Amine Linked Single Molecule Circuits: Systematic Measurements & Understanding

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Collaborators

Columbia: Latha Venkataraman, Michael Steigerwald
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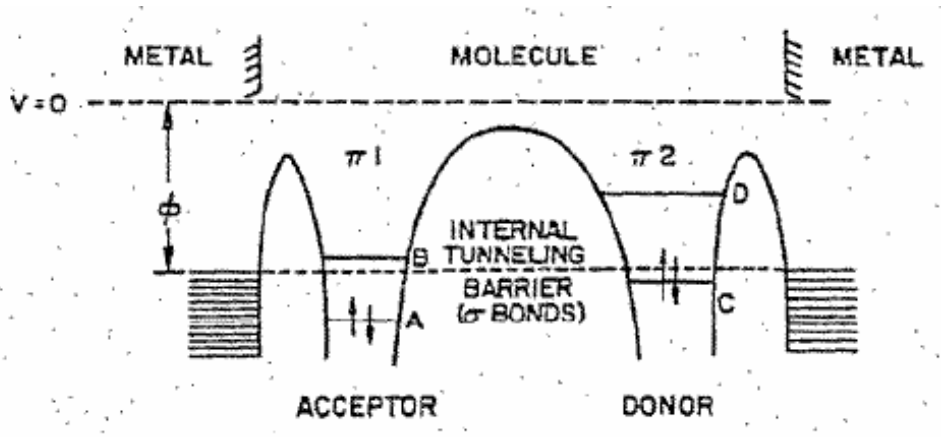
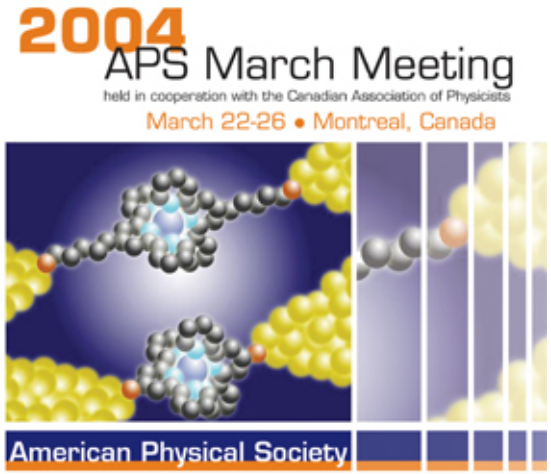
Molecular Foundry (LBNL): Su Ying Quek, Jeffrey Neaton
H.K. Choi, Steven Louie

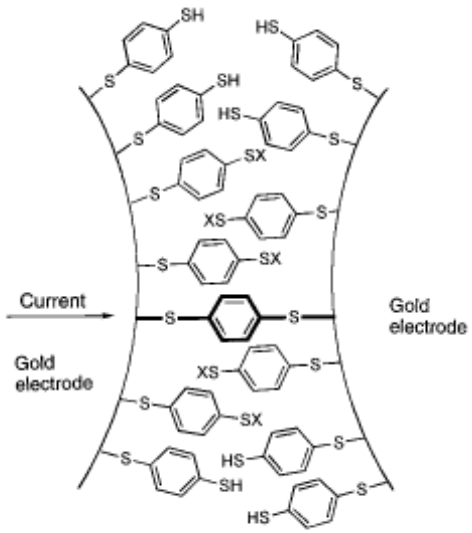
Funding: NSF, NYSTAR, DOE

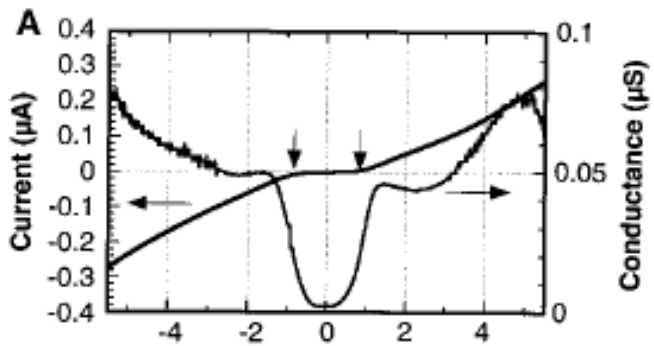
Vision: Functional Molecular Devices



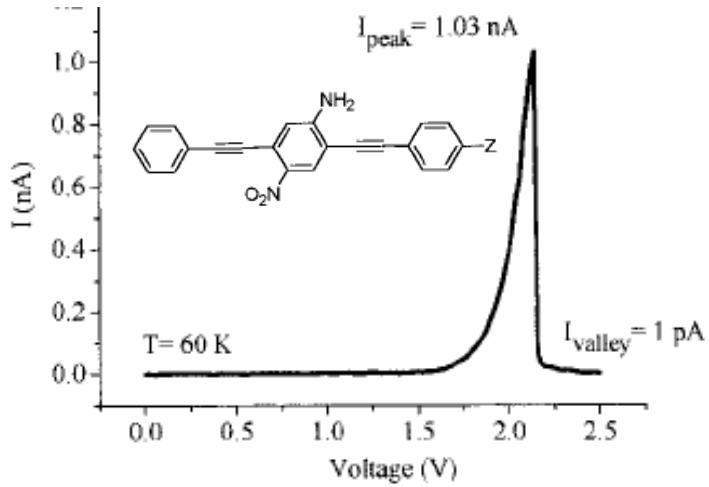
Aviram & Ratner, Chem Phys Lett, 1974







Reed et al, Science, 1997



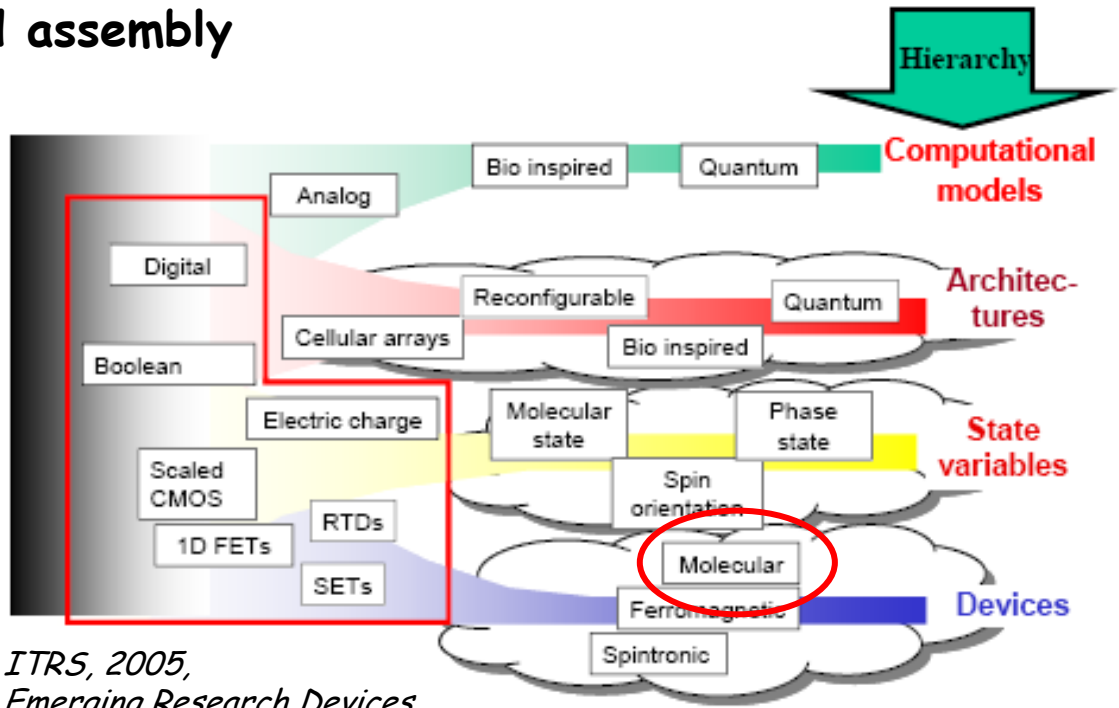
Chen, Reed, Rawlett & Tour, Science, 1999

Nanoelectronics Research Initiative

Research Vectors

- Alternate state variables
- Non-equilibrium systems
- Novel energy transfer
- Nanoscale thermal design
- Directed assembly

Active role for functional molecular devices ?

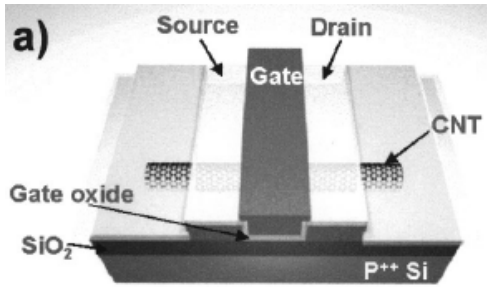


ITRS, 2005, Emerging Research Devices

Figure 51 A Taxonomy for Nano Information Processing

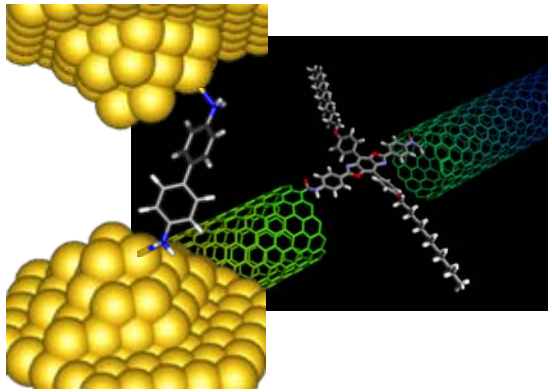
Scope of Materials

Carbon Nanotubes



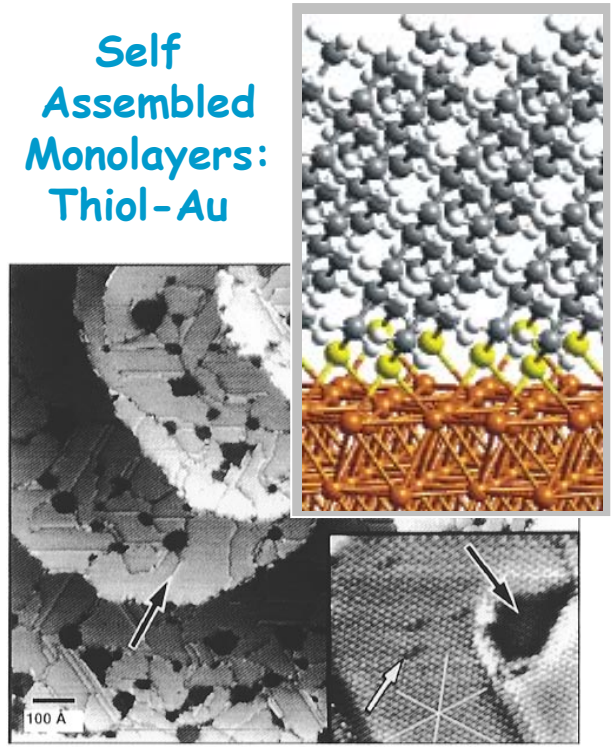
Avouris, et al, Proc. IEEE, 2003

Single Organic Molecule



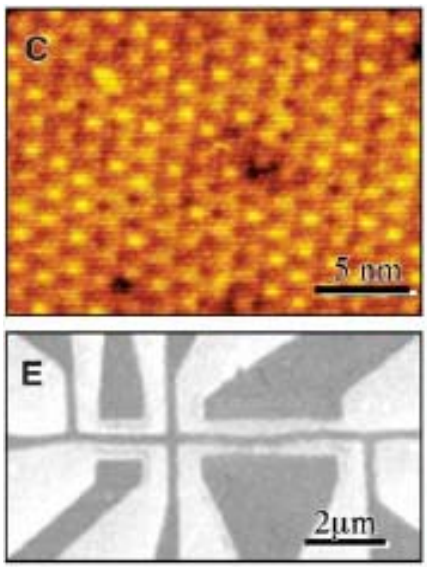
Venkataraman, et al, Nature, 2006
Guo, et al, Science, 2006

Self Assembled Monolayers: Thiol-Au



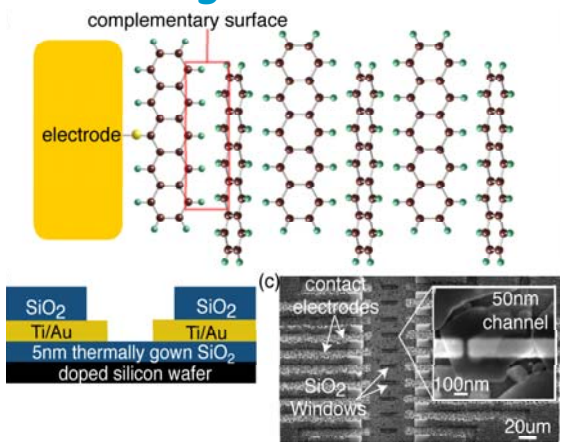
Poirier, Chem Rev, 1997
Fischer, et al., Langmuir, 2003

