Exploring Trends in Conductance for Well-Defined Single Molecule Circuits

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Collaborators

Columbia: Michael Steigerwald
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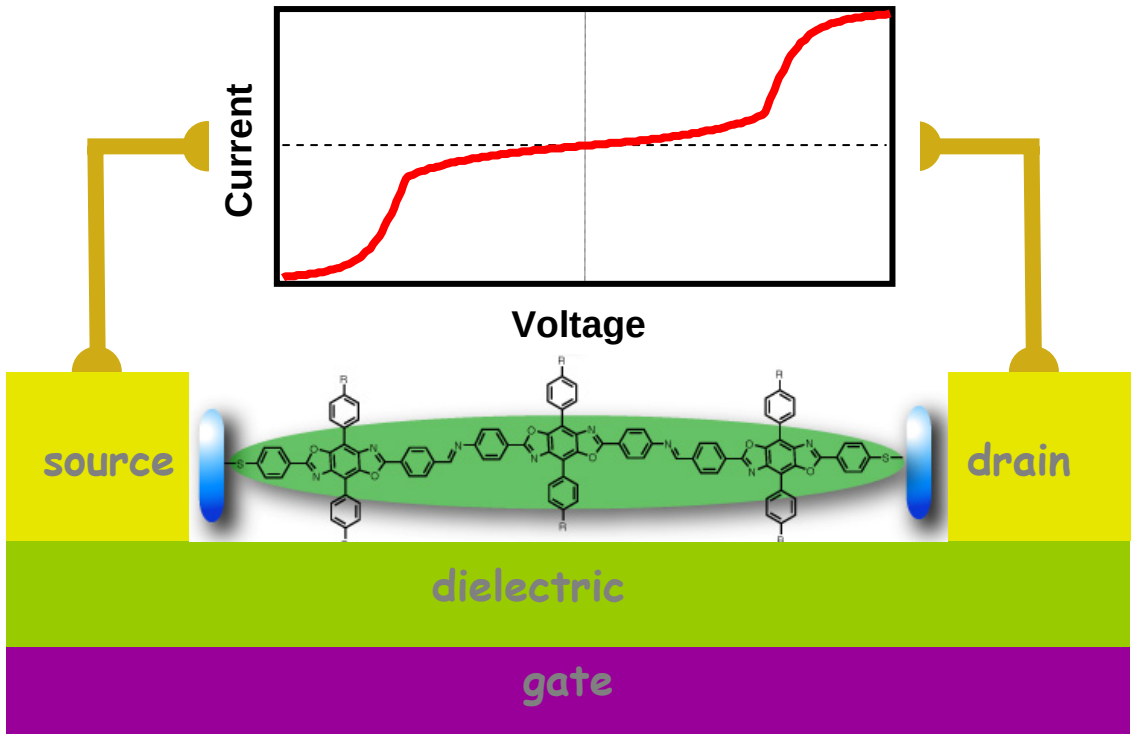
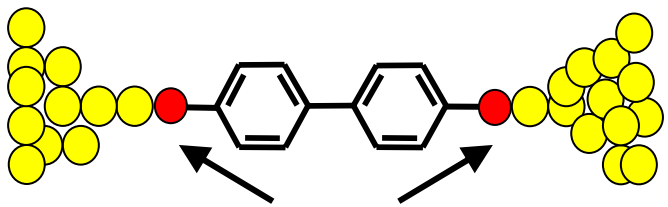
Also: Talks by Su-Ying Quek & Jeff Neaton
Molecular Foundry, LBNL

Funding: NSF, NYSTAR, DOE

Probing Single Molecule "Devices"



Transport Questions



Structure-Property Questions

Outline

Amines: New Alligator Clips for Single Molecule Junctions

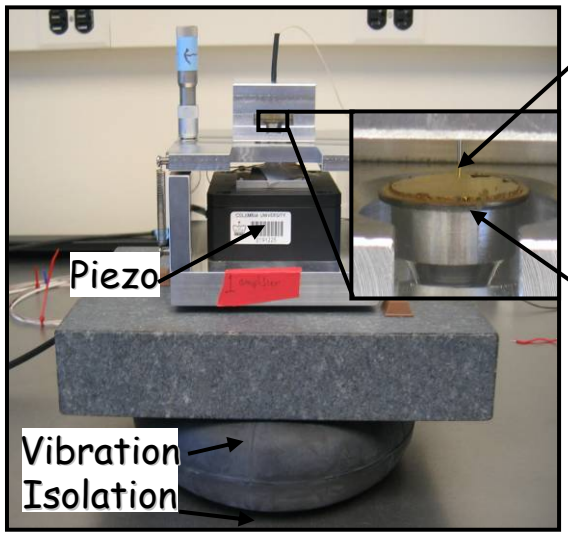
- Trends in single molecule conductance with molecular structure
  - Length & conjugation
  - Conformation
  - Substituents
  - Attachment point: fused ring systems

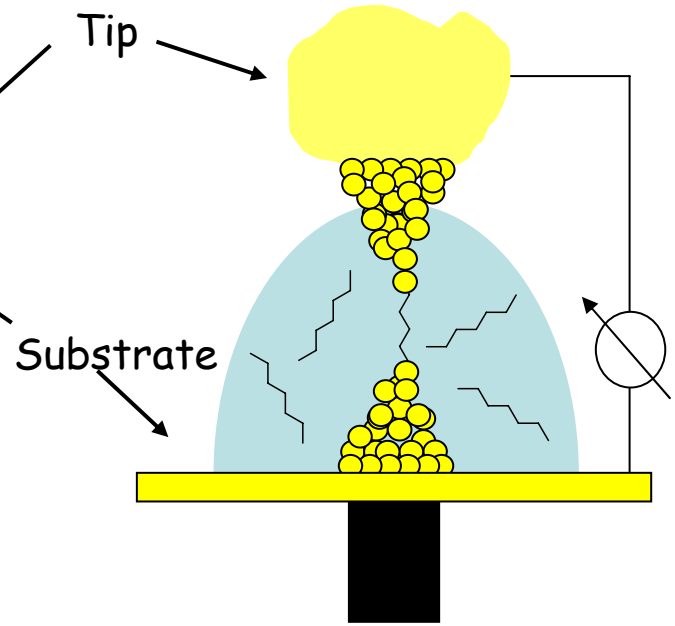
Link Chemistry: Does the Donor-Acceptor bond scheme generalize?

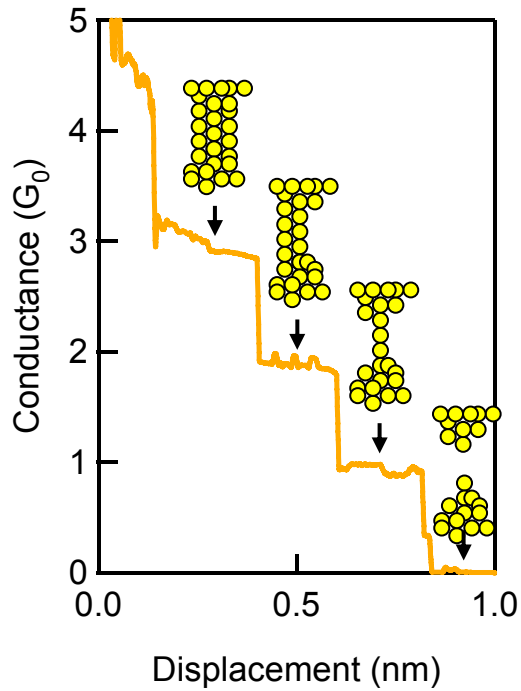
- Comparison of NH2, PMe2, & SMe

Experimental Method

STM based mechanically controlled break junction
Latha Venkataraman





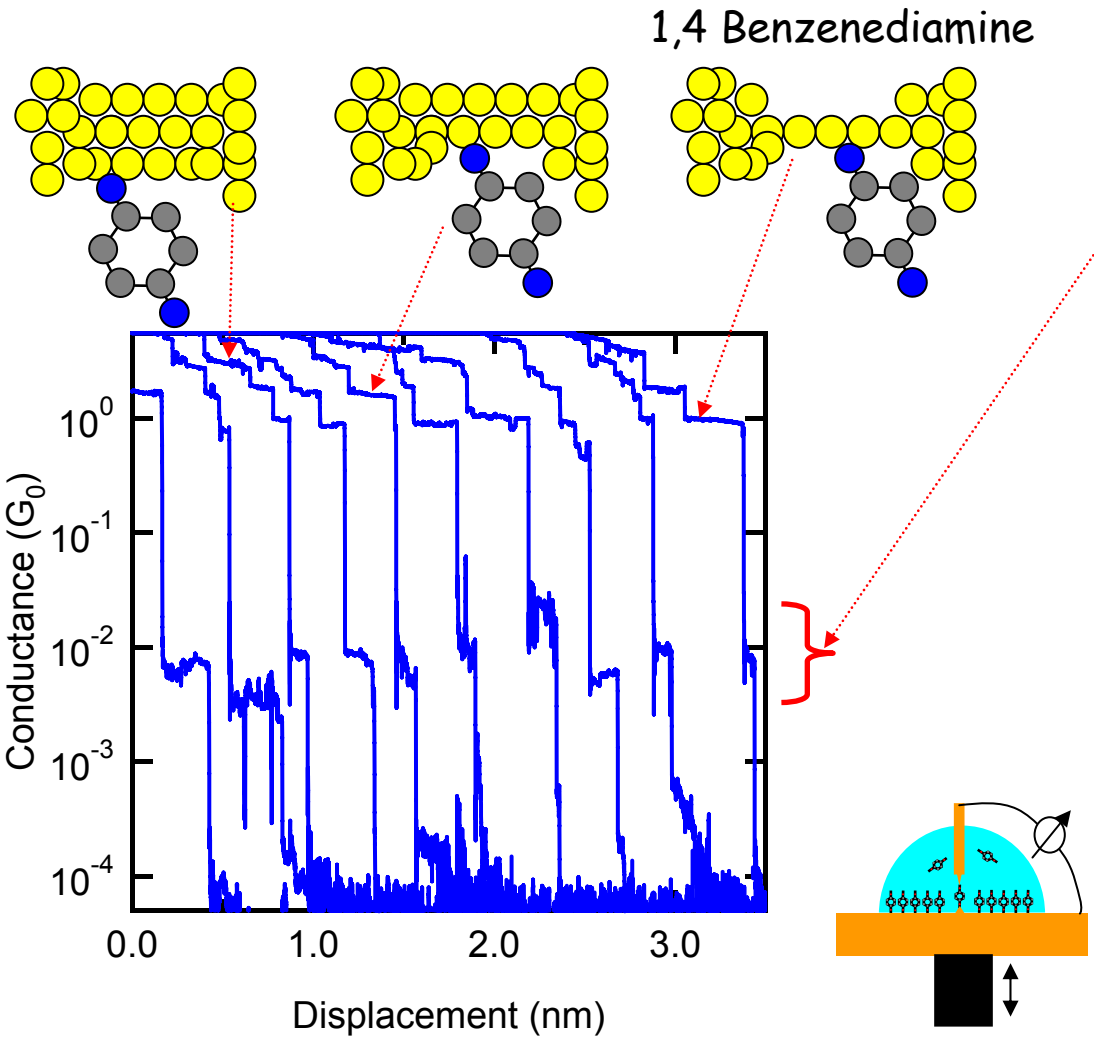


Key Points:
- Good vibration and acoustic isolation
- Low voltage noise for piezo
- Clean substrate & high purity solvents

