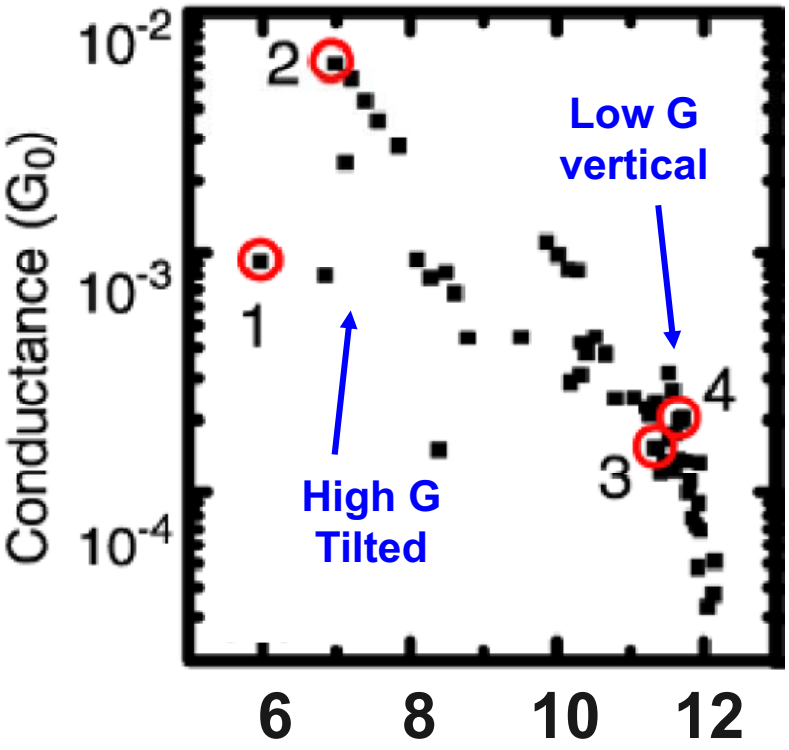
'High G' (5.4×10^{-4} G_0)

'Low G' (1.6×10^{-4} G_0)

Quantitative Comparison: Theory & Exp.

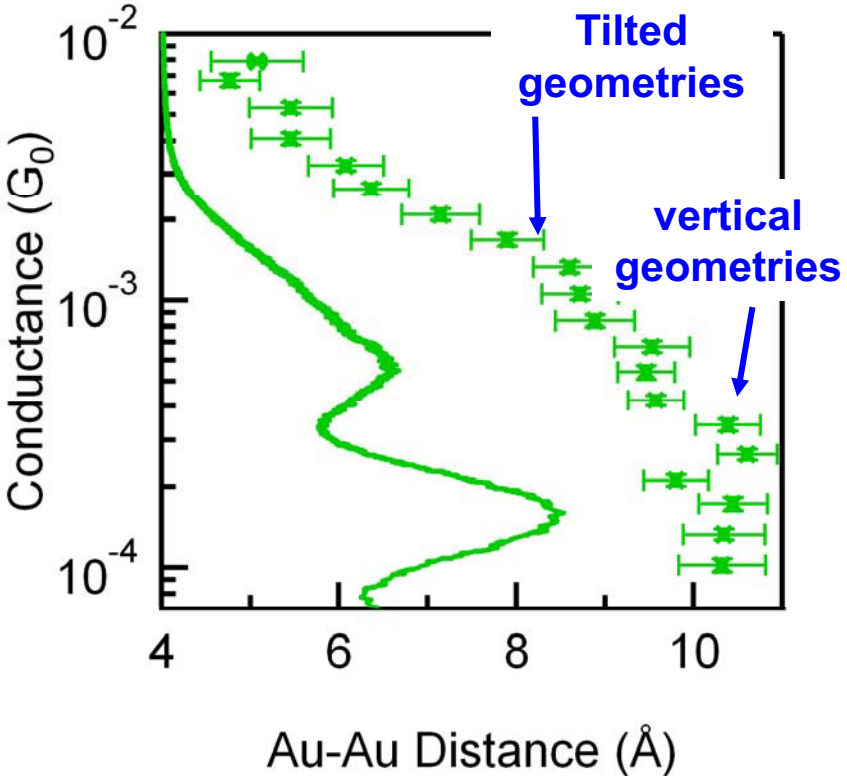
(Quek, Kamenetska et al, Nature Nanotechnology 2009)