Ultrathin Graphite



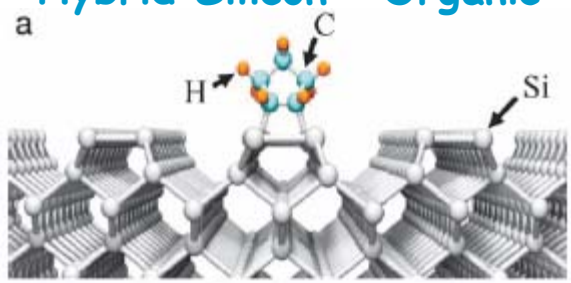
Berger, et al, Science, 2006

Organic Films



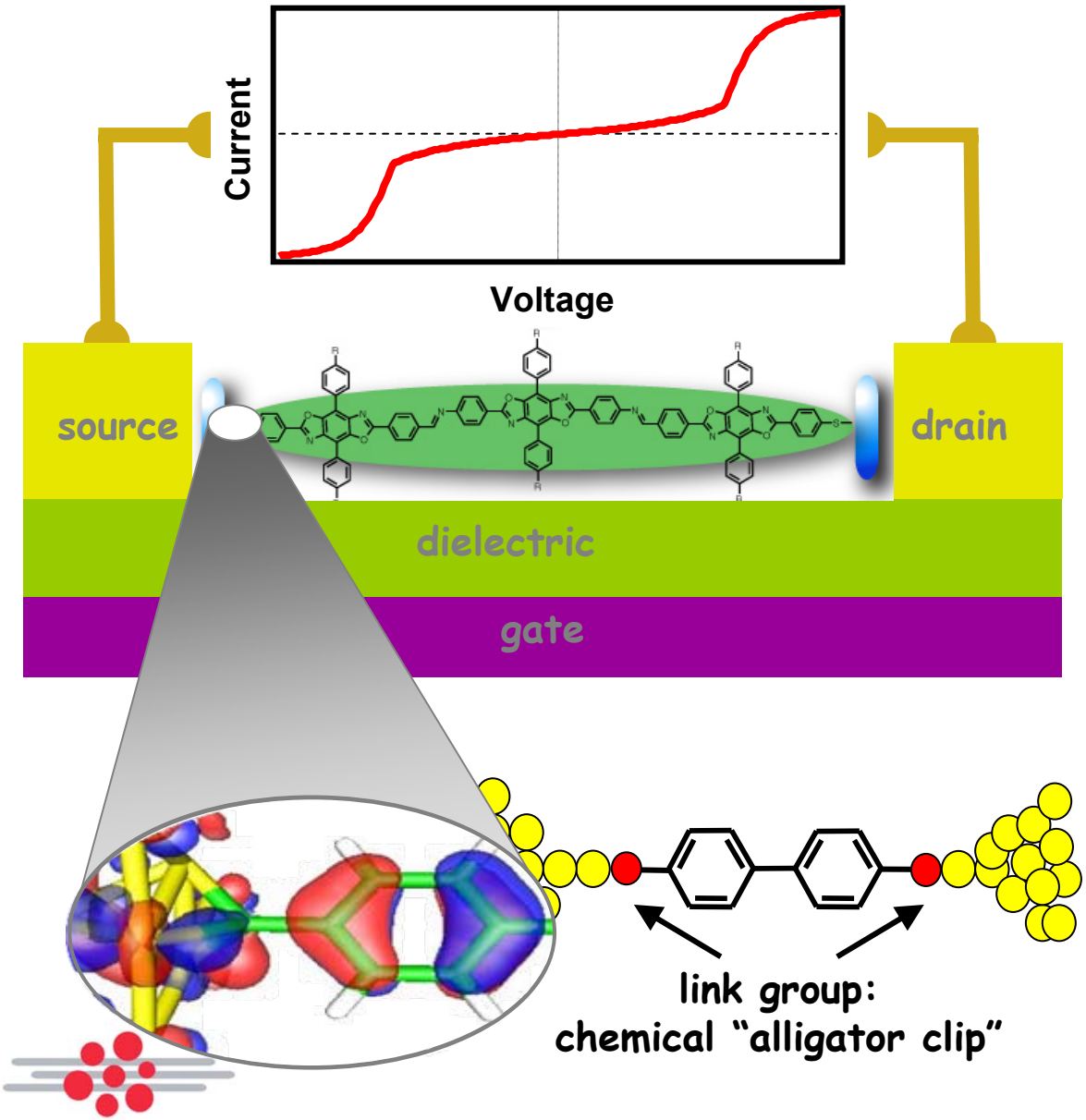
Tulevski, et al, JACS 2006

Hybrid Silicon – Organic



Guisinger, Yoder & Hersam, PNAS 2005

Probing Single Molecule "Devices"



Transport Questions

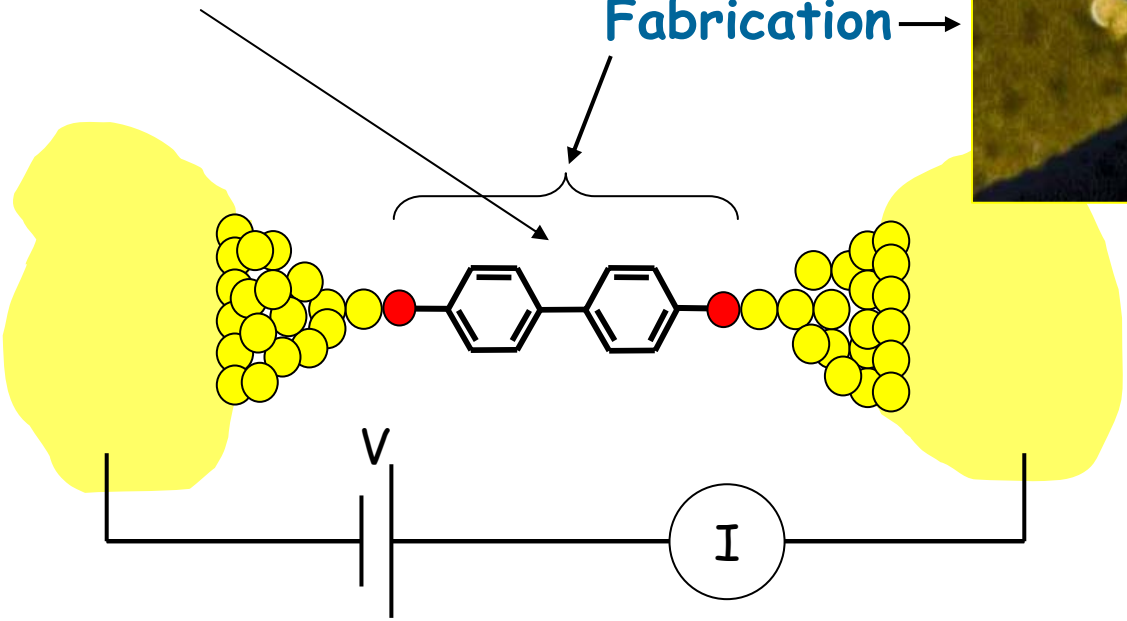
- Low bias conductance
- Non-linear conductance
- Gate control

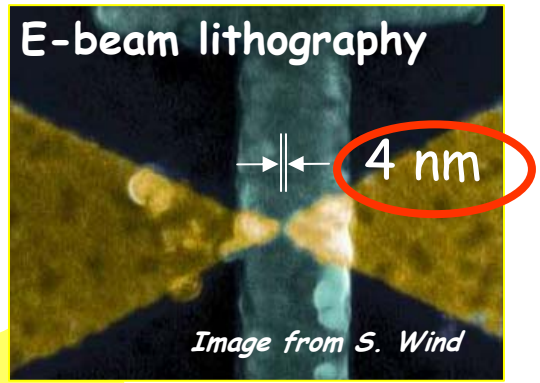
Structure-Property Questions

- Molecule-metal bonding
- Electronic coupling
- Energy level alignment

Where is the Experimental Challenge?

Biphenyl: ~ 7 Å

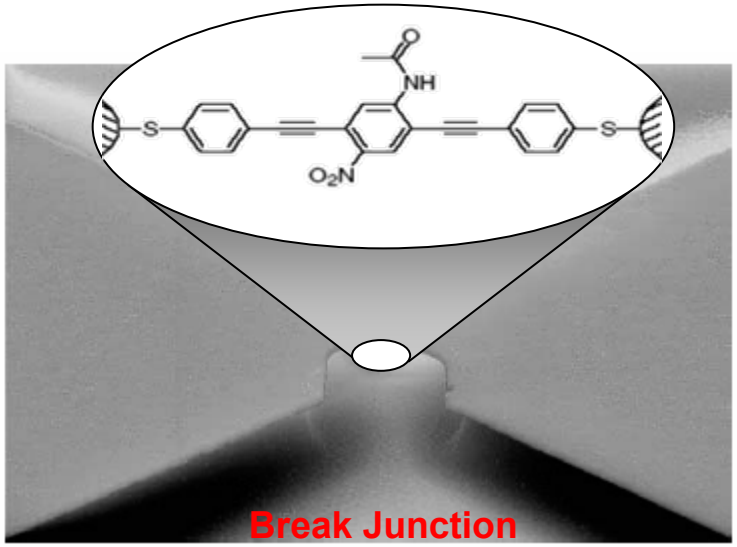




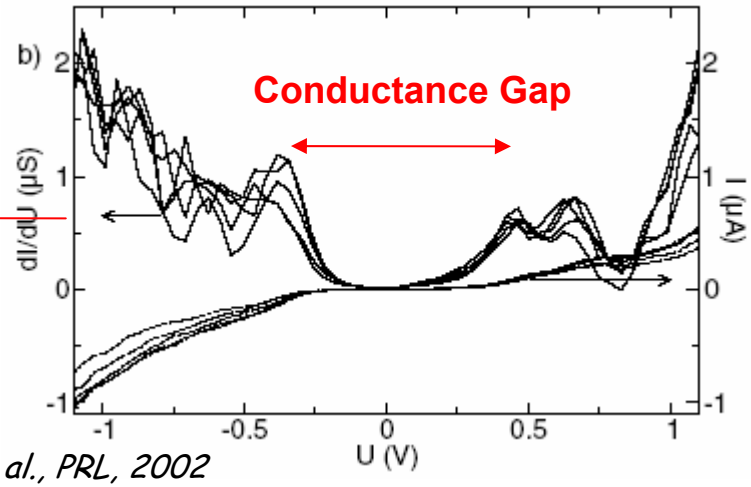
Key Experimental Issues:

- Reproducibility
- Clear Molecular Signatures

Molecular Scale Conduction

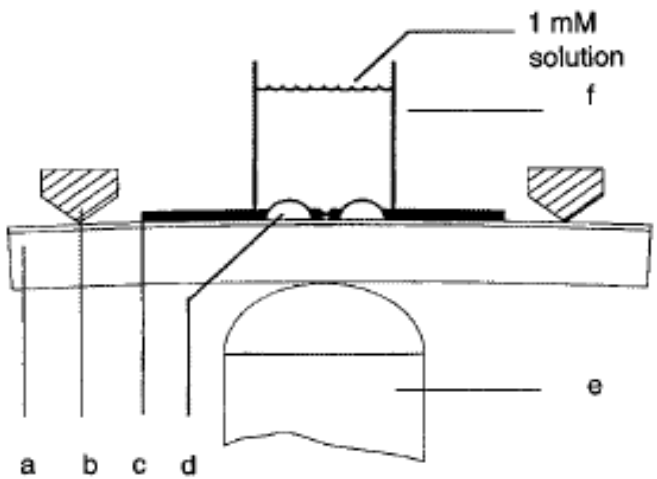


1 MΩ

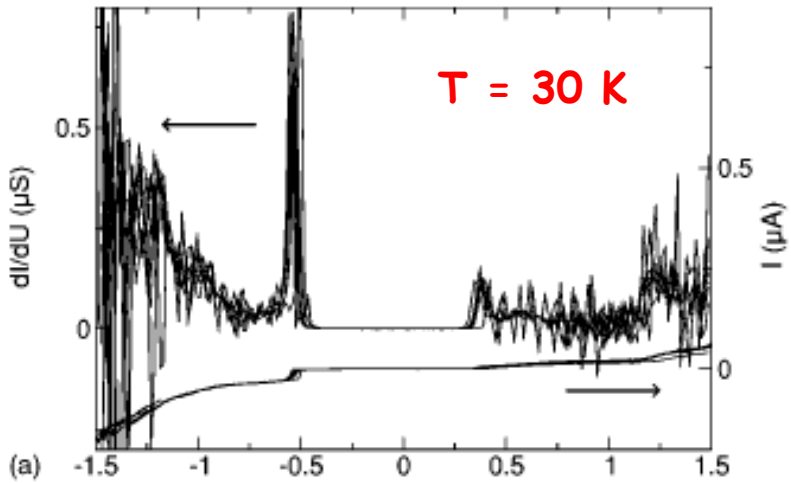


Reichart, et al., PRL, 2002

$G \ll G_0 = 2e^2/h = 1/13k\Omega$

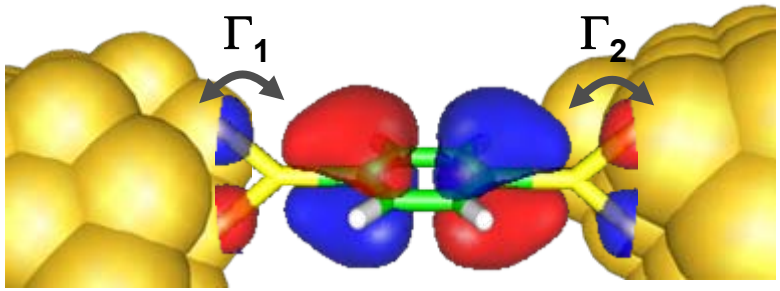


Reed, et al., Science, 1997

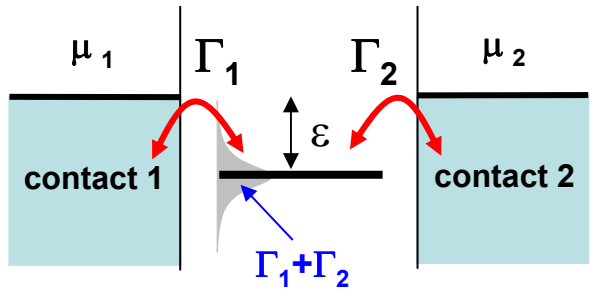


Reichart, et al., APL, 2003

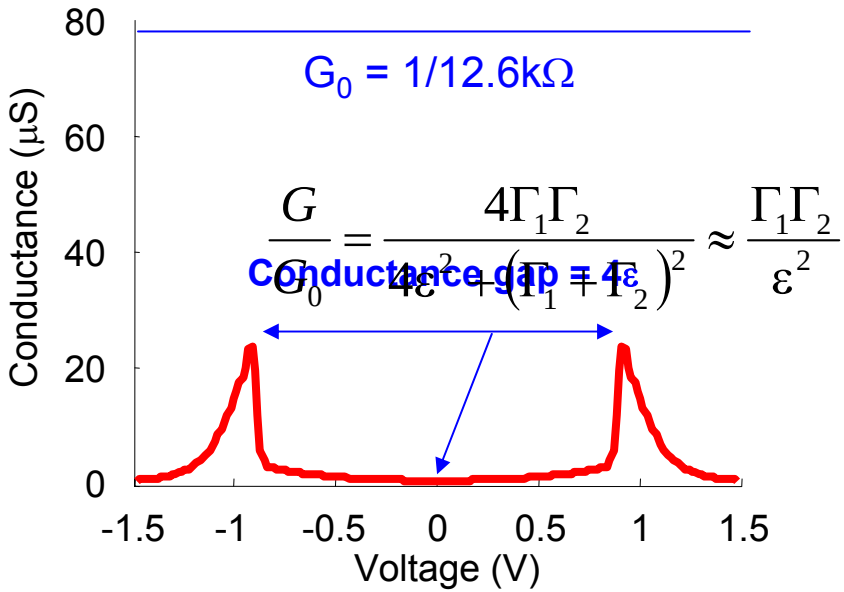
Resonant Tunneling Via Frontier States



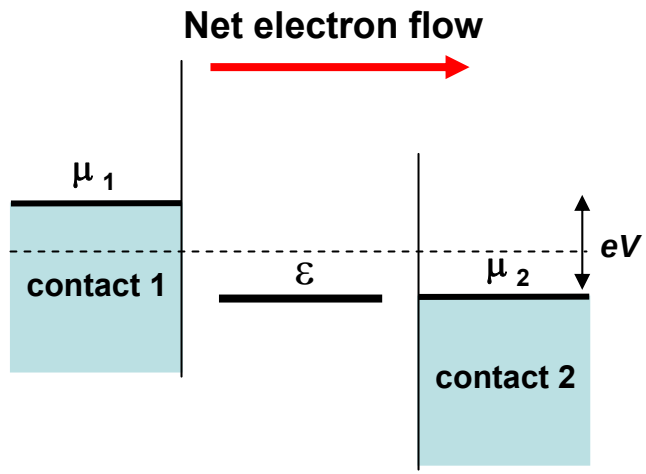
Zero Applied Bias



Weak Coupling: $\Gamma_{1,2} / \varepsilon << 1$



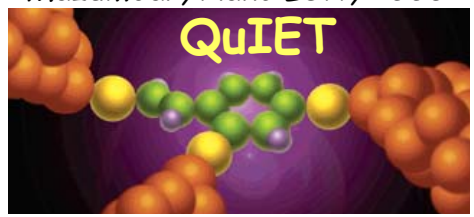
Positive Applied Bias



Molecular Electronics: Post CMOS Technology ?