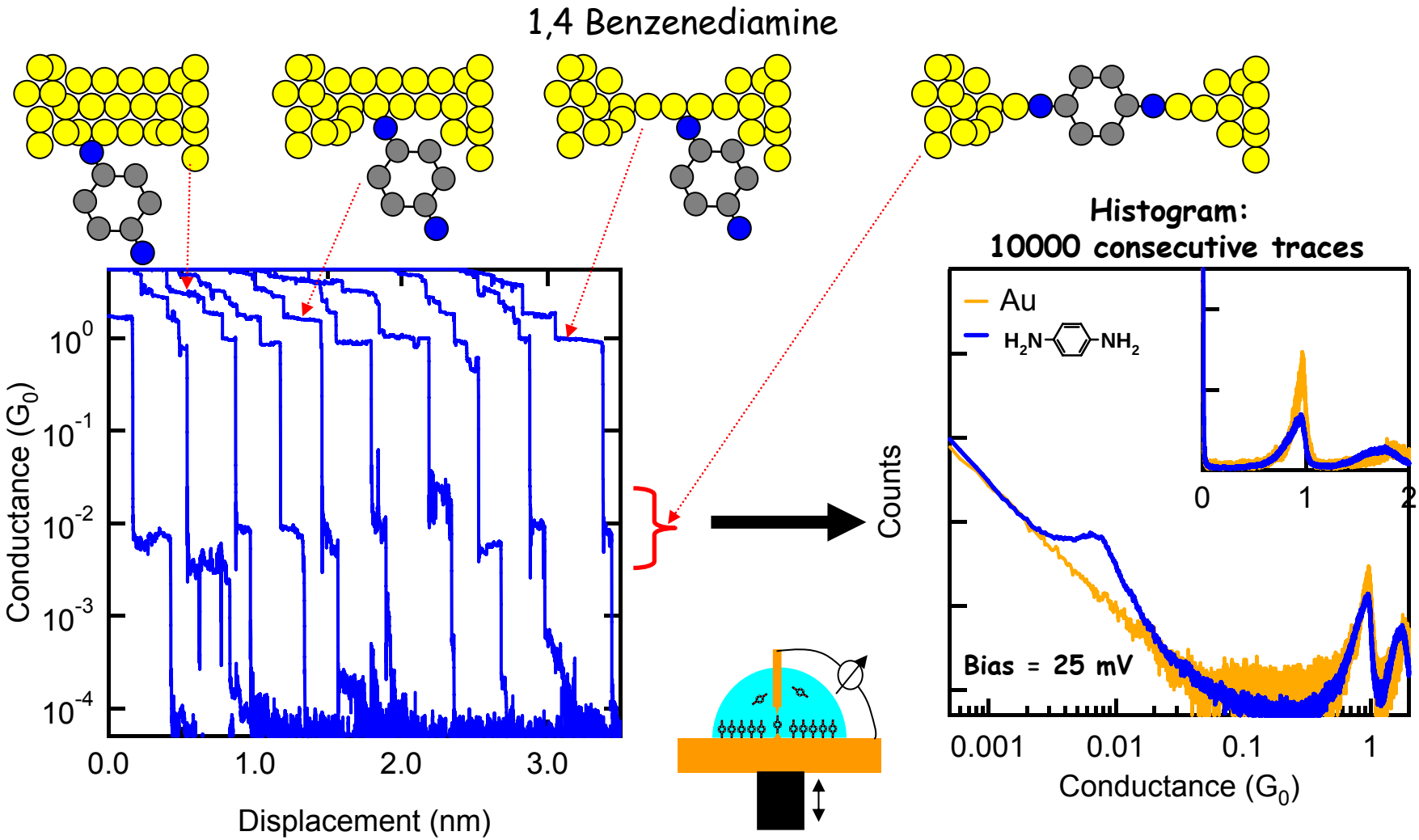
Advantages:
- Statistics
- Same platform for different molecules
- Variable Environment

Based on Xu & Tao, Science 2003

Diamines: NH2 Link Group



Diamines: NH2 Link Group



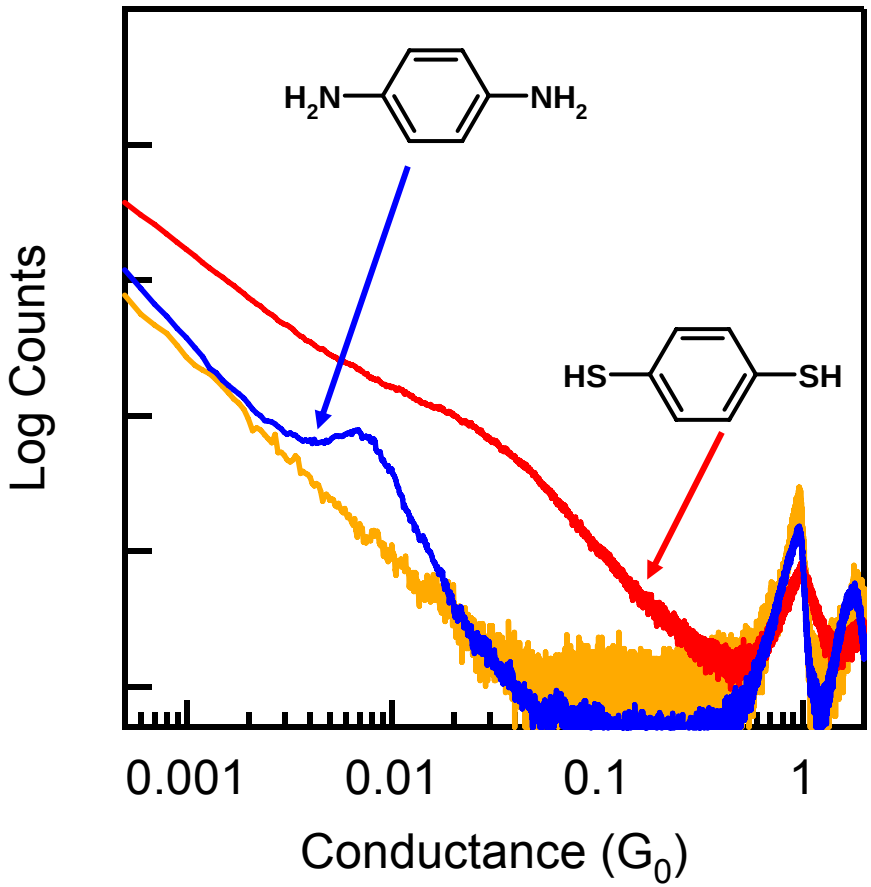
Characteristic Benzenediamine-Au conductance !!

Link Chemistry: A Comparison

Thiols do not give clear molecular signature

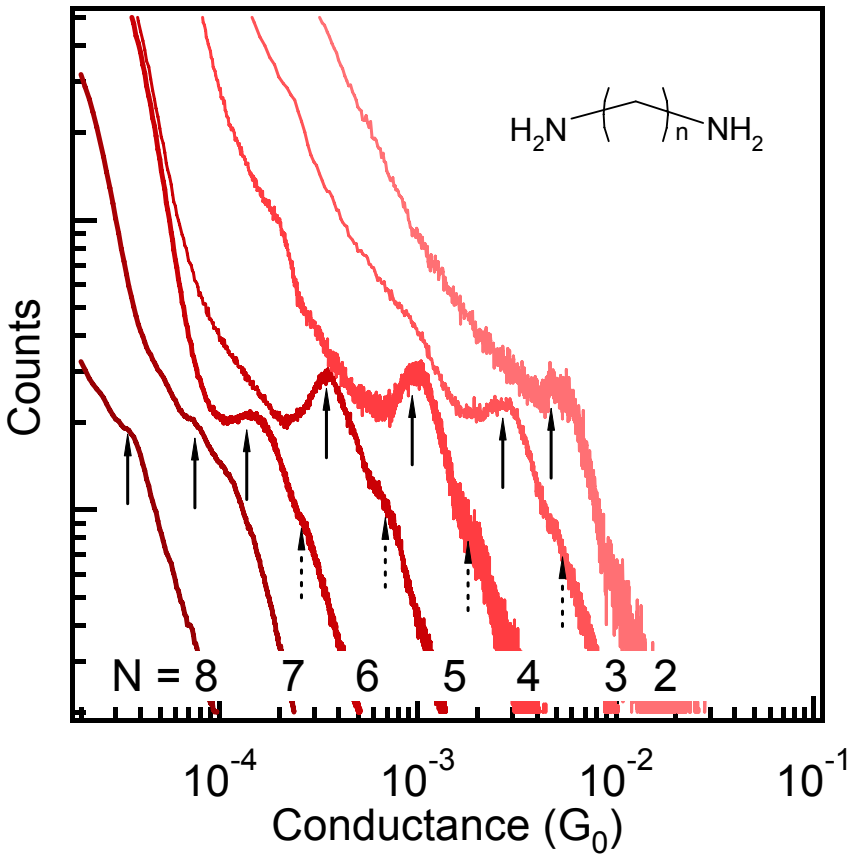
Histograms constructed without any data selection

Amine experiments work with multiple tip/sample pairs and with different solvents.