Theory

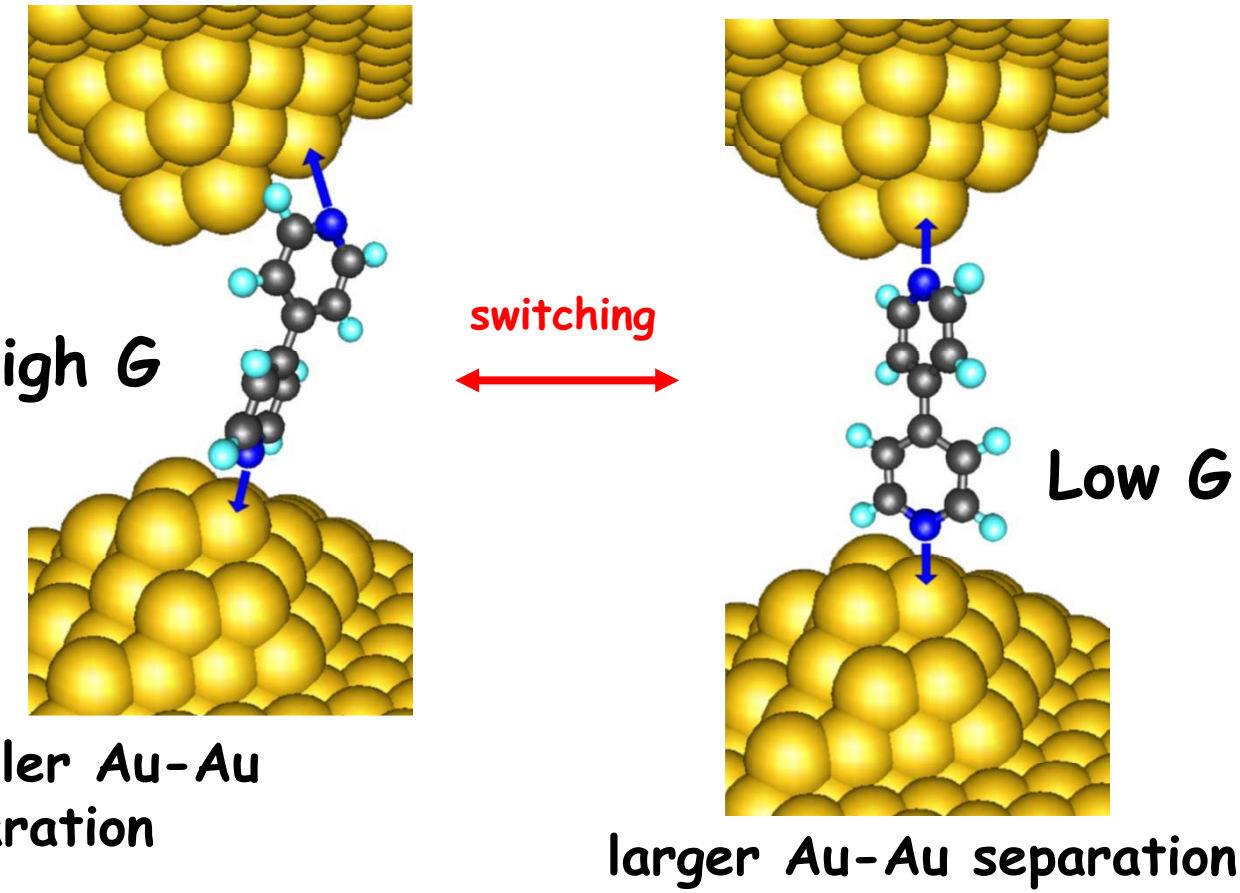


Vertical distance between Au binding sites (Å)