Will functional single-molecule devices ever be the core of an information processing technology ?

Cardamone, Stafford & Mazumdar, Nano Lett, 2006



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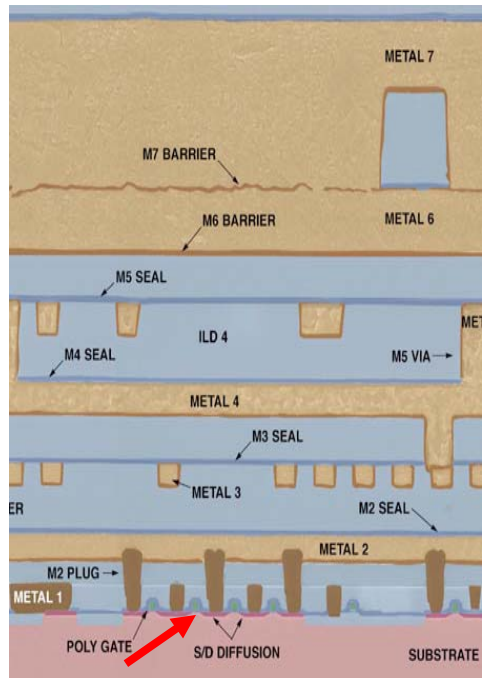


Narrow Assessment:

- For 2020, prototype now
- No compelling inventions to date –
  - Significant issues with switching concepts
  - Alternate architectures wide open

Broad Assessment:

- Investment in fundamental understanding of heterogeneous molecular systems is critical:

  electronics, sensors, energy, bio-interface, ….

"A knowledge gap exists between materials behaviors and device functions."

- ITRS, 2005:,Emerging Research Devices

Molecular Electronics: Fundamental Questions

Conductance phenomena:

- Molecular structure–conductance relation ($G \rightarrow G_0$?)
- Role of electrode-molecule contacts ("alligator clips")
- Coupling to a molecular "state variable" (charge, spin, conform.)

Assembly of single molecule circuit elements:

- Reproducible electrode-molecule bonding motifs
- Distinguishable bonding to two (three) terminals
- Assembly of functional molecules in a junction

Characterization of heterogeneous nanostructures:

- Measurement of structure & conductance in a junction

Impact on Electronics:

- Reproducible function (switching, …)
- Compatible with a viable architecture (on/off ratio, …)

Outline

Themes:

- Link Chemistry: control, utility & reproducibility
- Molecule Structure–Conductance Function: mapping "design rules"

Amines: the new alligator clips

Trends: Impact of Molecular Properties on Conductance

DFT Based Conductance Calculations: How Wrong ?

Experiments: Point Contact Technique

Atomic scale junction formation:

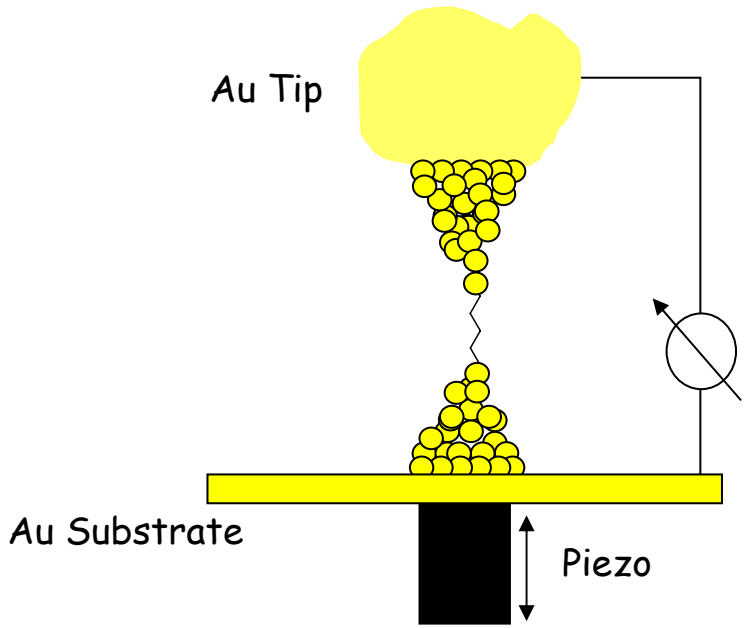
- Calibrated point contact

Junction size varies:

- Continuously during pulling
- Statistically

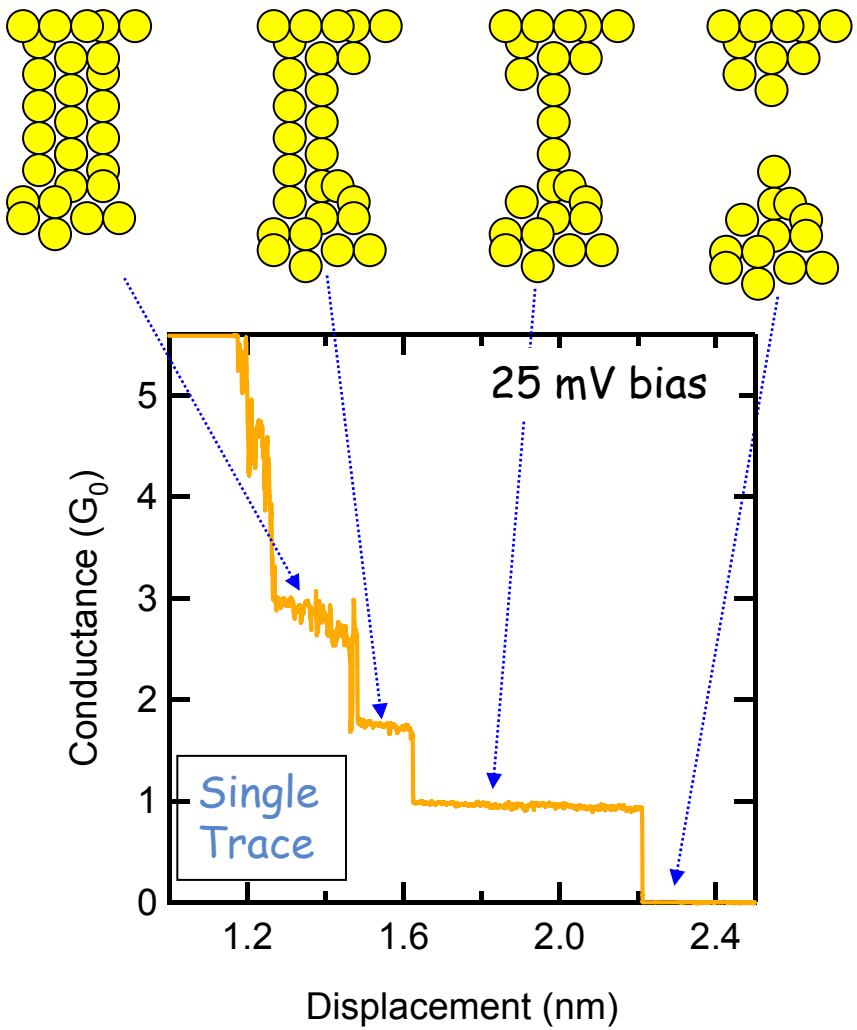
Transport data:

- Thousands of experiments
- Statistical sample



Molecules in solution:
Xu & Tao, Science, 2003

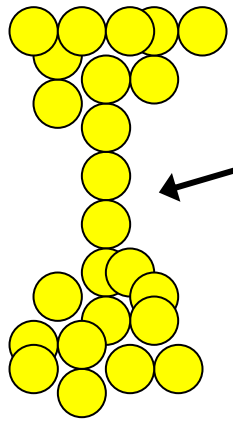
Breaking A Gold Contact



Landauer formalism:

$G = G_0 \times \Sigma t_i$

$G_o = 2e^2/h$ (12.9 kΩ)

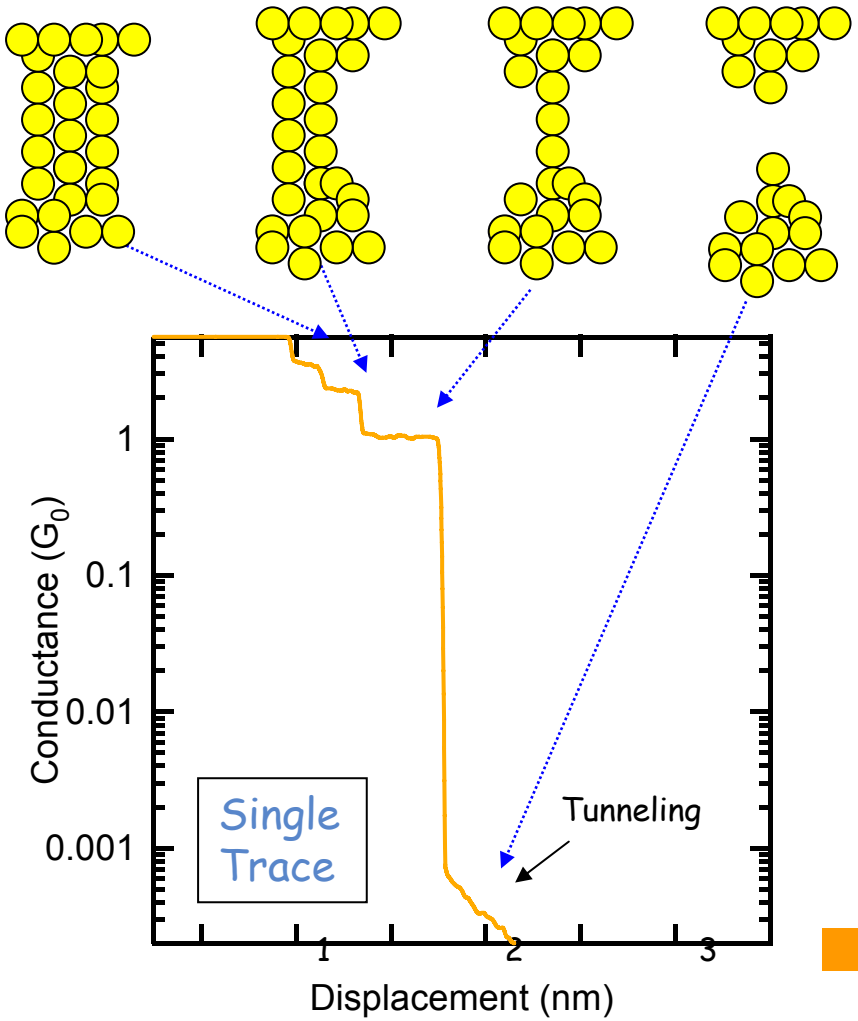


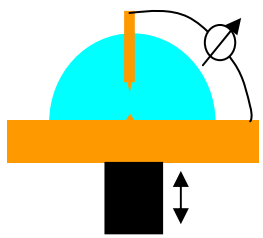
Au single atom chain has only 1 channel → Au 6s