Venkataraman et al, Nano Letters, 2006

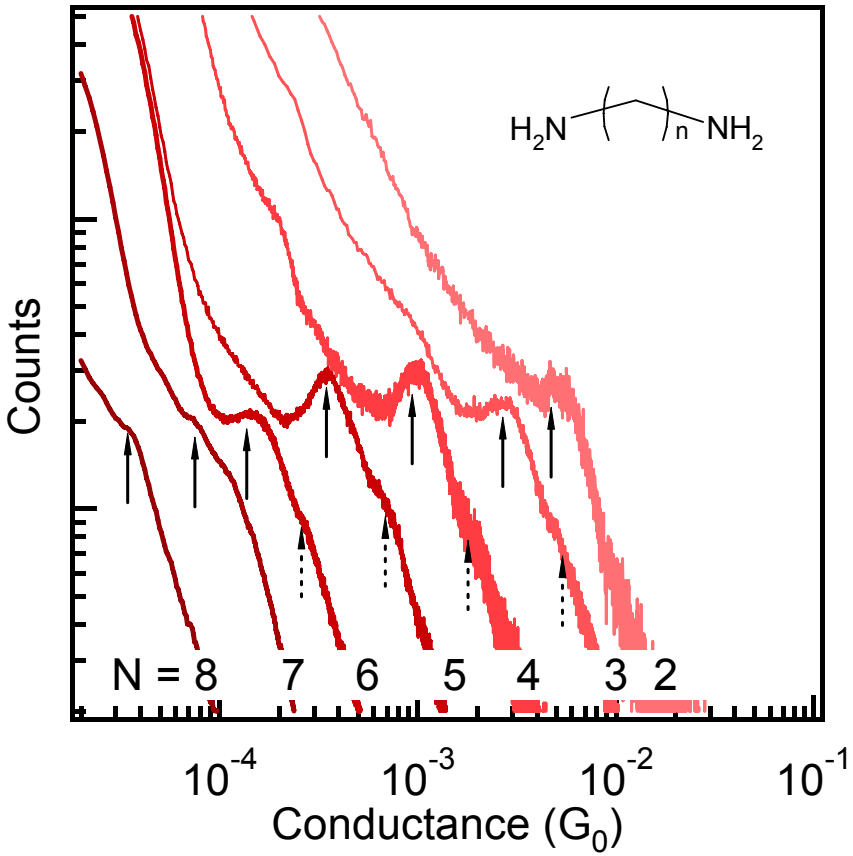
Conductance of Alkanes



Data offset vertically for clarity

N:	Alkane Chains Attempted
2	H_2N NH_2
3	H_2N NH_2
4	H_2N NH_2
5	H_2N NH_2
6	H_2N NH_2
7	H_2N NH_2
8	H_2N NH_2

Conductance vs Length



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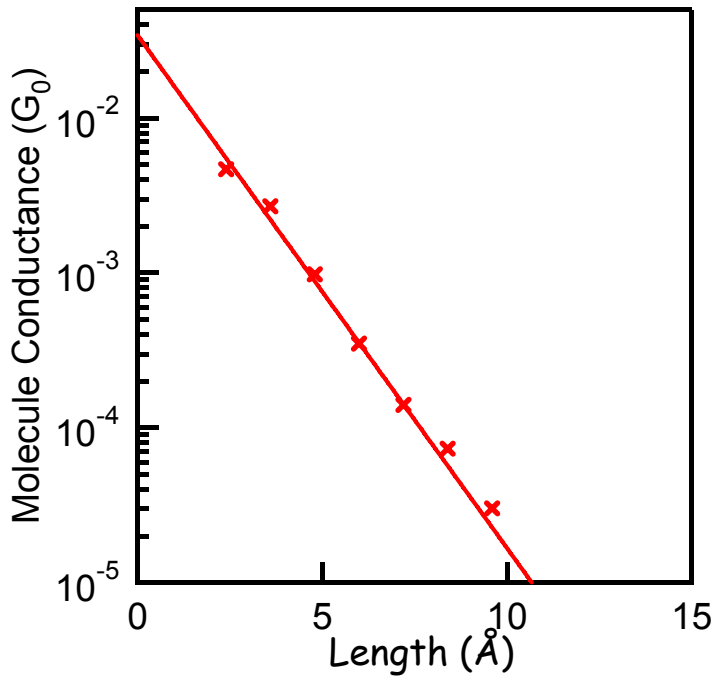
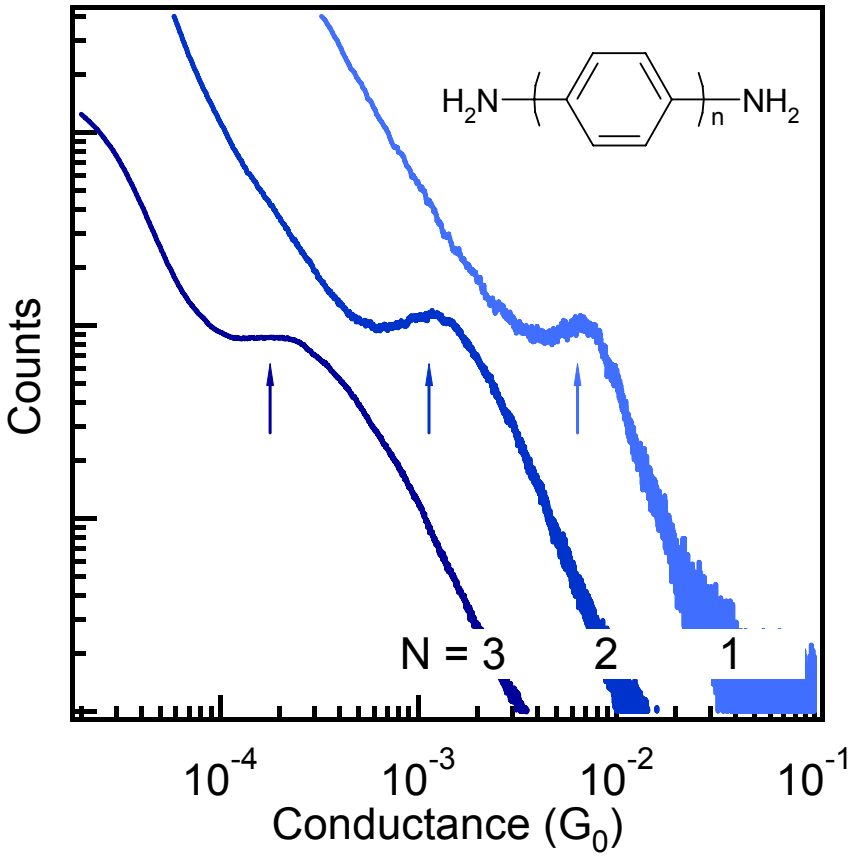