Experiment



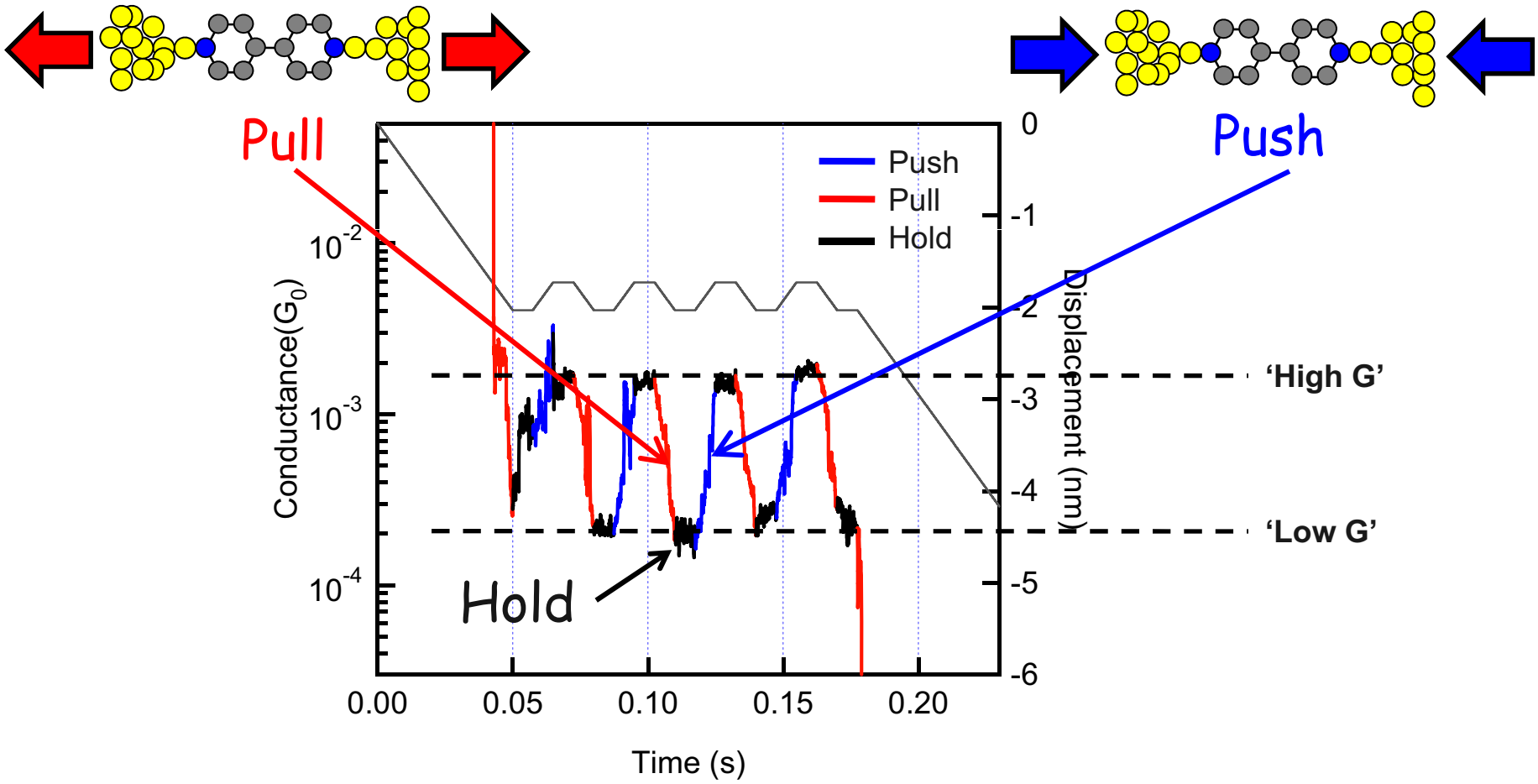
Mechanically-Controlled Switching



Chemical control of a nanoscale interface via mechanical manipulation: Au-pyridine contact geometry dictates conductance!

Reversible, controllable mechanical switching!

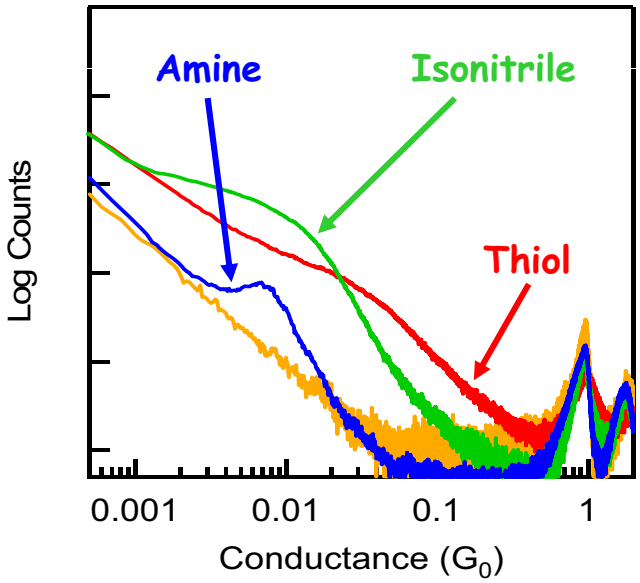
(Quek, Kamenetska et al, Nature Nanotechnology 2009)



Toggle between low & high G by mechanical manipulation

Summary

Amine links provide a bottom-up approach to form single molecule with reproducible characteristics.