$T(E_F) \sim 1$

H. Ohnishi et al. Nature (1998)
V. Rodrigues et al. PRL (2000)

Data on a Log scale

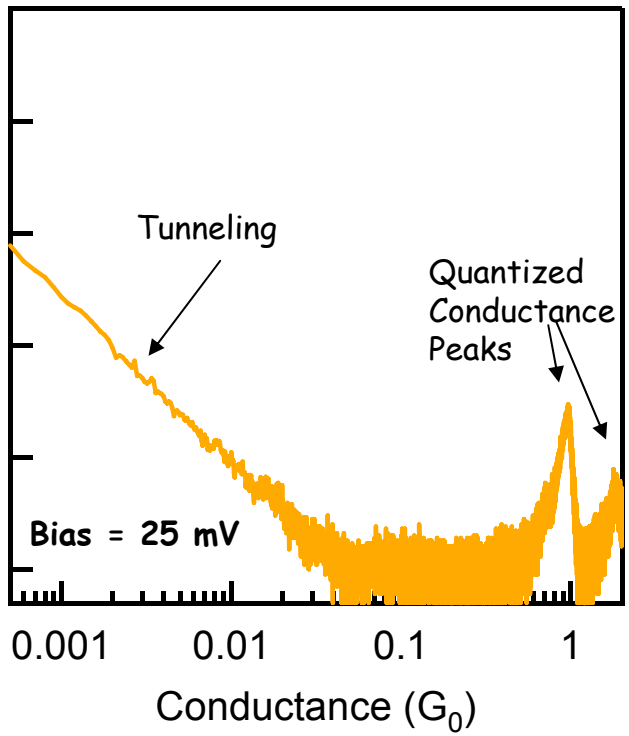




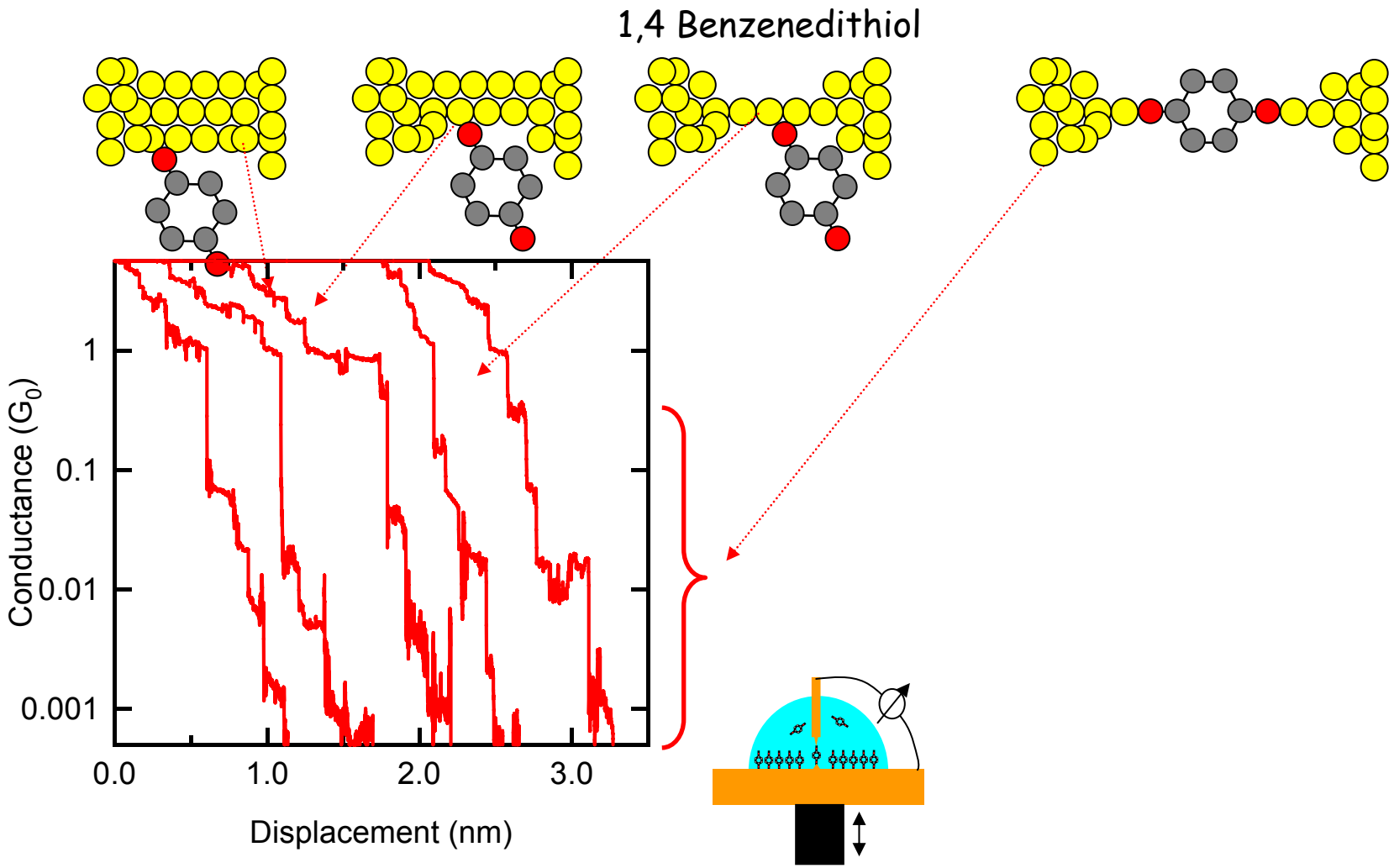
Log Counts

Peaks:
Multiples of $G_o = 2e^2/h$

Histogram:
1000 traces



Dithiols: SH Link Group



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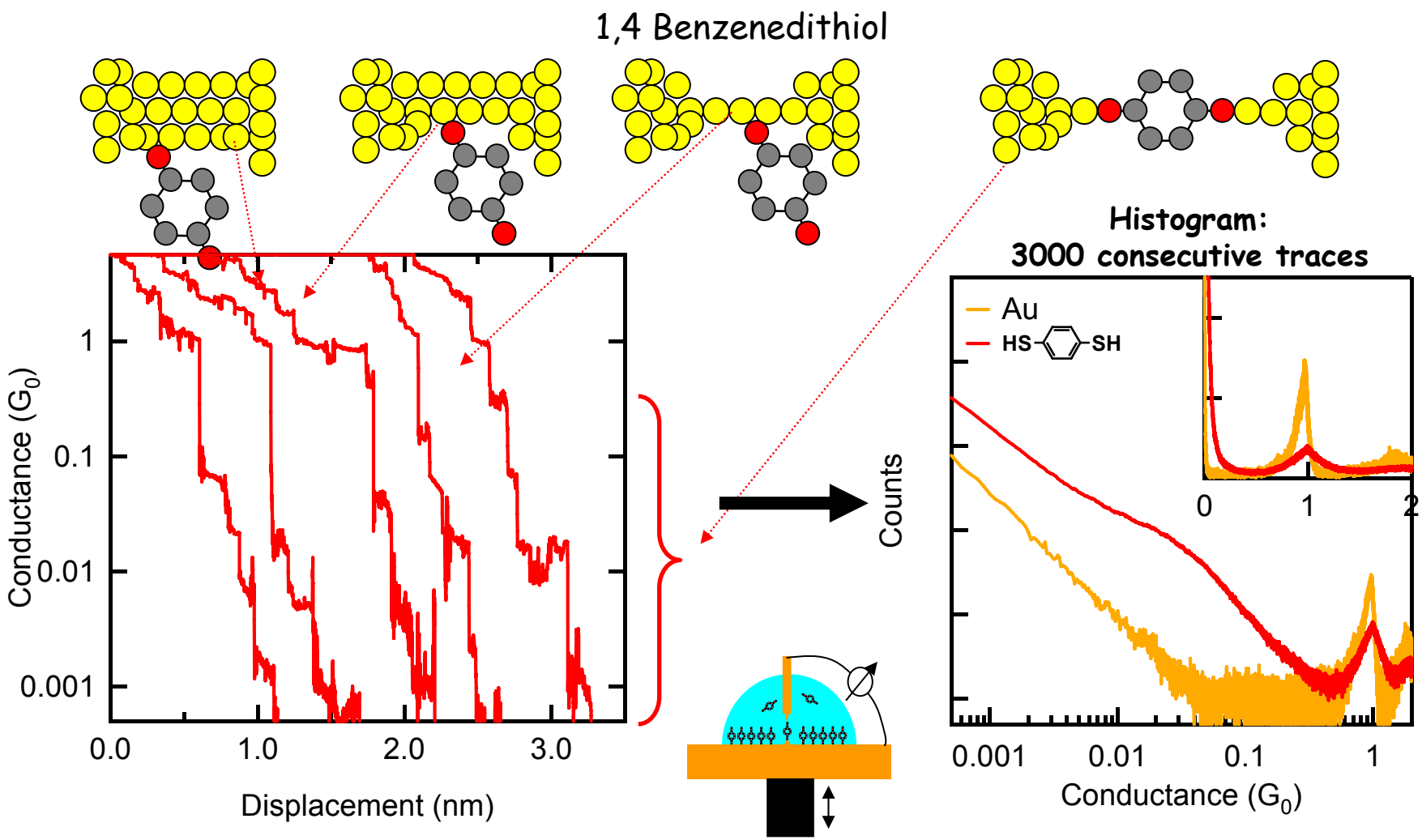
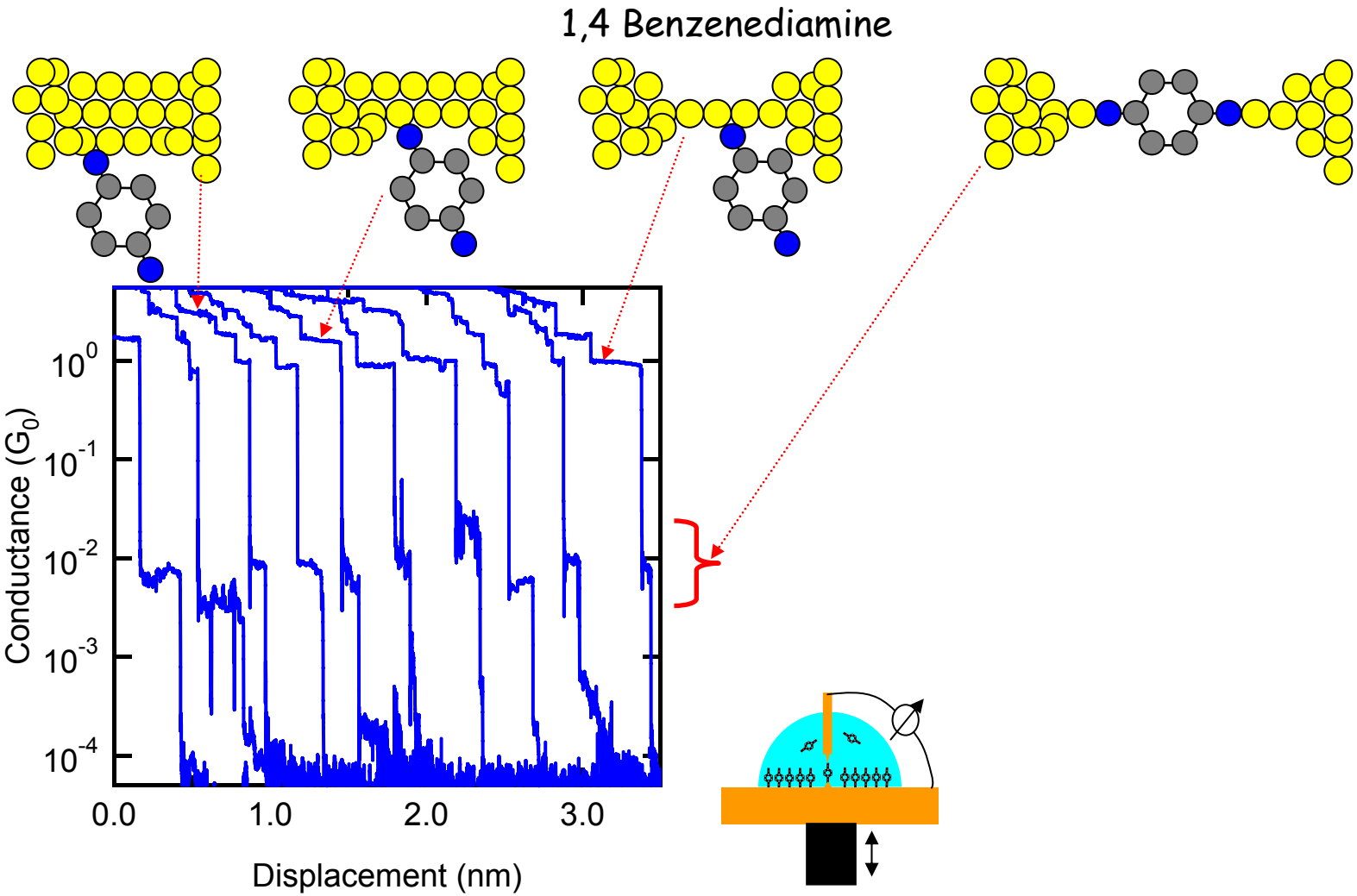


Characteristic benzenedithiol conductance ??

Diamines: NH2 Link Group



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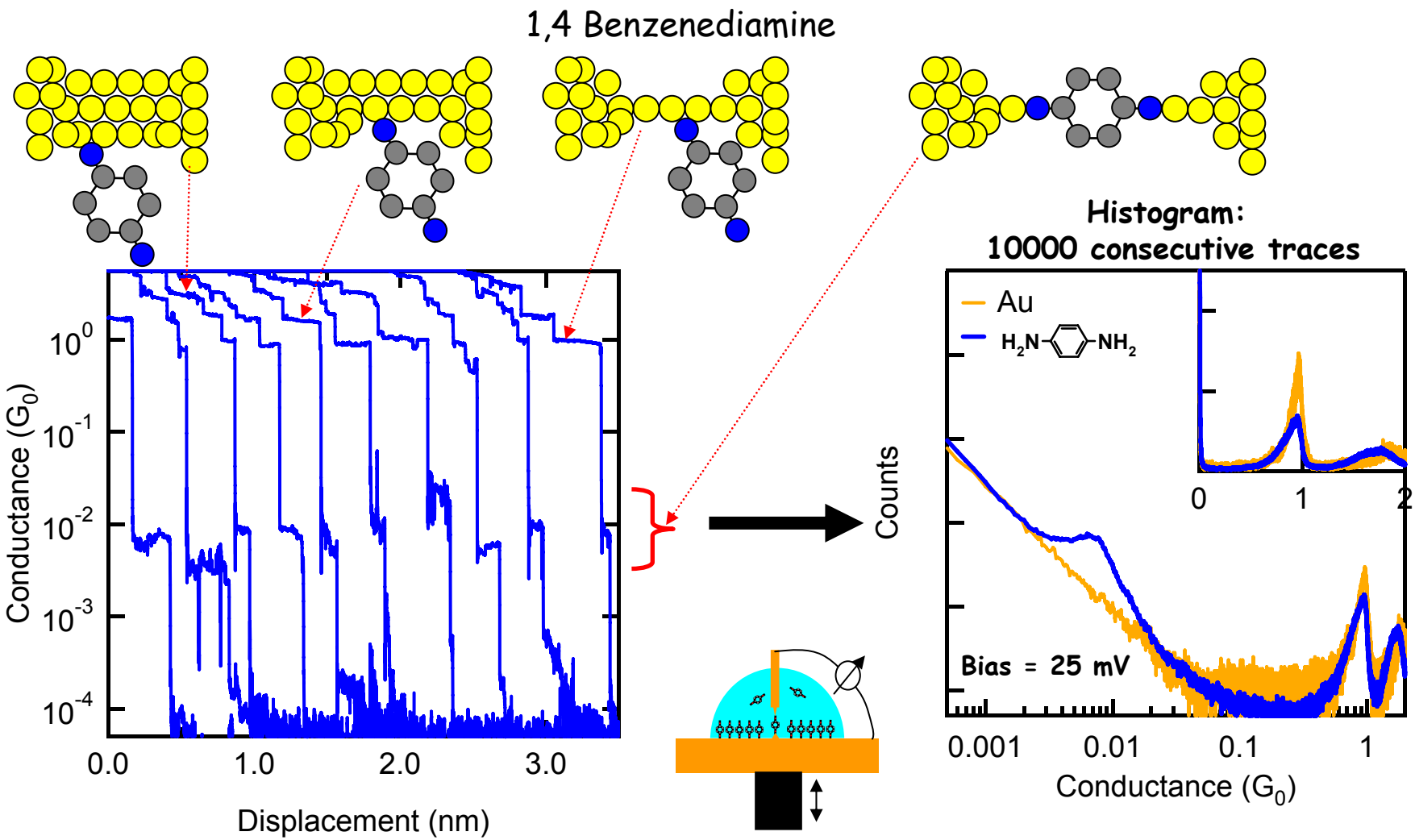
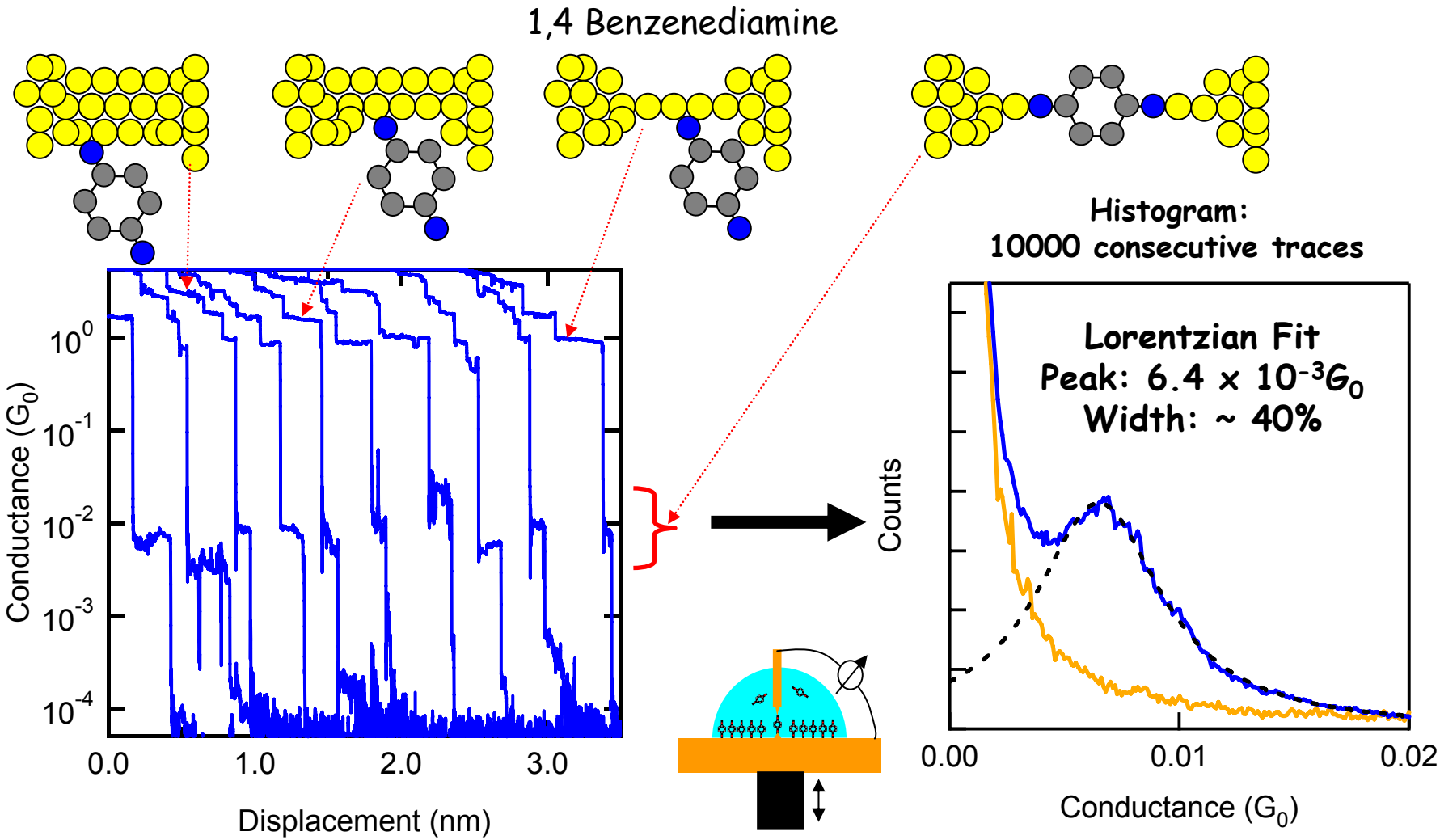