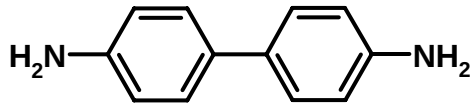
Conductance of Polyphenyls

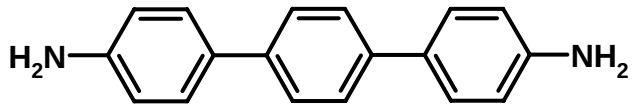


Data offset vertically for clarity

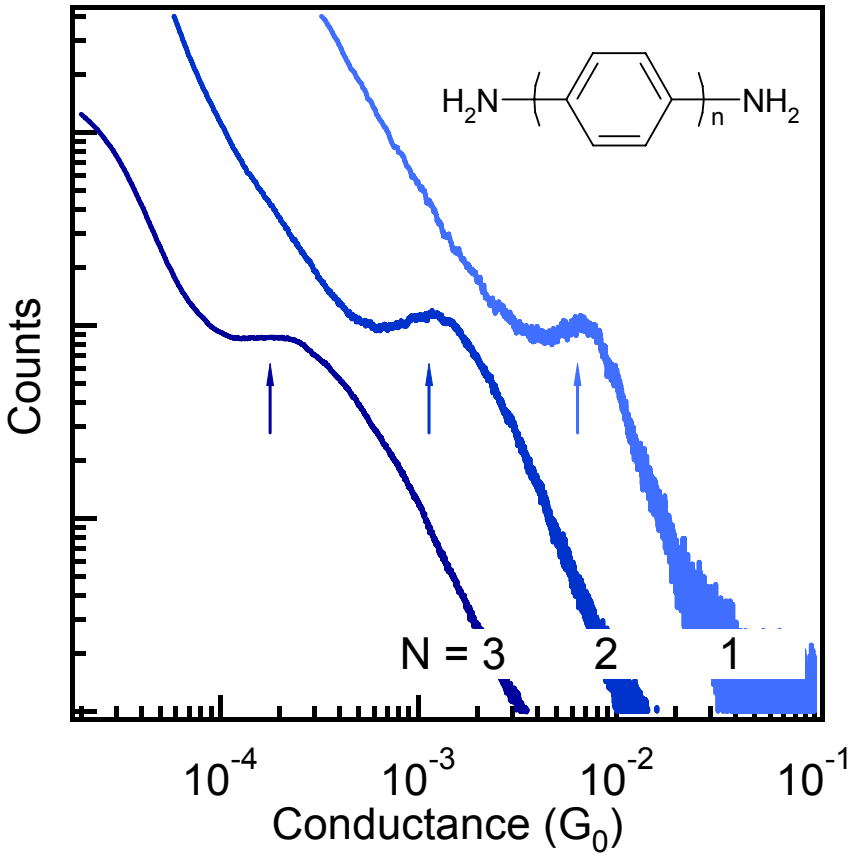
N: Phenyl Chains Attempted

1 

2 

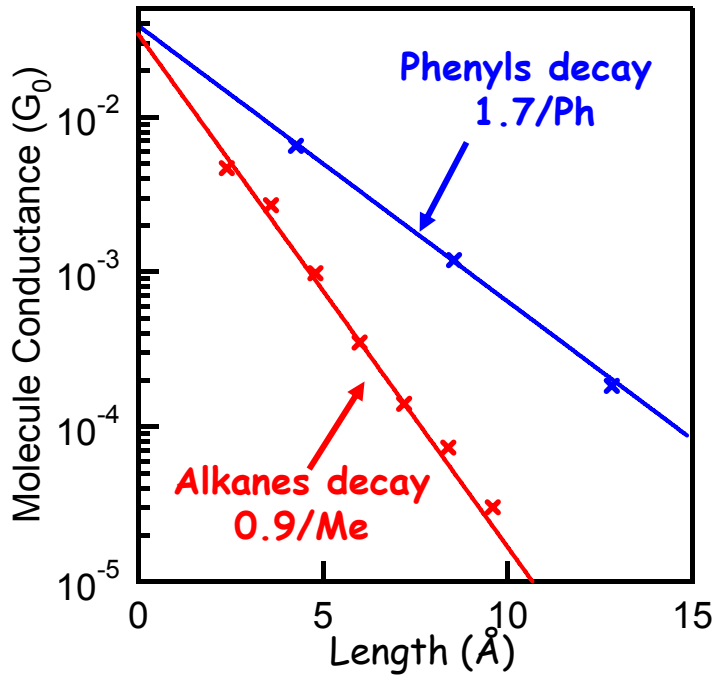
3 

Conductance vs Length



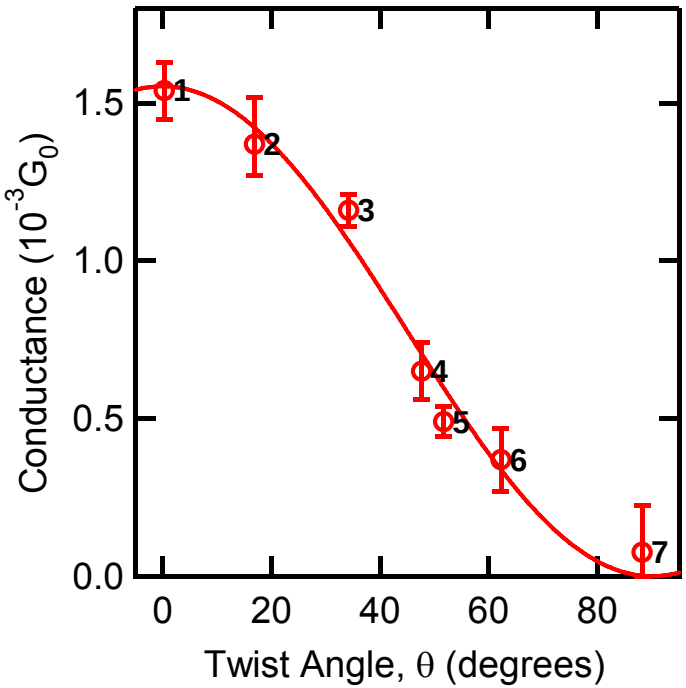
Data offset vertically for clarity

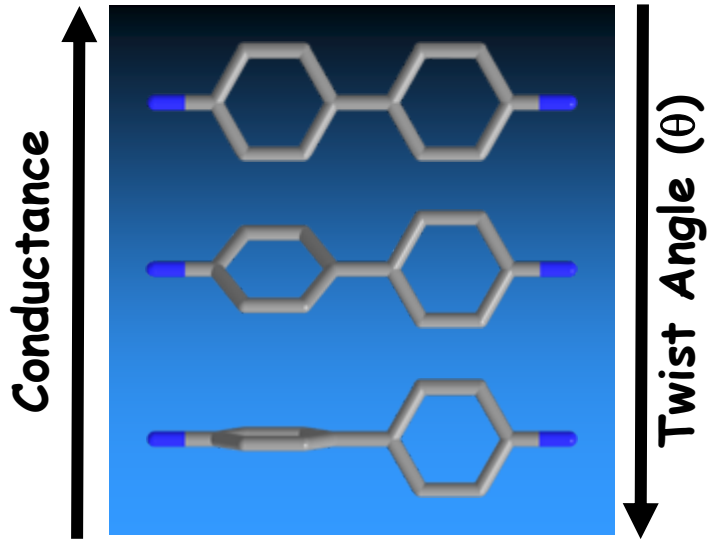
$G \sim e^{-\beta L}$

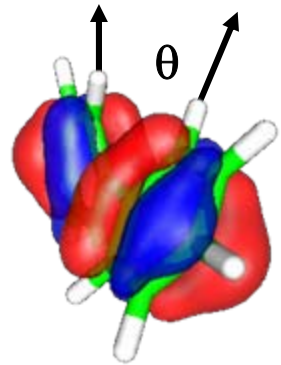


Direct evidence: Non-resonant tunneling

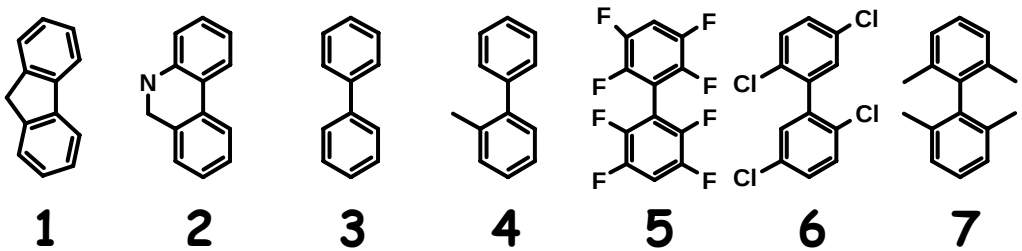
Conductance vs Molecular Conformation







Amine link not shown



Structure – Function: Cosine square dependence measured

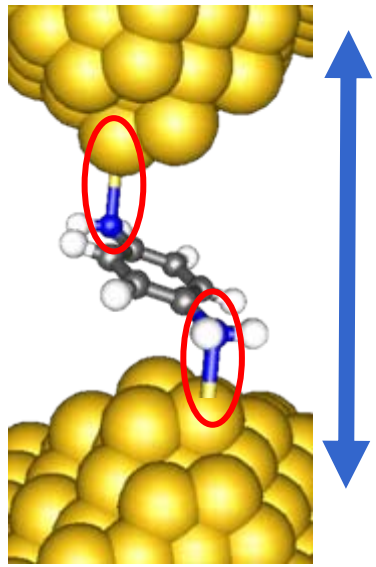
Venkataraman, Klare, Nuckolls, Hybertsen & Steigerwald, Nature, 2006

Theory Perspective: Amine-Gold Linked Junctions

How do amines bond in the junction ?

Selective bonding motif

- N lone pair to under coordinated Au site: bond energy ~ 0.5 eV
- No binding to bridge or hollow sites (S.Y. Quek)



Are the links stable and flexible ?

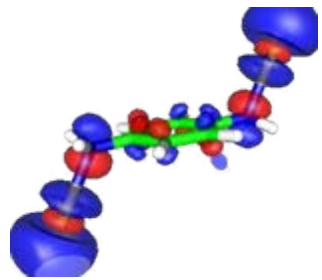
N-Au bond controls the junction

- Estimated maximum force 0.5-0.7 nN
- N-Au bond breaks

Is the electronic coupling reproducible ?

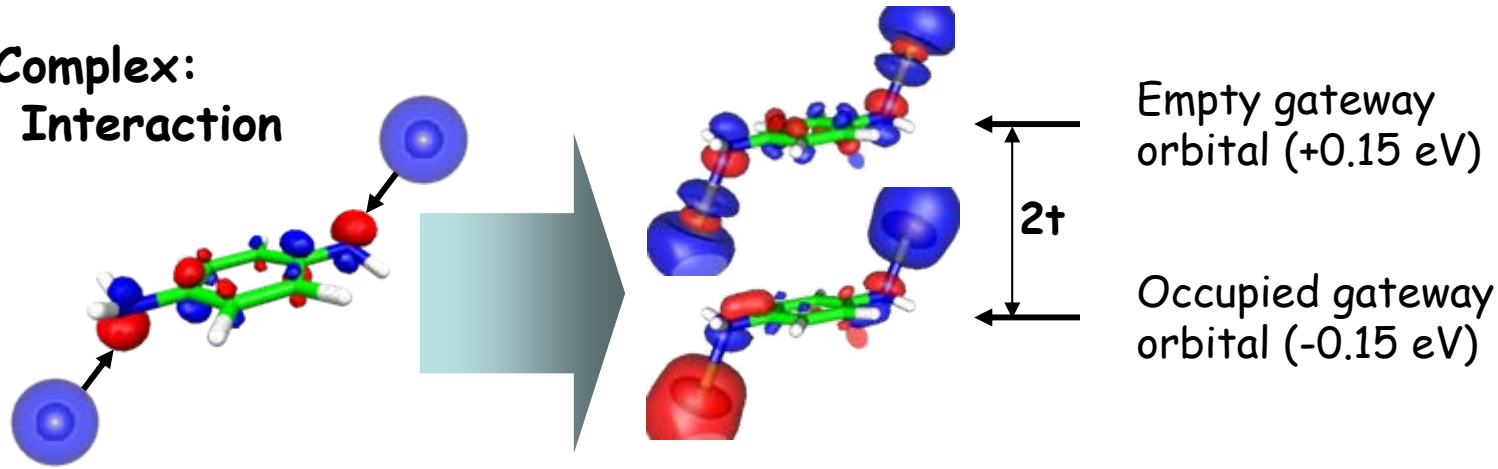
N lone pair coupling to isotropic Au s orbital

- Tunnel coupling mediated through N-Au bond explains trends across molecular families
- Conductance varies modestly with local Au and molecule structure (S.Y. Quek)



Tunnel Coupling: Role of N-Au States

Model Complex:
Amine-Au Interaction

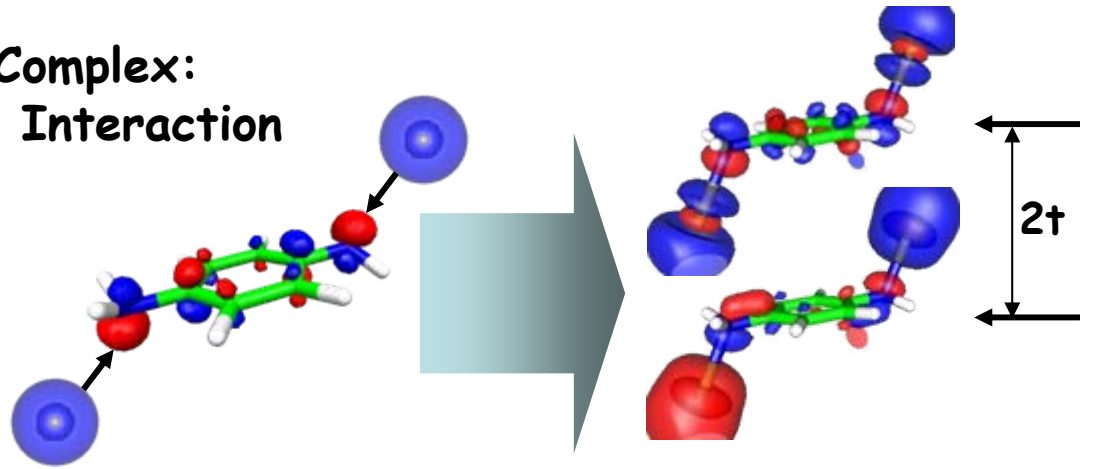


DFT Studies

- **Molecules –**
  - **Jaguar 5.0: gaussian basis all electron**
- **Gradient corrected DFT (Perdew, Burke & Ernzerhof)**

Tunnel Coupling: Role of N-Au States

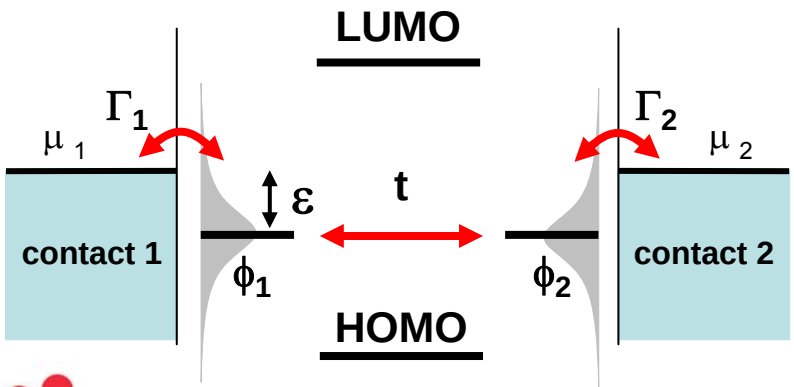
Model Complex:
Amine-Au Interaction



Empty gateway orbital (+0.15 eV)