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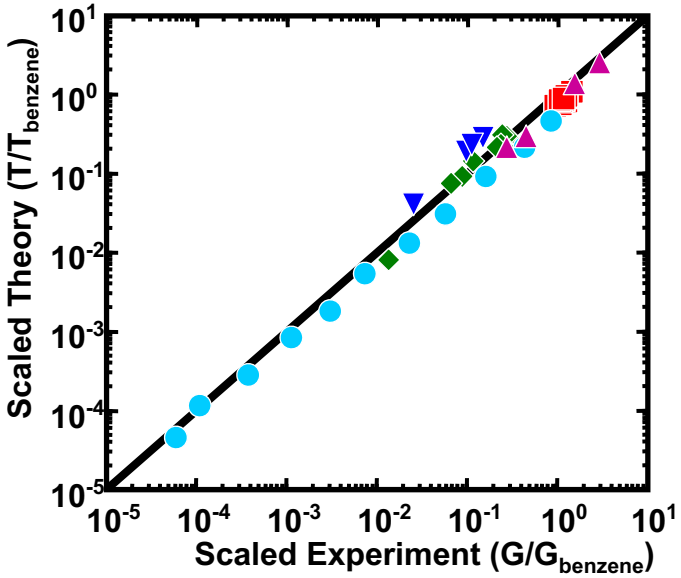
Structure conductance relations can be mapped using Amine-Gold link chemistry



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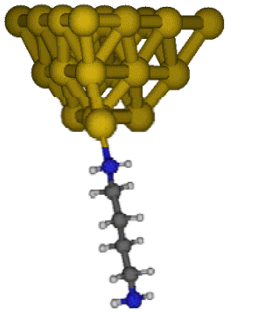

Electronics and mechanics depend on contact linker as well as molecule length.

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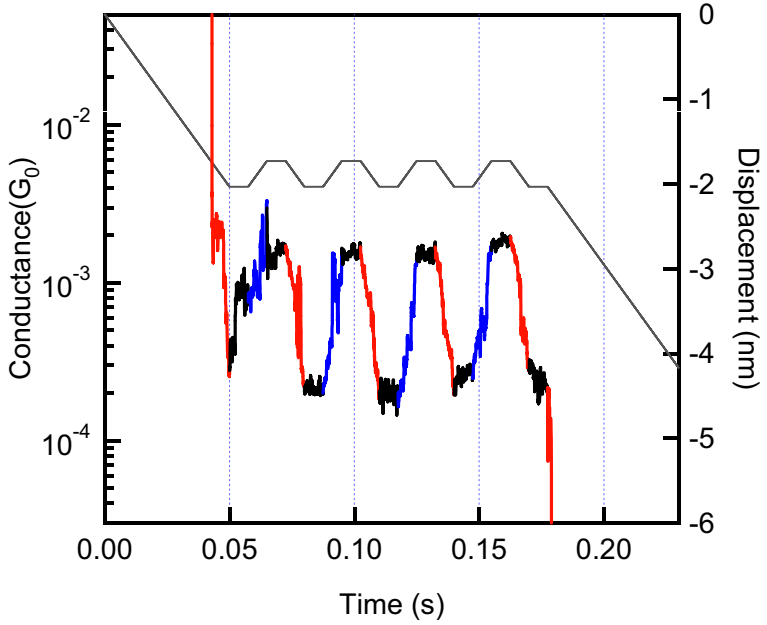

Electronics and mechanics depend on contact linker as well as molecule length.

We can use contact properties to demonstrate single molecule switching.

Thanks

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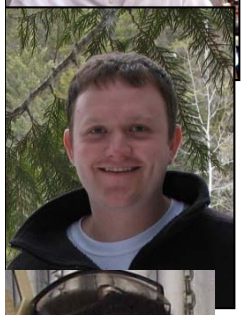

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