Diamines: NH2 Link Group



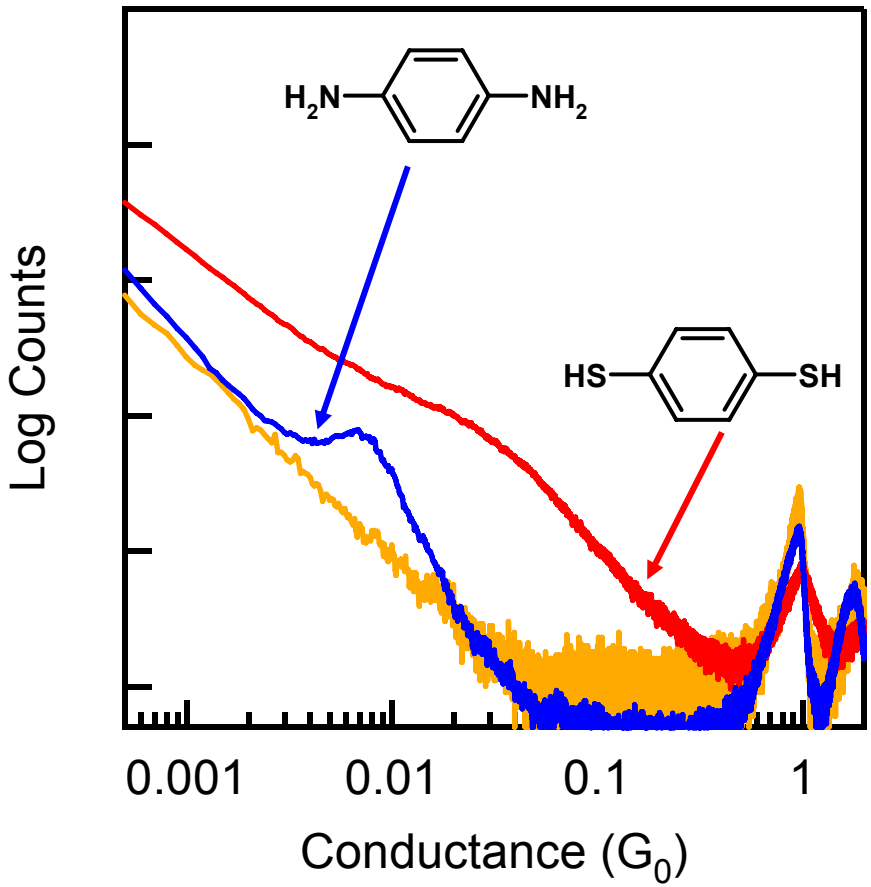
Characteristic Benzenediamine-Au conductance !!

Link Chemistry: A Comparison

Thiols do not give clear molecular signature

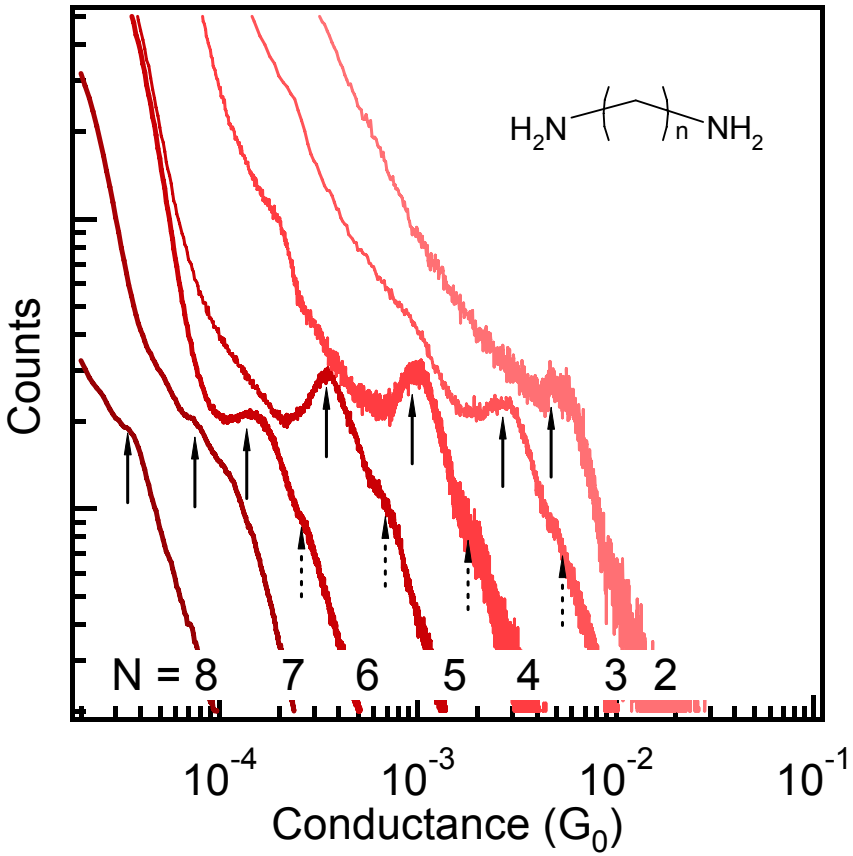
Histograms constructed without any data selection

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

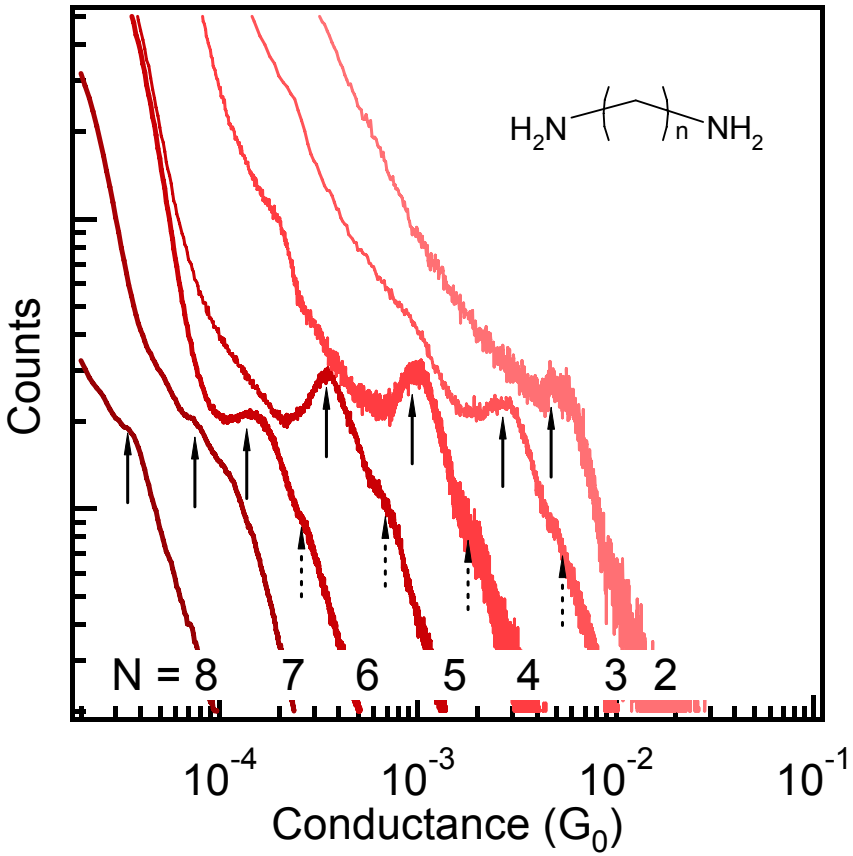
5 H_2N–NH_2

6 H_2N–NH_2

7 H_2N–NH_2

8 H_2N–NH_2

Conductance vs Length



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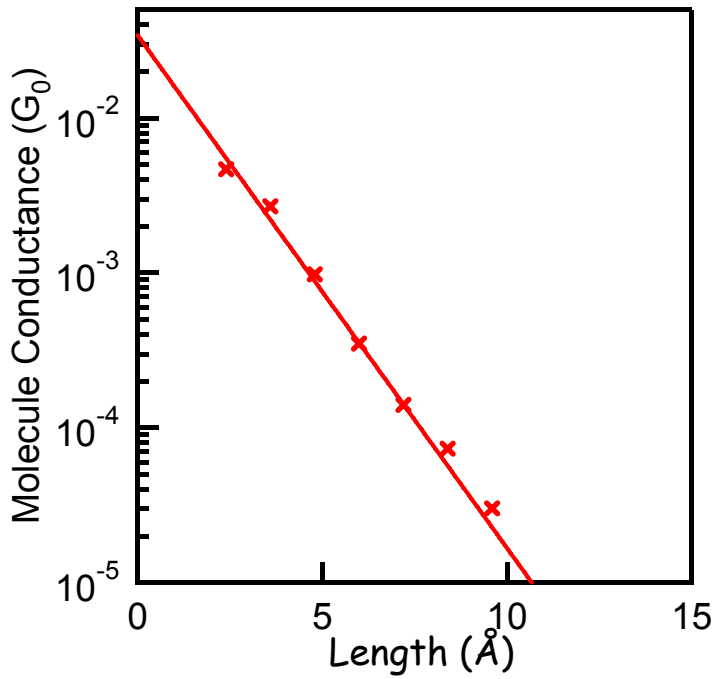
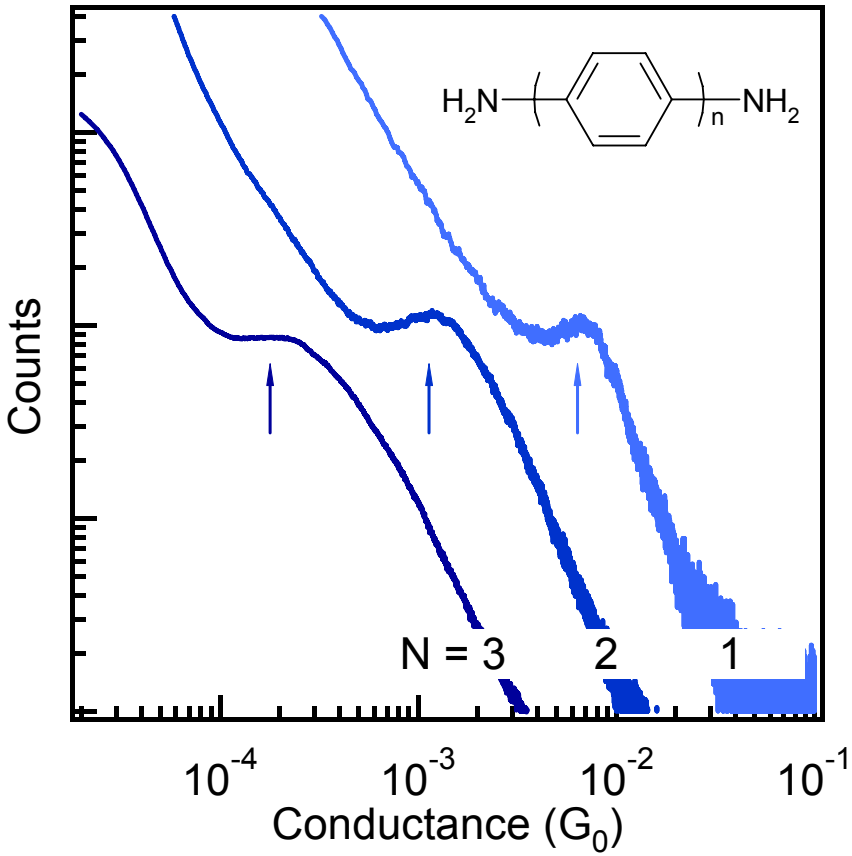