Occupied gateway orbital (-0.15 eV)

Donor-Bridge-Acceptor Picture



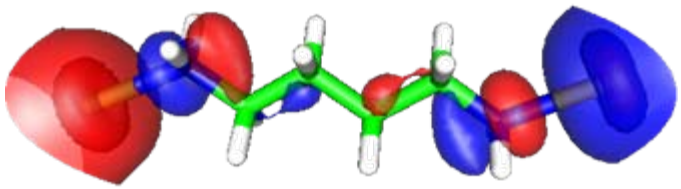
Low Bias Conductance

$$\frac{G}{G_0} \approx \frac{16\Gamma_1\Gamma_2 t^2}{16\varepsilon^4 + \Gamma_1^2\Gamma_2^2} \propto t^2$$

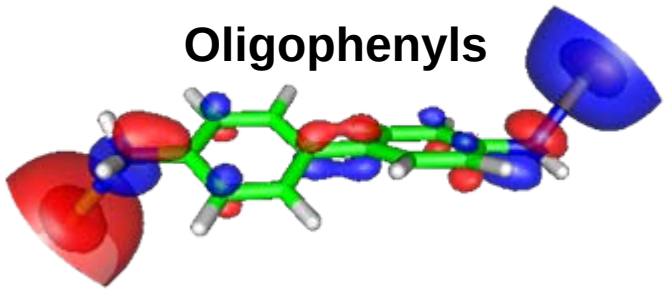
Trends: Tunneling Conductance vs. Length

Tunnel splitting from Au_1 cluster terminated

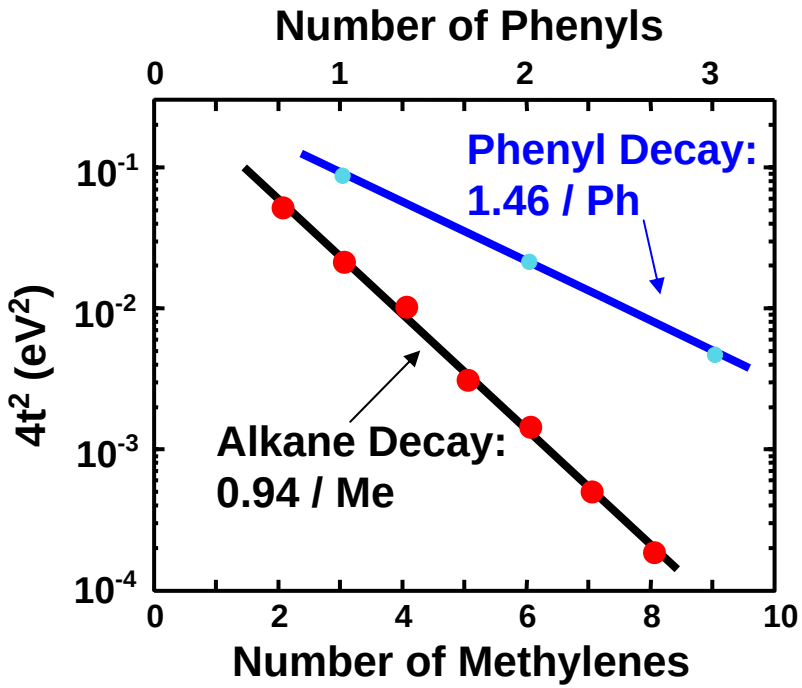
Alkanes



Oligophenyls



Calculated tunnel splitting

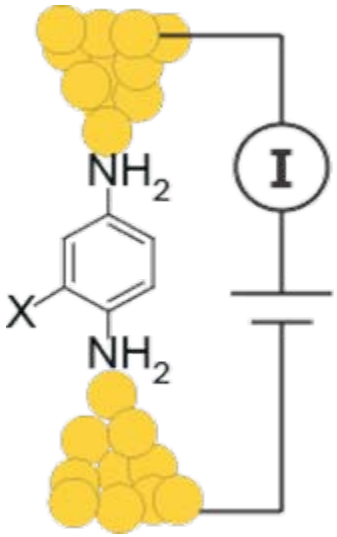


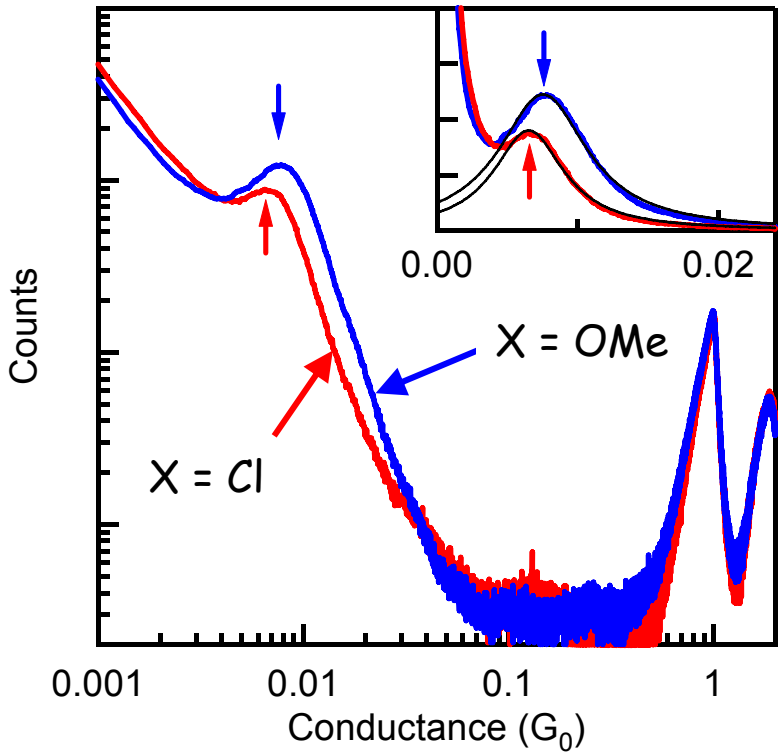
Experiment:

0.91 ± 0.03 / Me

1.68 ± 0.03 / Ph

Substituent Effects

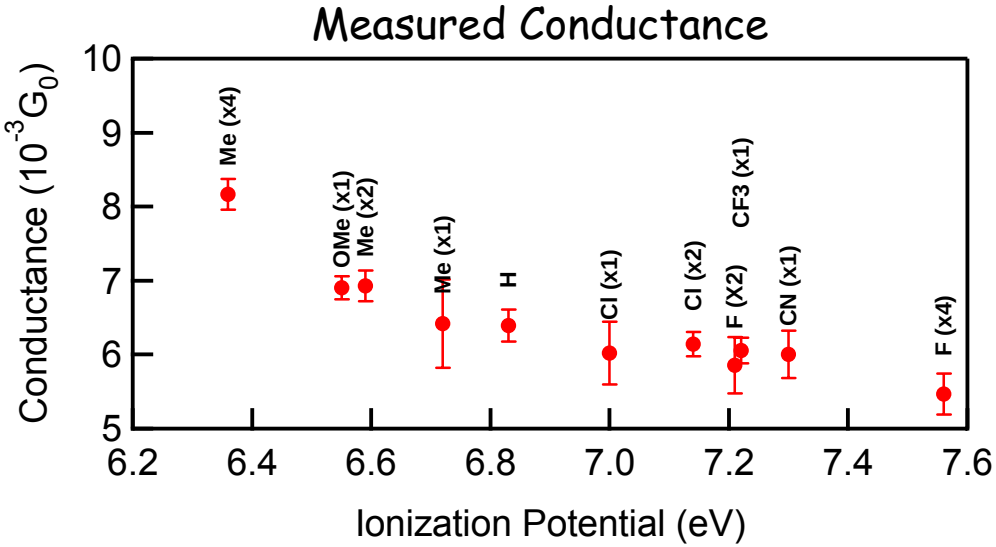


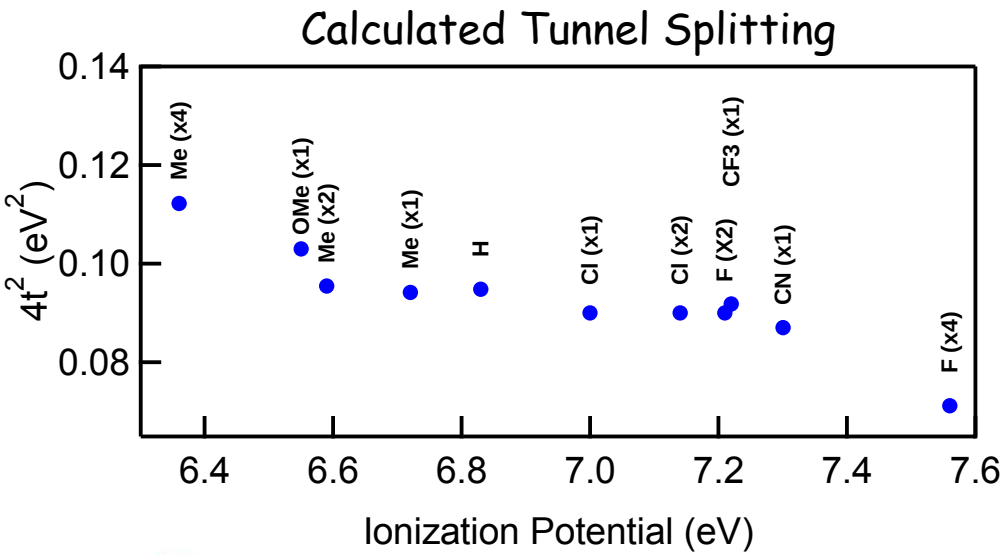


OMe → electron donating → increases conductance

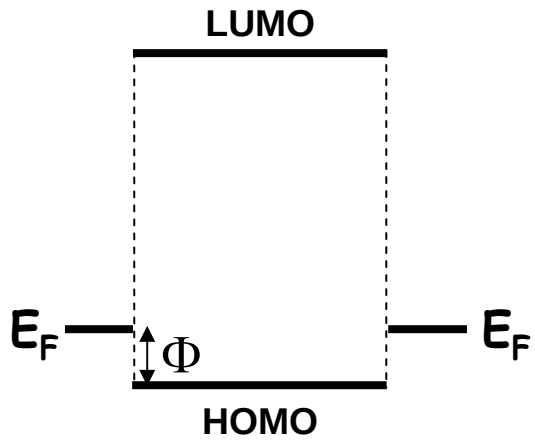
Cl → electron withdrawing → decreases conductance

Trend Demonstrates HOMO Dominated Tunneling





Hypothesized Alignment: Simmons Picture

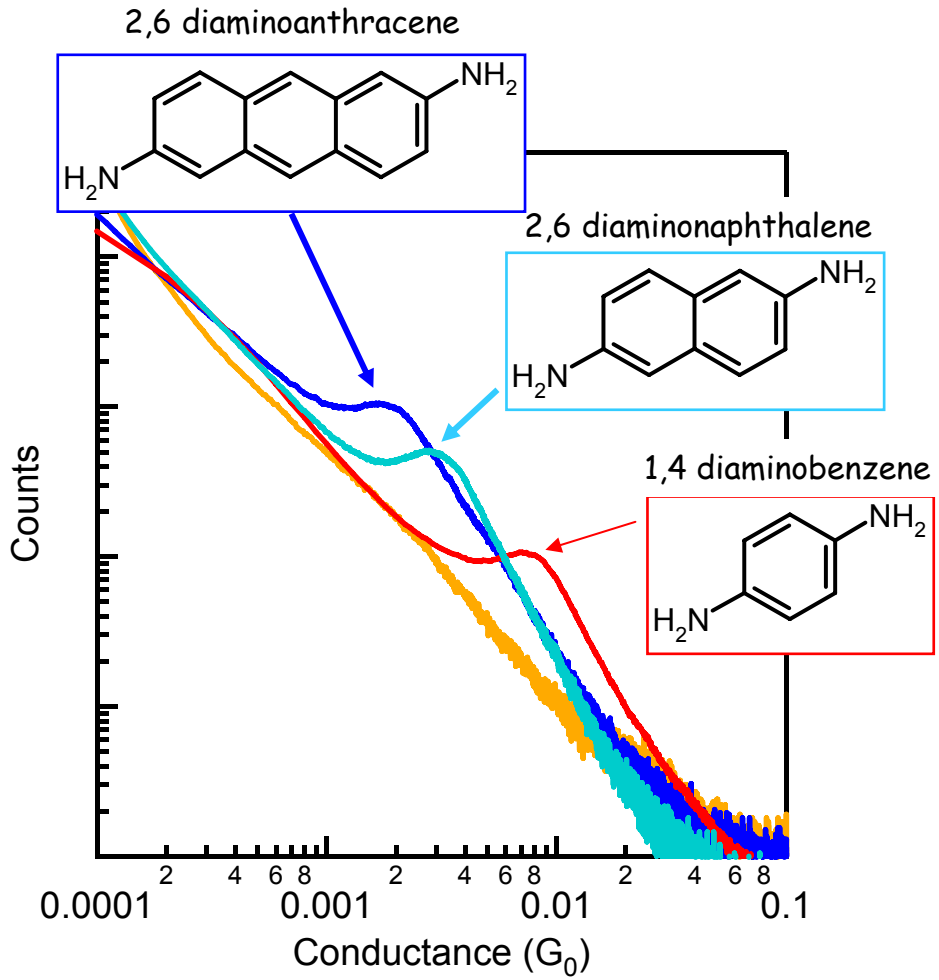


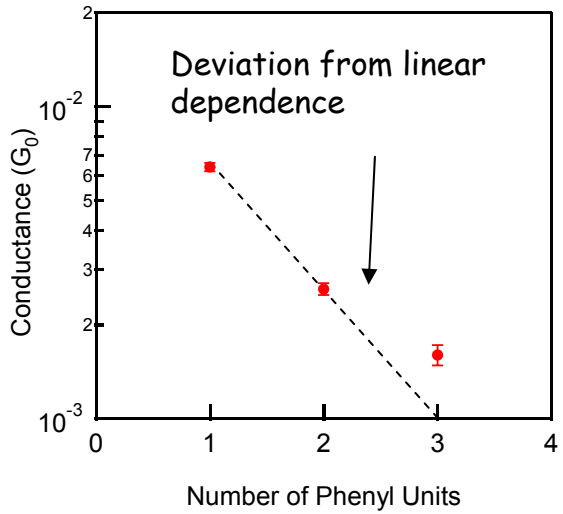
Electron donating group:

- **Raise HOMO (lower IP)**
- **Reduce Φ**
- **Increase G**

Venkataraman, et al, Nano Letters, 2007

Fused Ring Systems

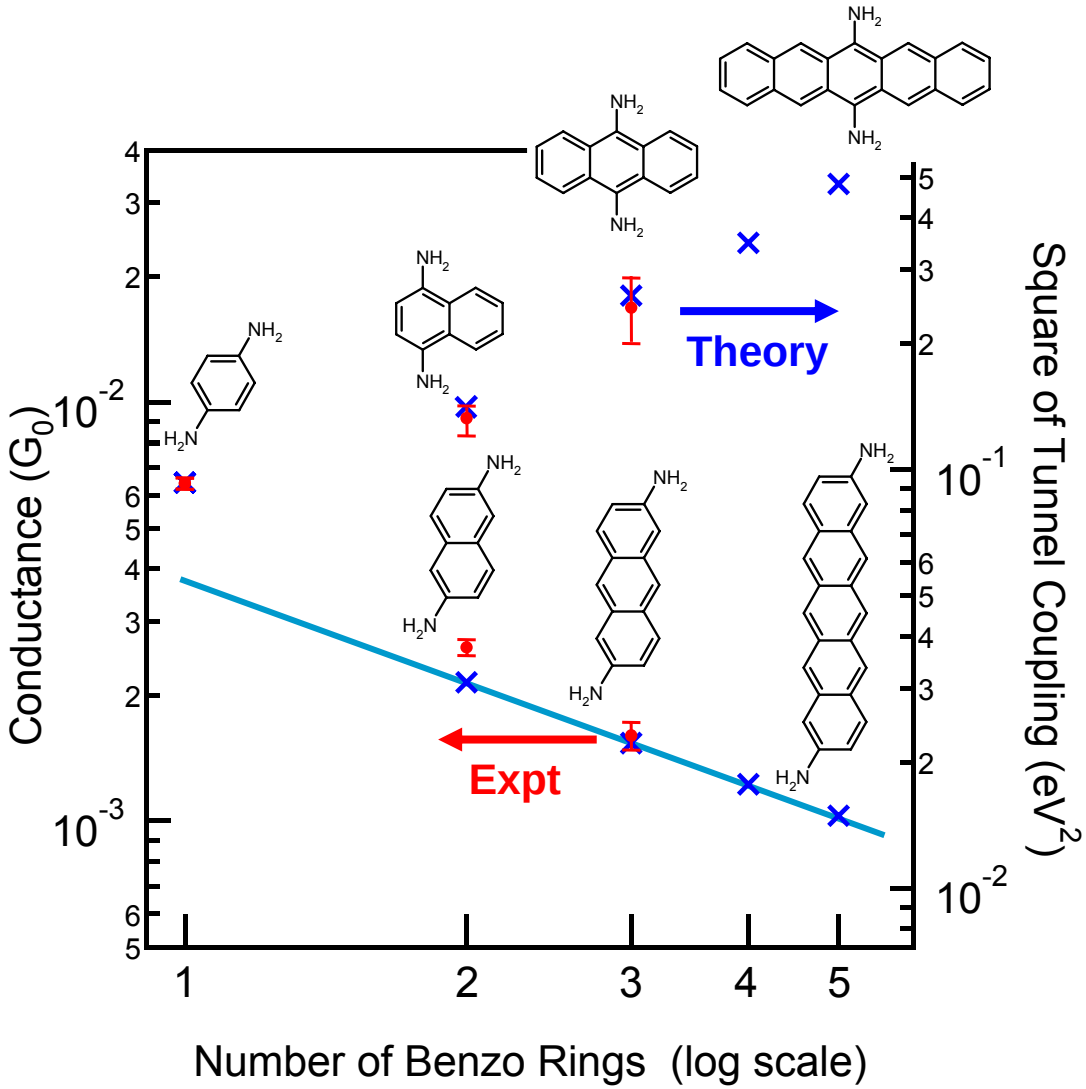




	HOMO-LUMO Gap
Benzene	~ 10.3 eV
Naphthalene	~ 8.3 eV
Anthracene	~ 6.9 eV

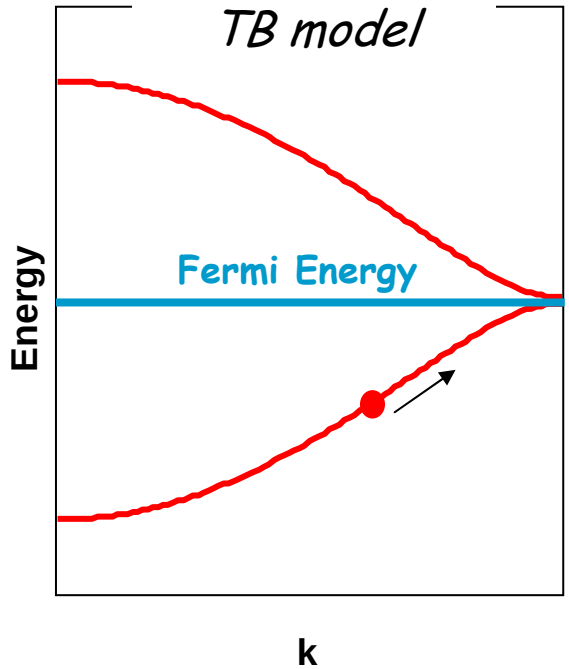
J. Quinn et al, JACS Comm. 2007

Tunneling: Fused Ring Aromatics



Power Law Length Dependence

Infinite Chain: TB model



J. Quinn et al, JACS Comm. 2007

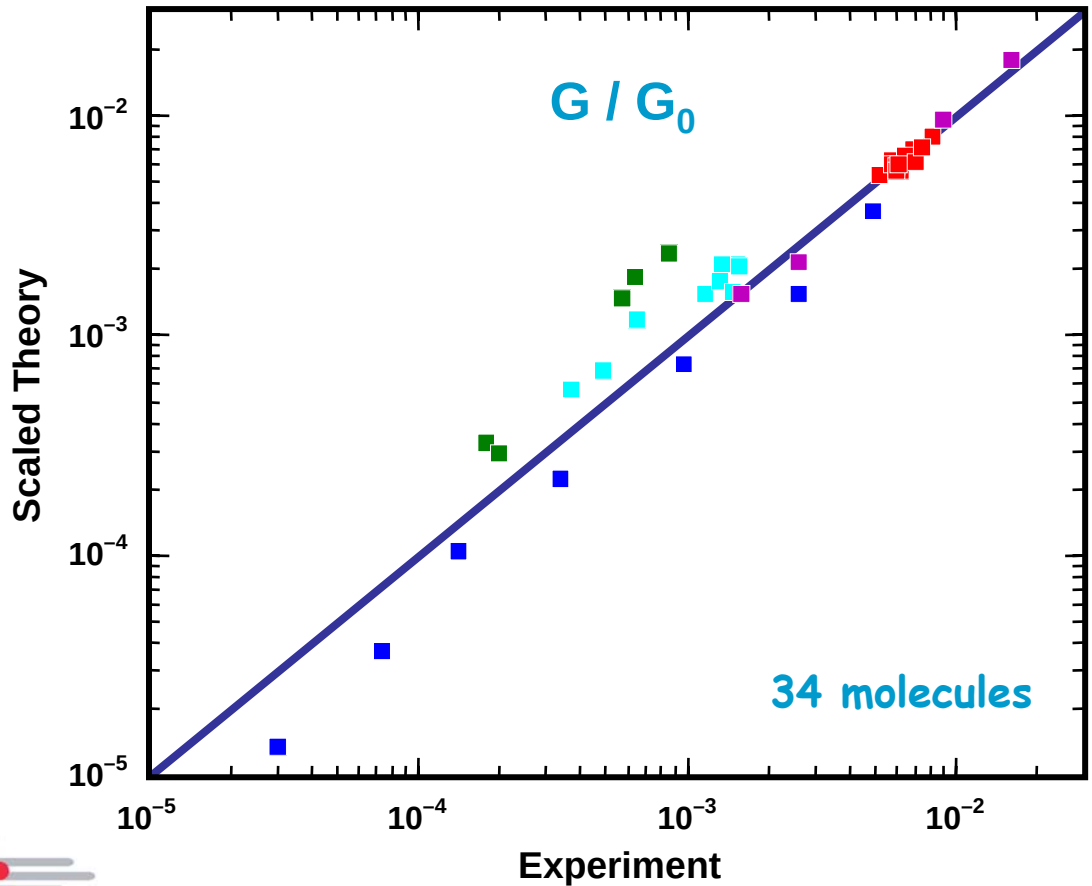
Tunneling Theory vs Experiment

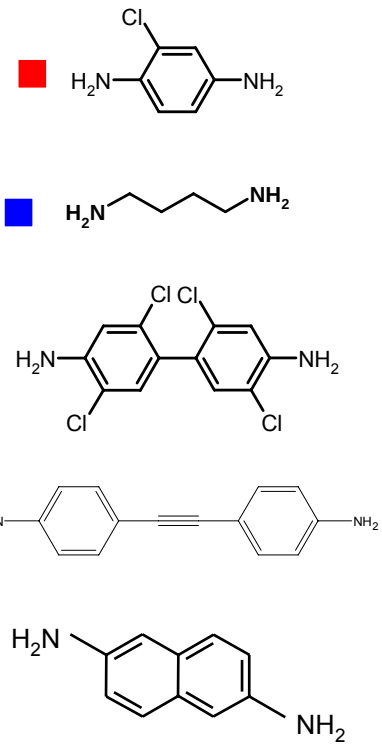
Reference Junction

Measured:
$G = 6.4 \times 10^{-3}\ G_0$

Scaled Theory

- Calculate $4t^2$ (model complex)
- Assume Γ_1, Γ_2, ε constant
- Scale to benzene (2t = 0.305 eV)

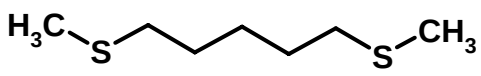




Generalize Donor-Acceptor Link Motif ?

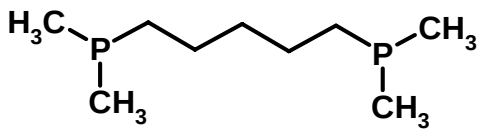
Examples

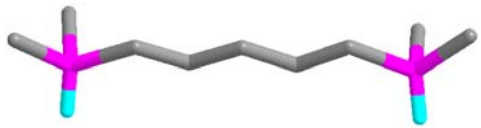
Thio-ether (S-CH_3)



Lone Pair

Phosphine (P-(CH_3)$_2$)

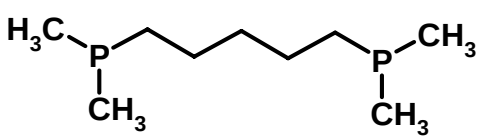


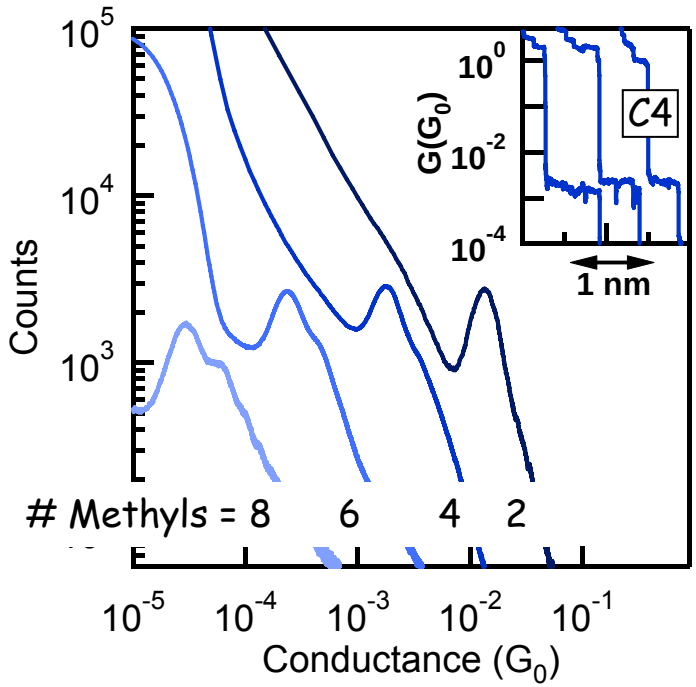


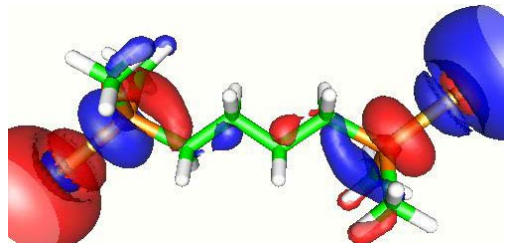
Requires synthesis:

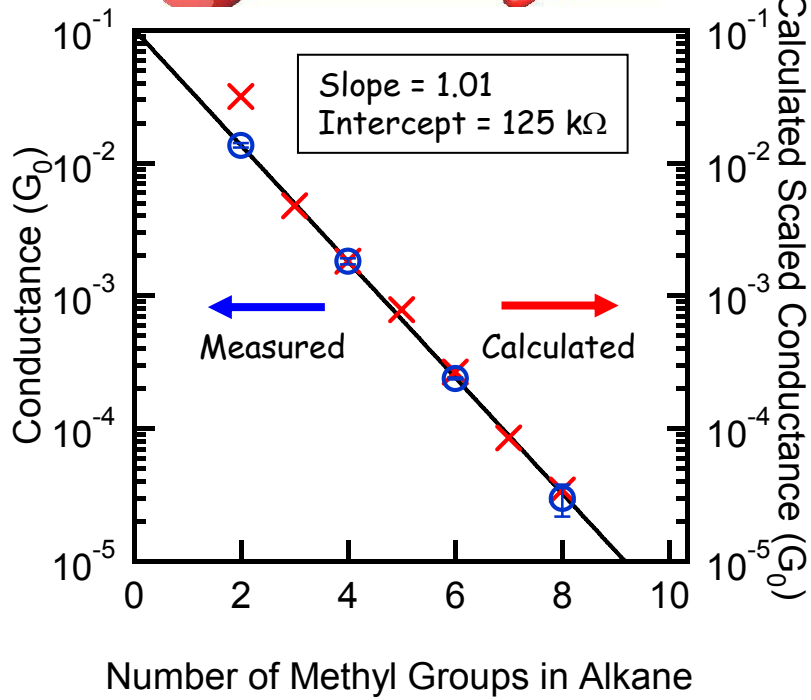
Adam Whalley & Young Suk Park
(Nuckolls Group, Columbia)