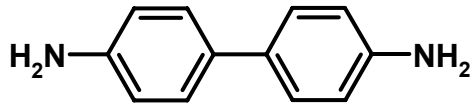
Conductance of Polyphenyls

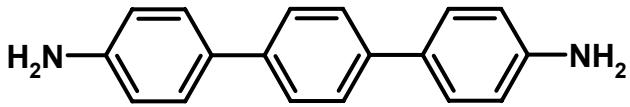


Data offset vertically for clarity

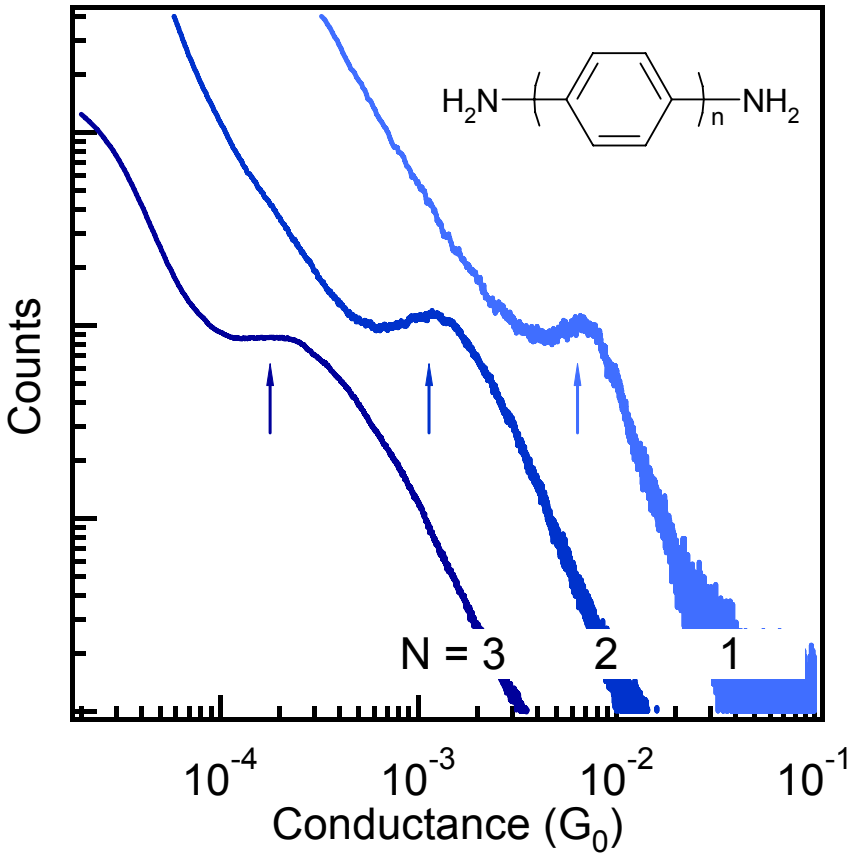
N: Phenyl Chains Attempted

1

2 

3 

Conductance vs Length



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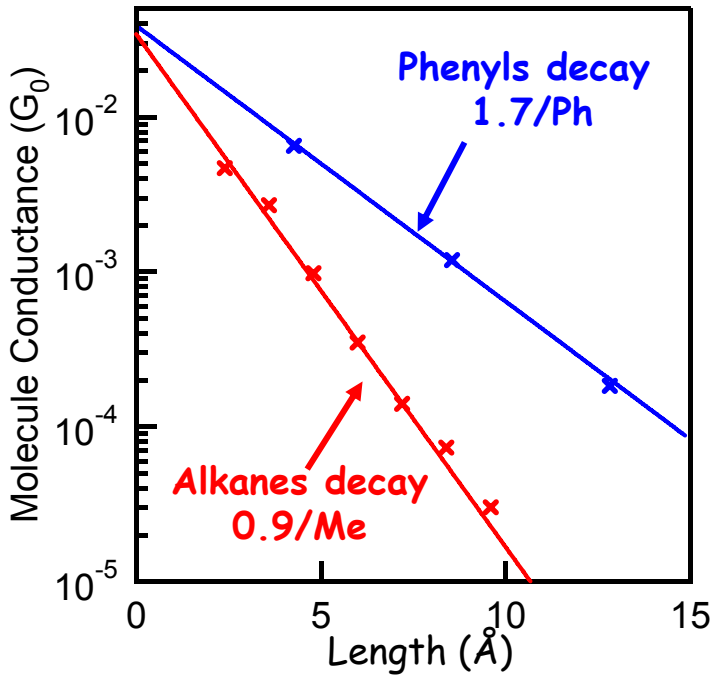


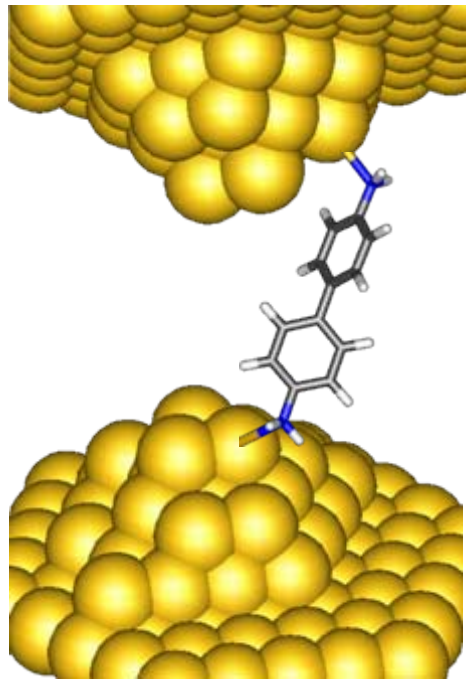
Direct evidence: Non-resonant tunneling

Why Do Amine-Gold Linkages Work ?

How do Amines bond to gold in the junction ?

Are the links stable & flexible ?

Why is the electronic coupling reproducible across different classes of molecules ?



Electronic Structure Tools Used

DFT Studies

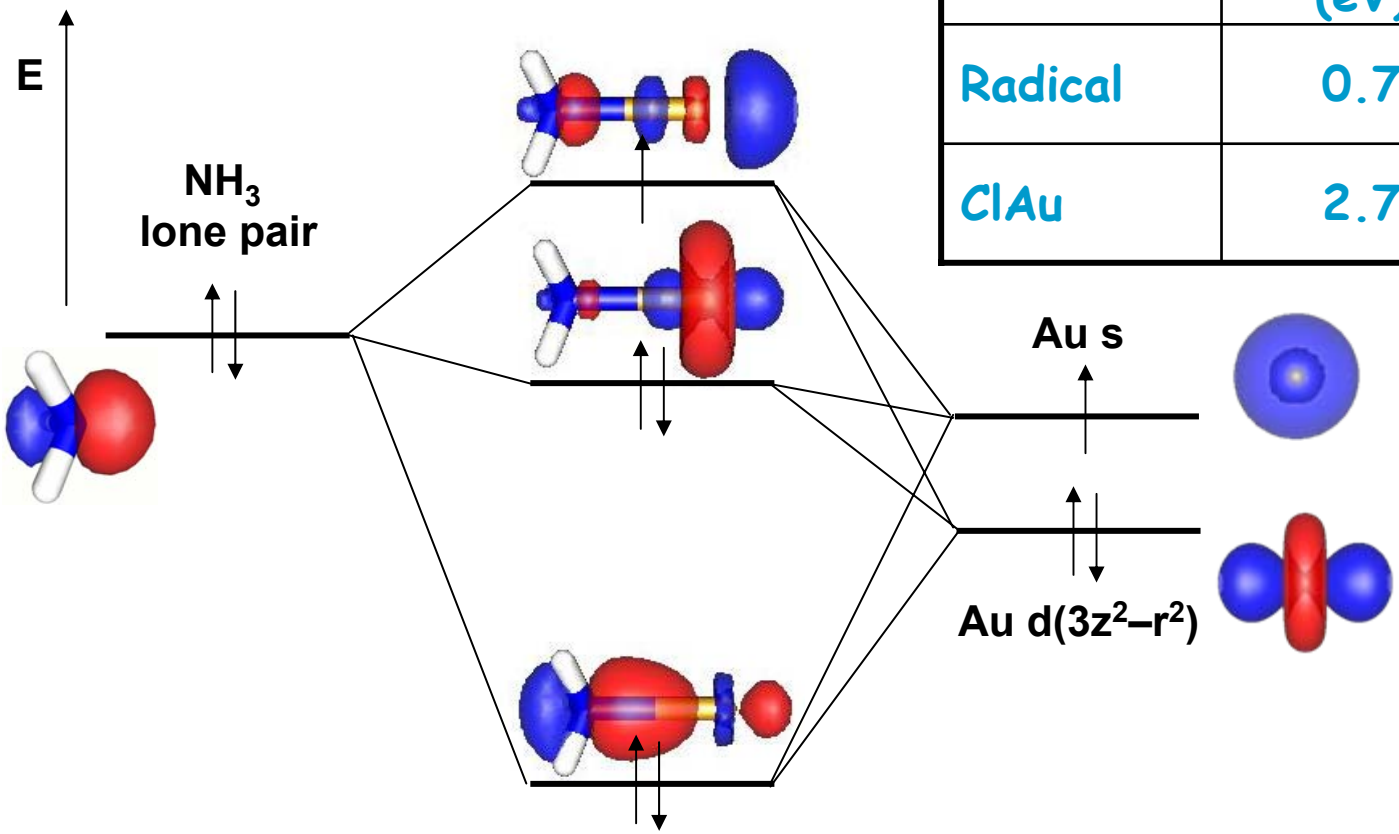
- Molecules: Jaguar 5.0 (gaussian basis all electron)
- Periodic slab models: Abinit v4.2 (planewave pseudopotential approach)
- Gradient corrected DFT (Perdew, Burke & Ernzerhof)

Transmission Calculations

- Pseudopotentials
- Numerical local orbital basis set (SIESTA)
- DFT-LDA
- Boundary matching, scattering theory
- Collaboration w/ Molecular Foundry

Character of Bonding: Au – Ammonia Example

Au Binding	Energy (eV)	d-Au-N (Å)
Radical	0.7	2.28
ClAu	2.7	2.14



Quantum chemistry study:

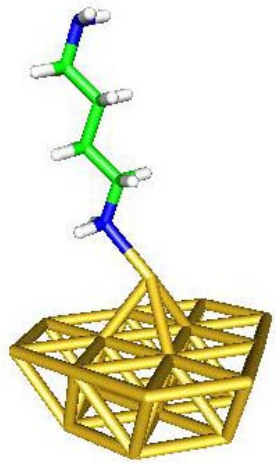
Radical Au binding: 0.78 eV

(Lambropoulos, Reimers & Hush, 2002)

Summary of Au – Amine Bonding

Preferential bonding to undercoordinated Au sites

- Butane diamine binding to Au(111):
  - Flat surface: no binding
  - Au adatom: 0.4 – 0.5 eV



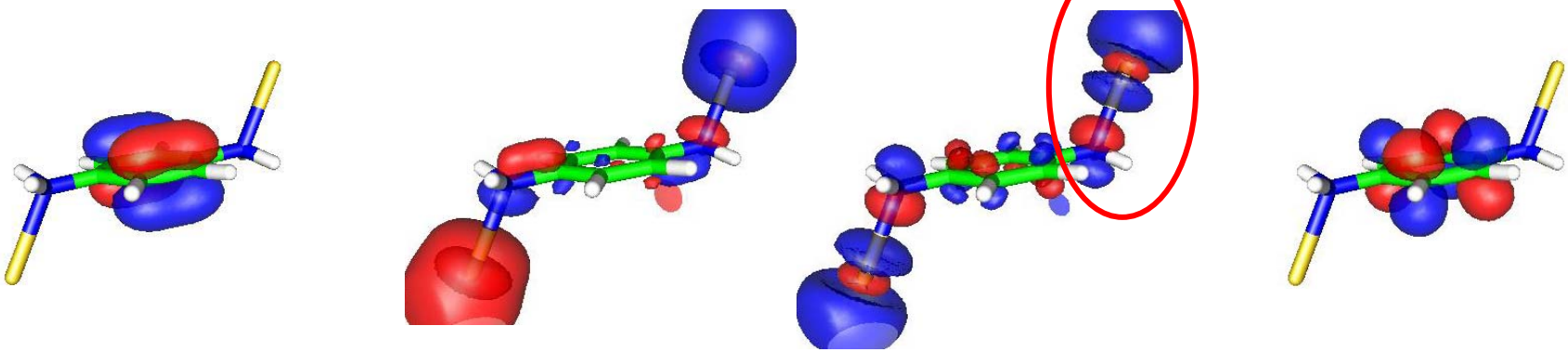
Consistent with passivation of Au nanoparticles by amines

Ad-atom properties

- S-state less constrained
  - more available for coupling
- Slightly positive
  - reduces workfunction
- Supports more charge transfer from N lone pair

Au Coupled Benzenediamine: Frontier Orbitals

Gateway state



– 2.9 eV
Occupied
phenyl π

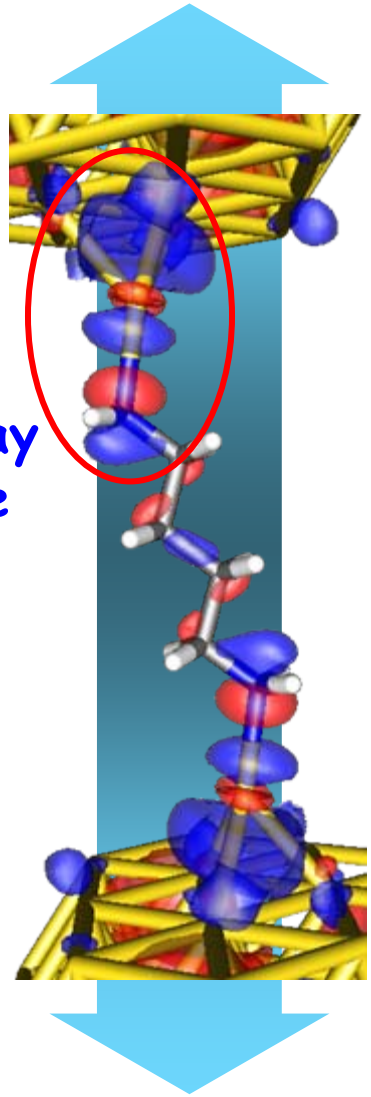
– 0.15 eV
HOMO

+ 0.15 eV
LUMO

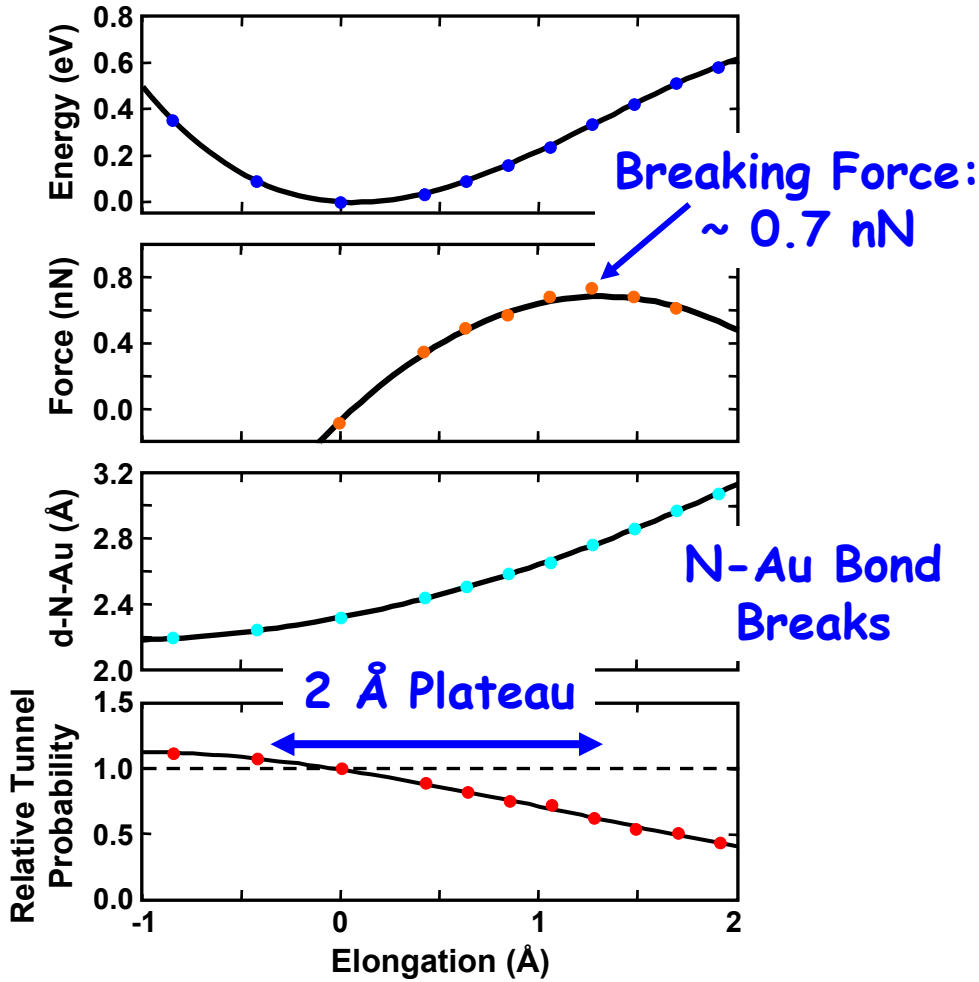
+ 2.4 eV
Empty
phenyl π

Near mid-gap
Au s – N lone pair orbital
Tunnel coupled through π system
→ small gap
→ bridge coupling 2t

Junction Evolution

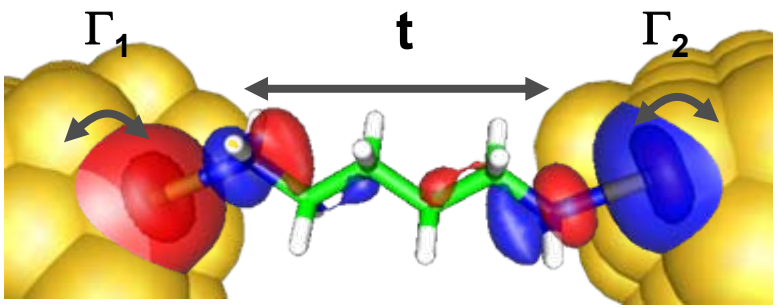


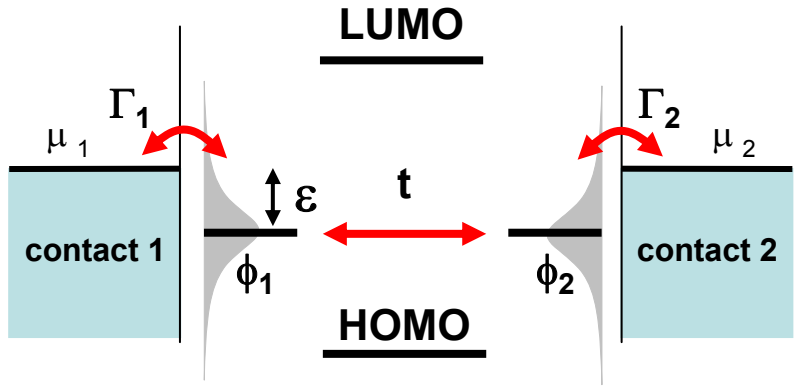
Gateway state



4 ML 2x2 periodic slab model

Conductance: Tunnel Coupling Via Gateway States





Low Bias Conductance

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

$$t \ << \ \Gamma_1, \Gamma_2, \varepsilon$$

Donor-Bridge-Acceptor Picture

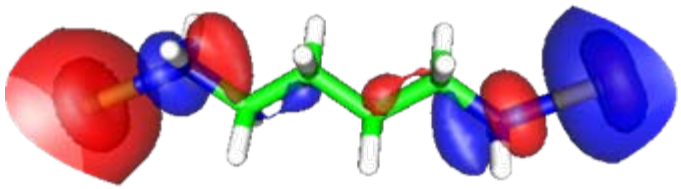
t: on-molecule coupling
Bridge

Γ: metal atom orbital coupling to electrode Fermi energy states
Donor / Acceptor

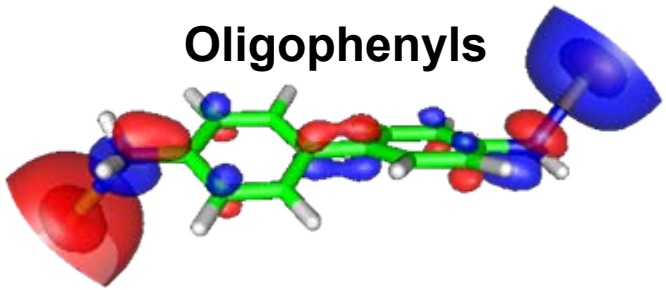
Trends: Tunneling Conductance vs. Length

Tunnel splitting from Au_1 cluster terminated

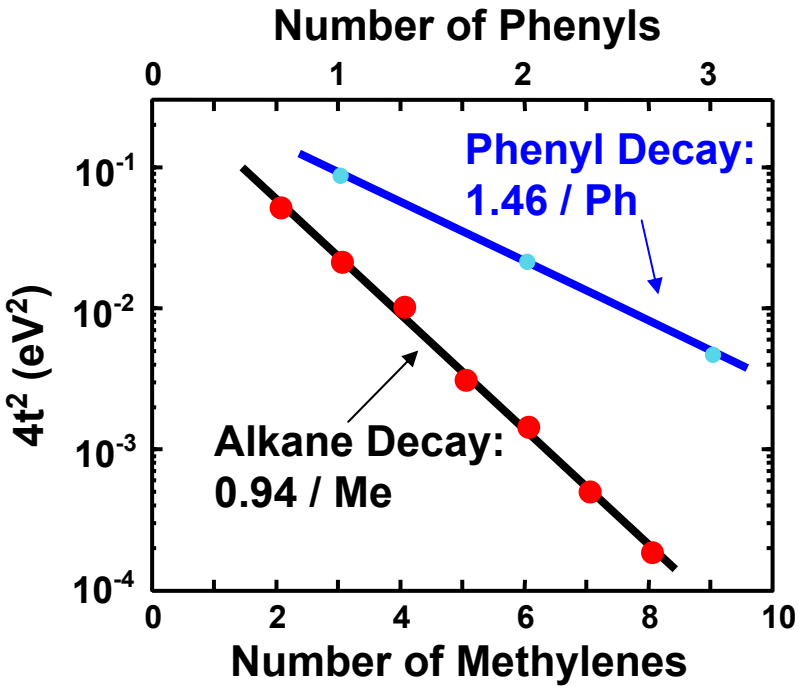
Alkanes



Oligophenyls



Calculated tunnel splitting



Complex polymer band structure –
Mid-gap decay constant

Alkane:	1.0 / Me
Oligophenyl:	2.0 / Ph

(Tomfohr & Sankey, Phys. Rev. B, 2002)

Experiment:

0.91 ± 0.03 / Me
1.68 ± 0.03 / Ph

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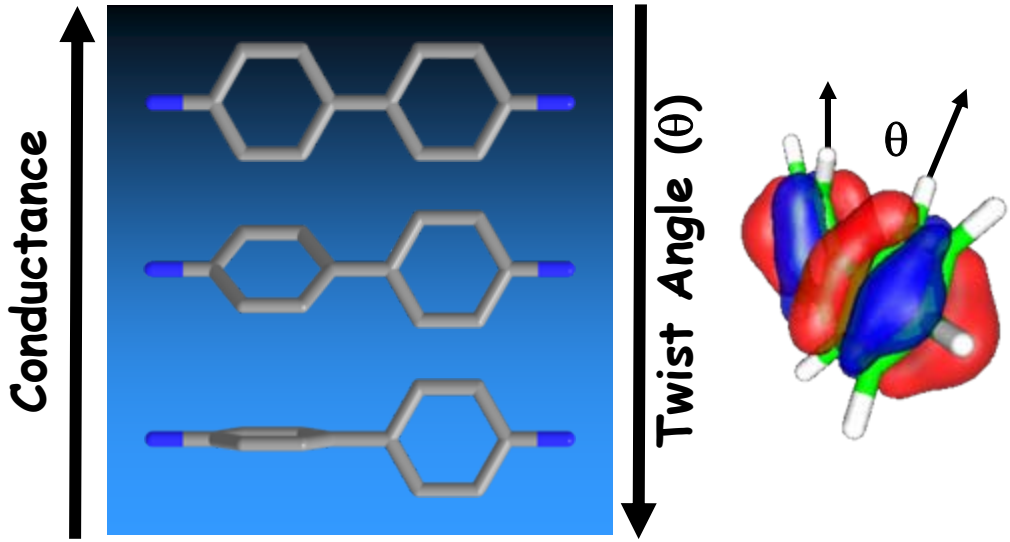
Trends: Impact of Molecular Properties on Conductance

DFT Based Conductance Calculations: How Wrong ?

Conductance vs Molecular Conformation



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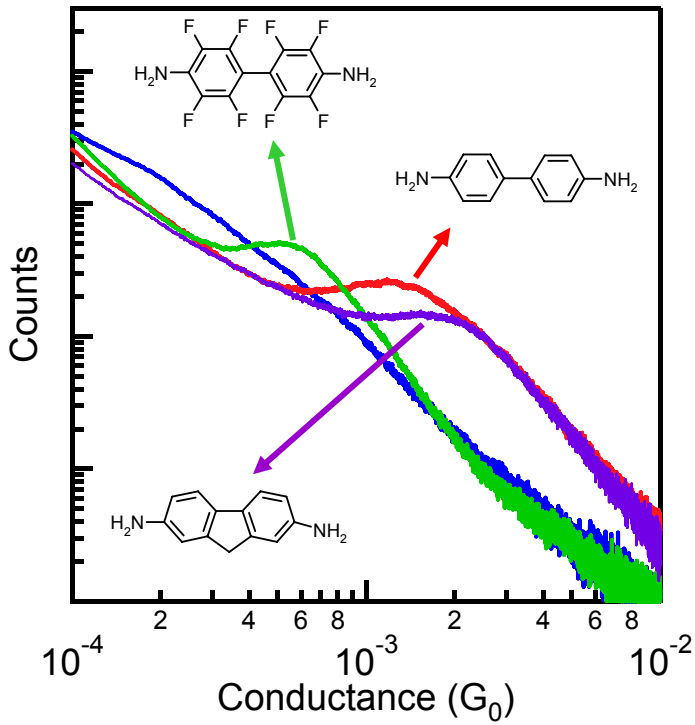