Dimethyl Phosphine Linked Alkanes

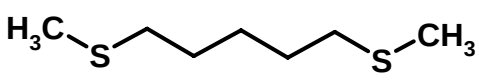


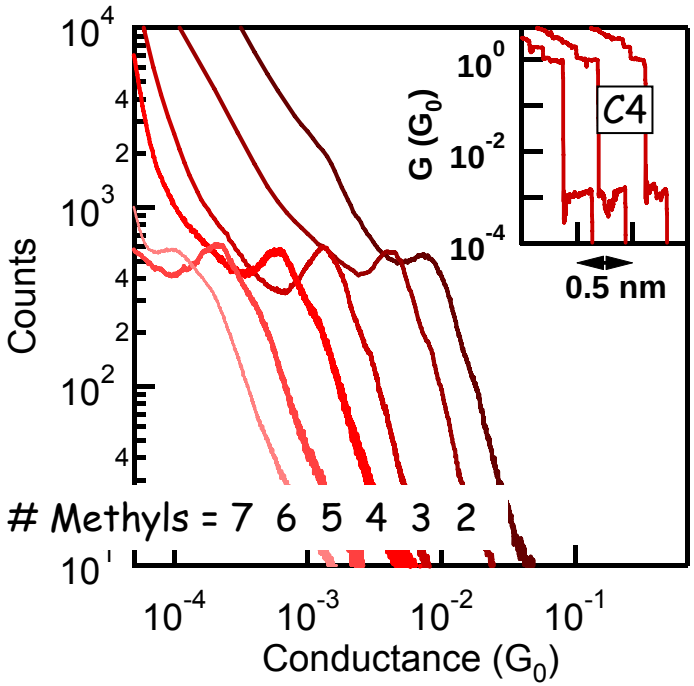


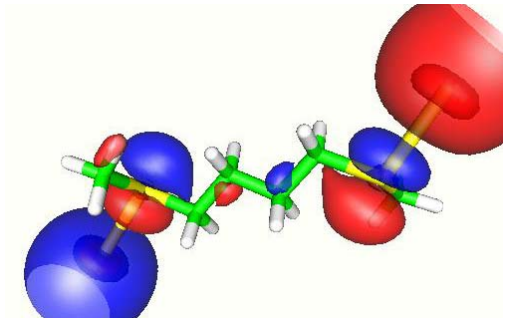


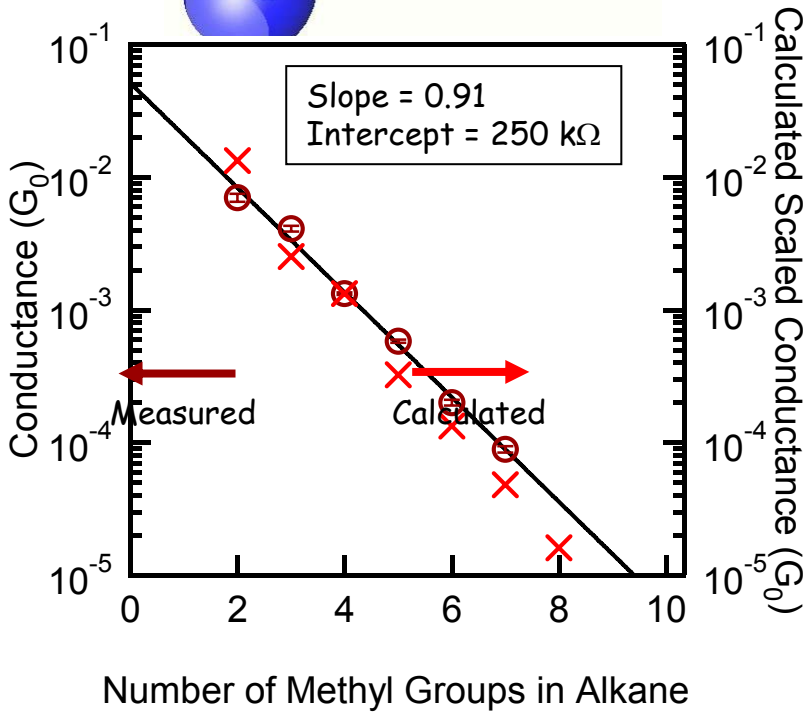


Methyl Thiol Linked Alkanes

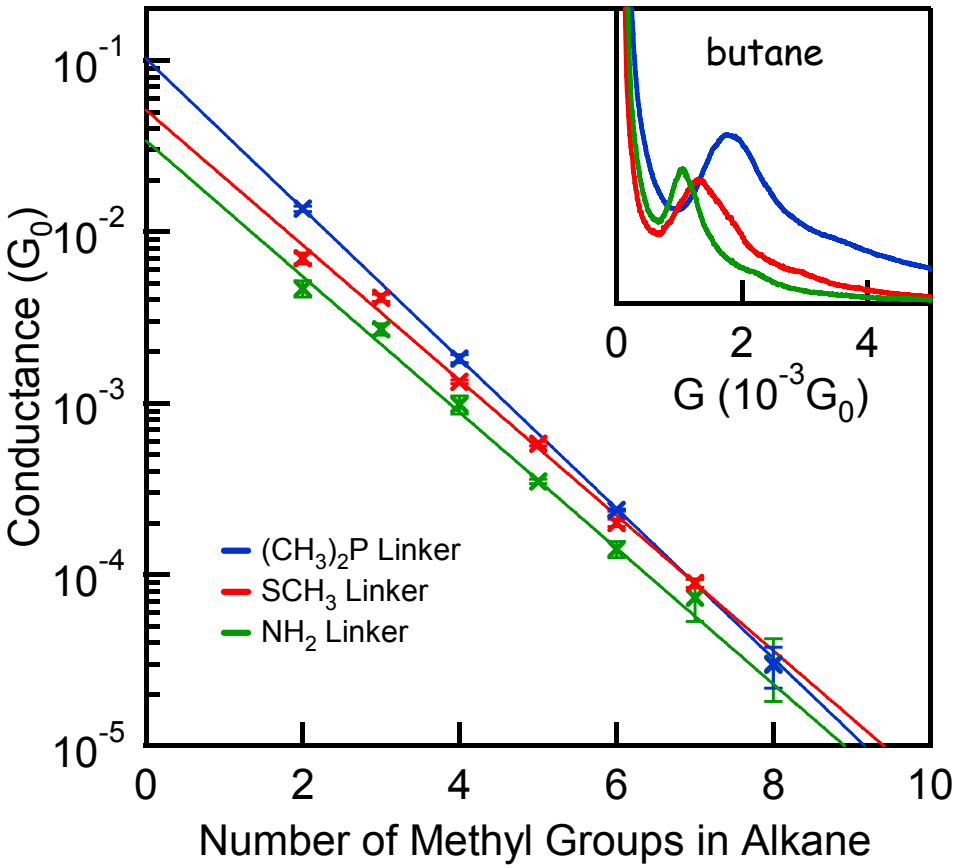








Donor-Acceptor Link Groups: Conductance Trends



Phosphines:
Contact Resistance = 125 kΩ
Link bond energy: 1.0 – 1.2 eV

Thioether:
Contact Resistance = 250 kΩ
Link bond energy: 0.5 – 0.7 eV

Amine:
Contact Resistance = 430 kΩ
Link bond energy: 0.6 – 0.8 eV

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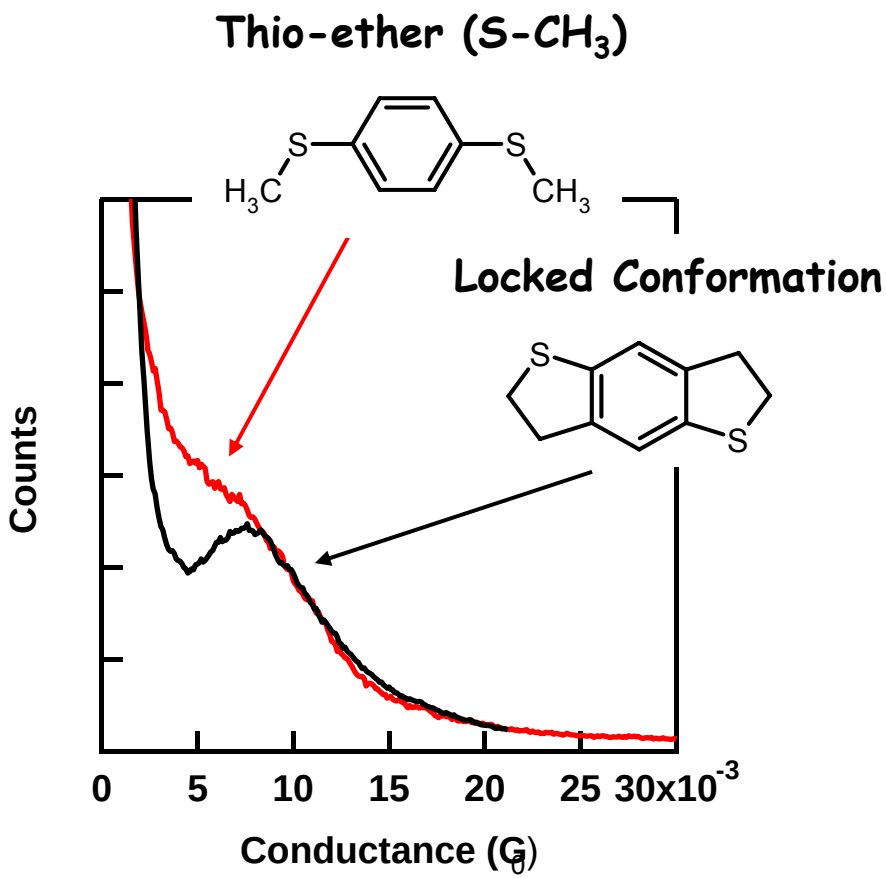
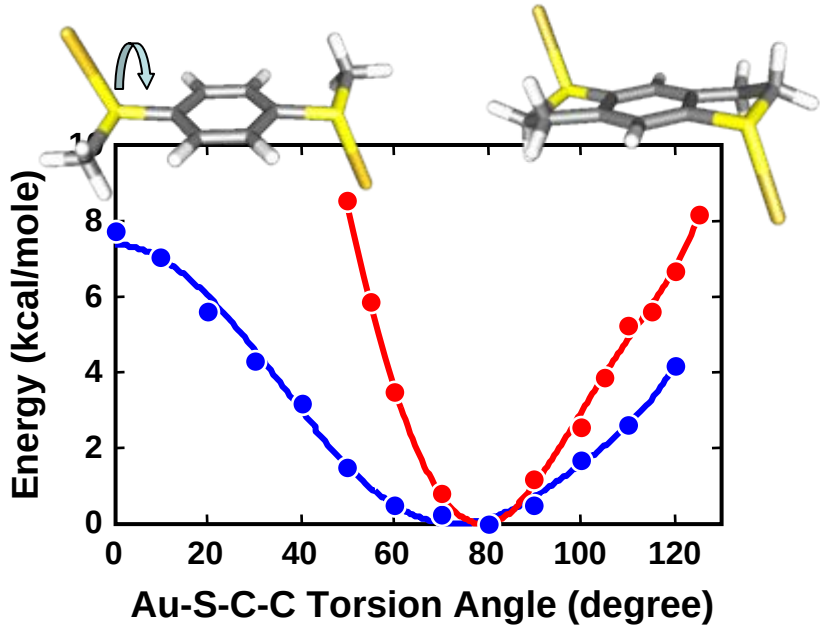
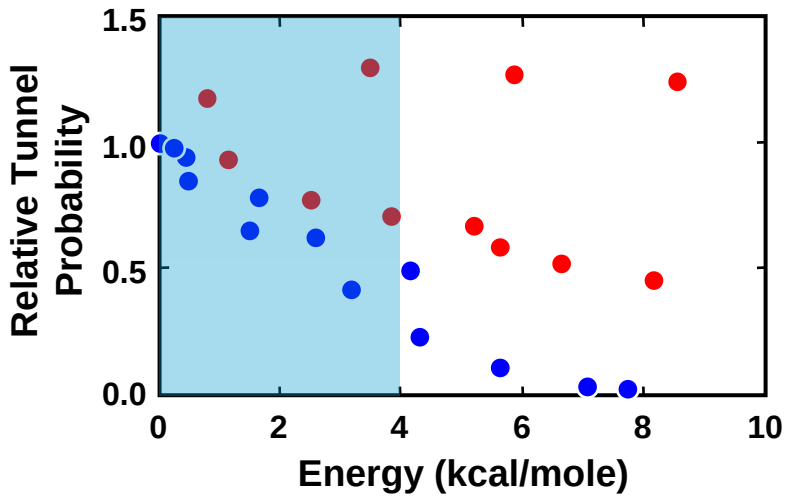
Control of Junction Conformation







Park, Whalley, Nuckolls, Hybertsen, Steigerwald, & Venkataraman
In Preparation

Summary & Outlook

Amine Linked Single Molecule Circuits

- Systematic trends in single molecule conductance correlate with molecular properties
- Emerging picture of bonding, electronic coupling, junctions, etc.

Donor-Acceptor Link Bonding Motif

- Generalizes to PMe2 & SMe
- Case study in control of junction structure

Fundamental Challenges

- Identify a link that combines selectivity with stronger binding
- Prediction of single molecule conductance (Talk by S.Y. Quek)