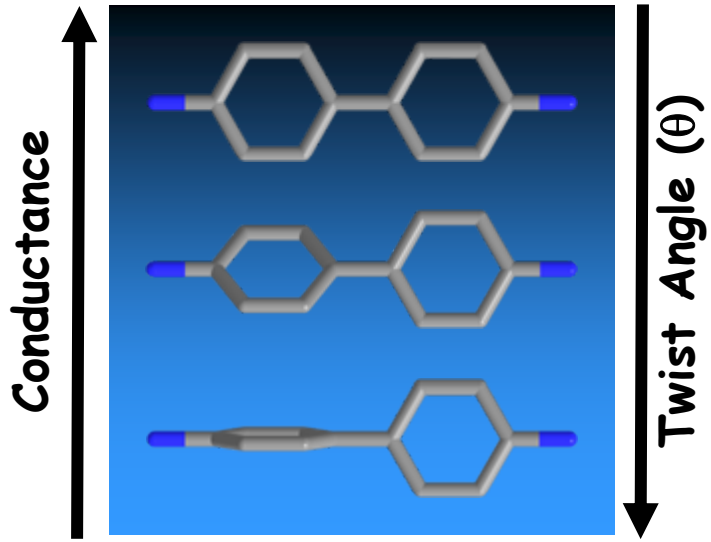

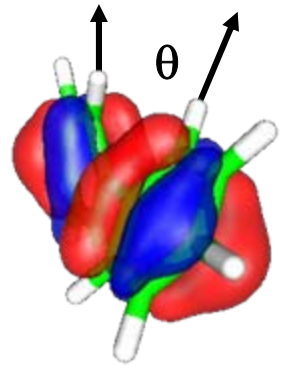

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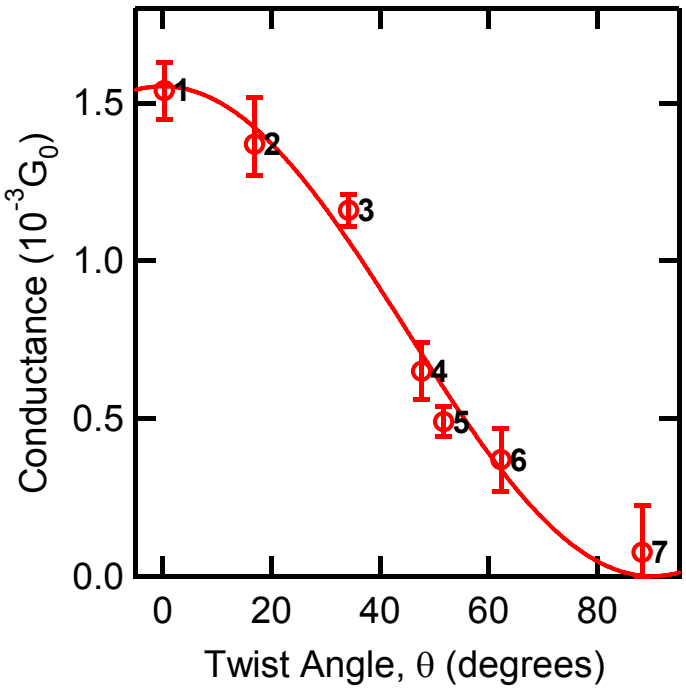
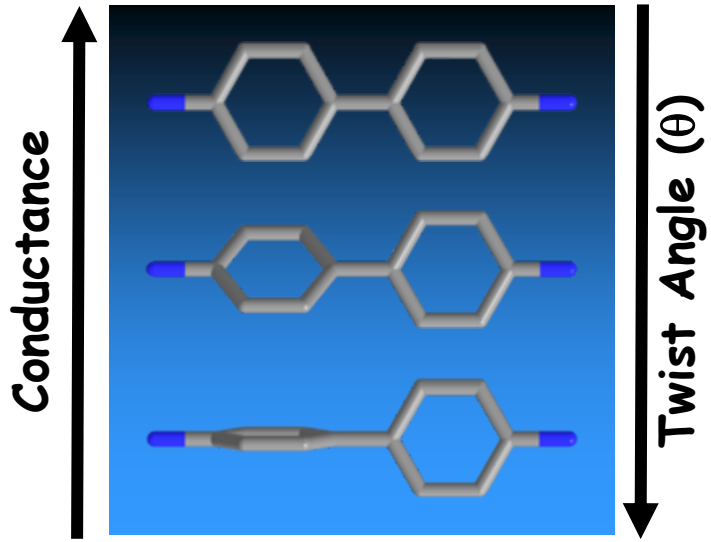
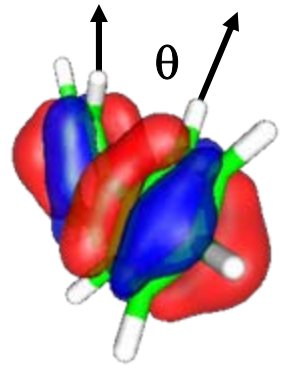
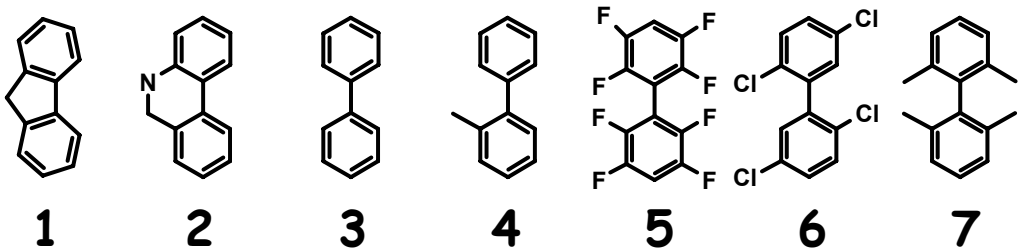






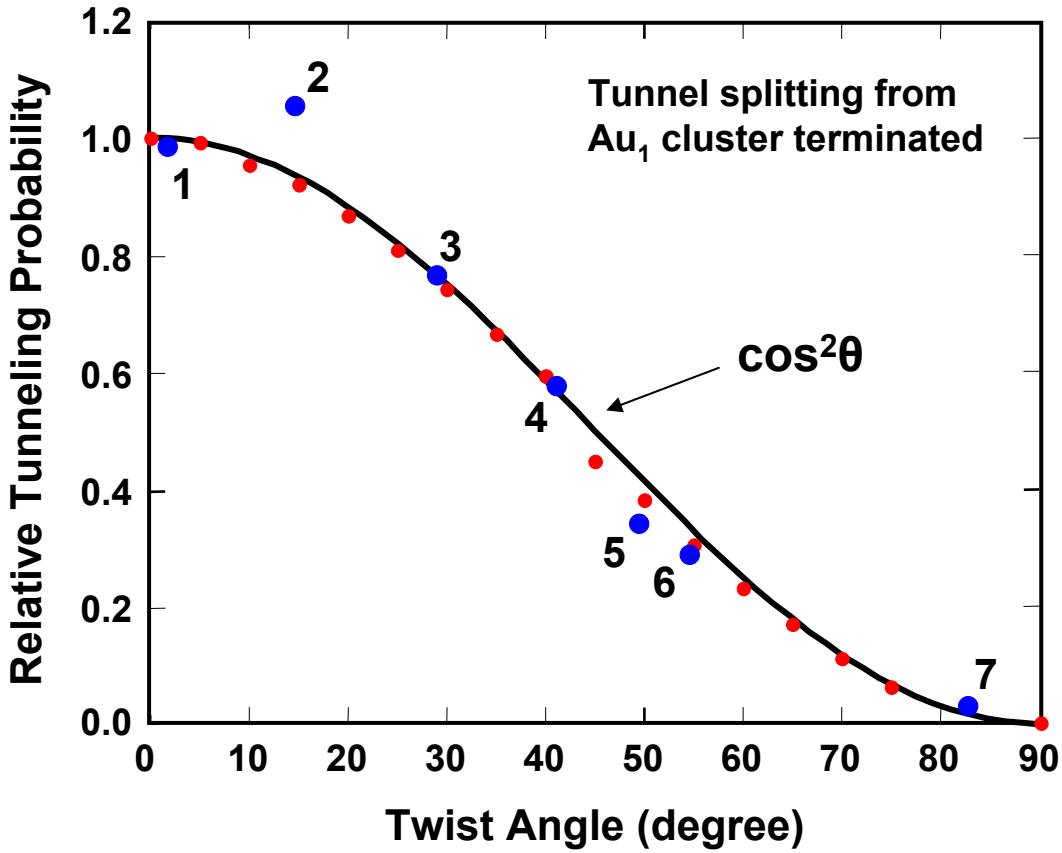
Amine link not shown



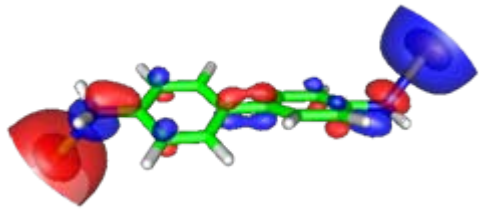
Structure – Function: Cosine square dependence measured

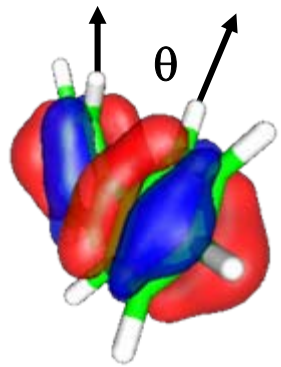
Venkataraman, et al, Nature, 2006

Tunneling Conductance vs. Twist Angle

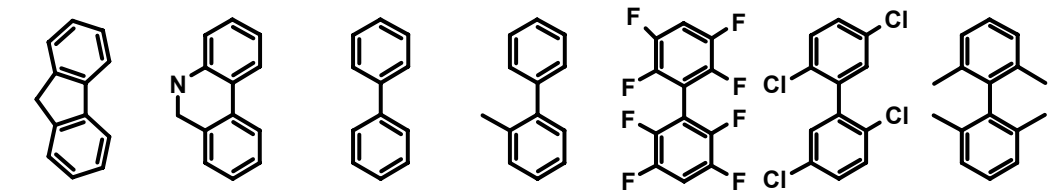


Biphenyldiamine





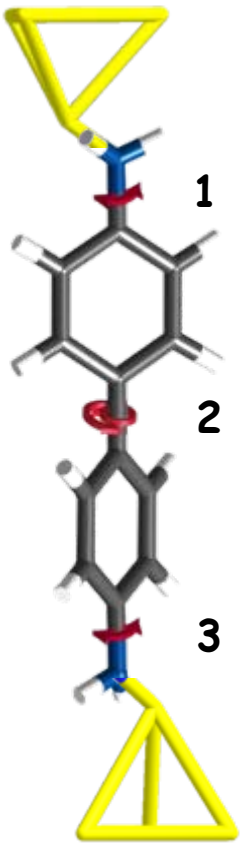
Amine link
not shown



1 2 3 4 5 6 7

Dynamical Effects

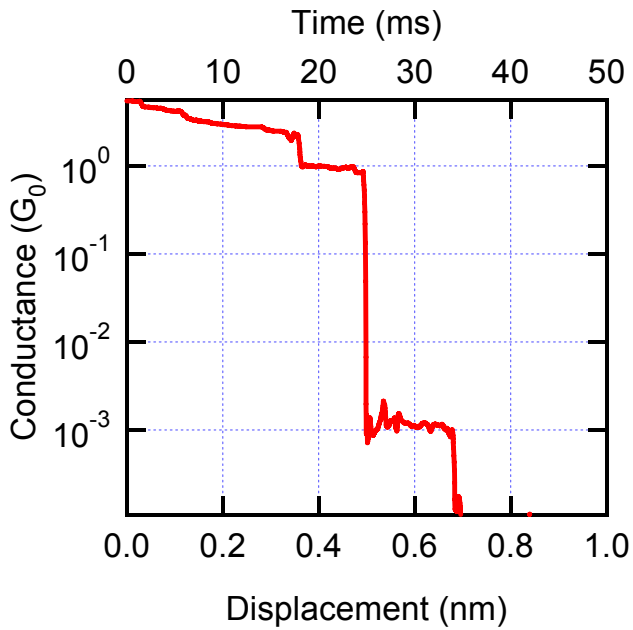
Soft rotations



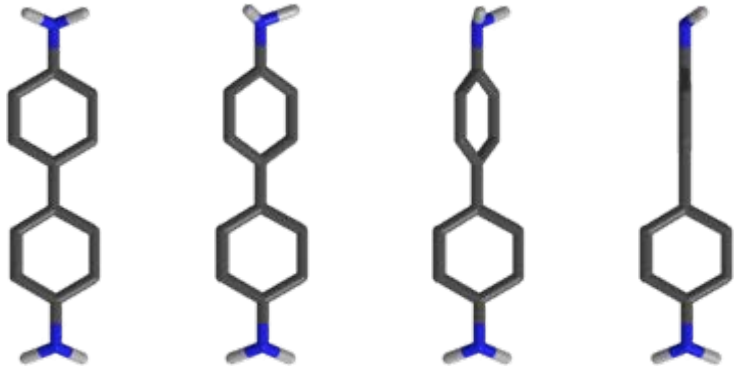
biphenyl

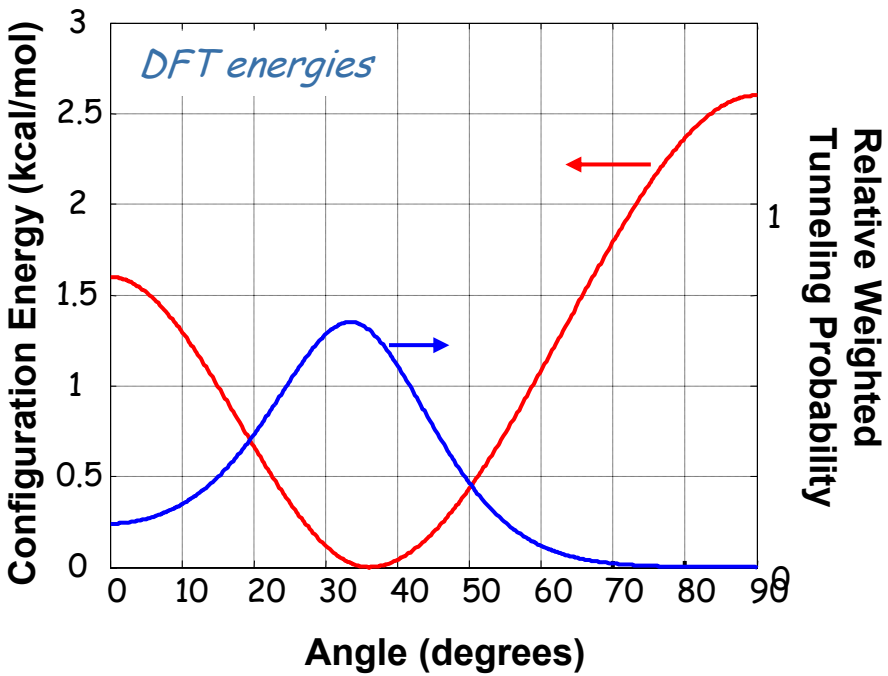
Time scales:

- Steps last ~ ms
- Molecule rotation times ~ ps
- Electron Tunneling times ~ fs



Thermal Average ~ Minimum





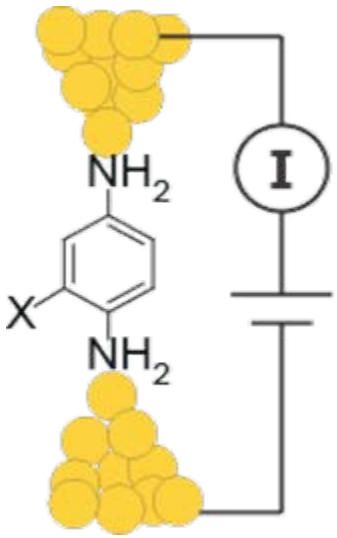
Rotational barrier: C-C bond
~ 3 kcal/mol ~ 0.1 eV
~ 4kT @ room T

Angle at barrier minimum: ~ 36°

Average conductance
→ Twist angle ~ 38°

Substituent Effects

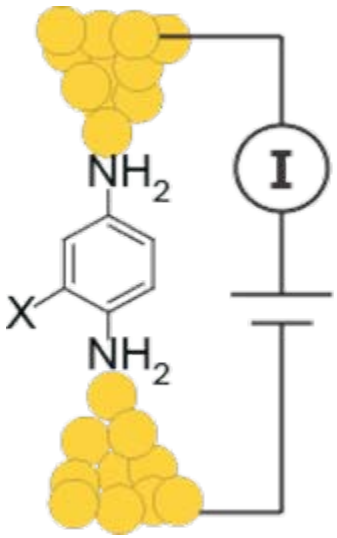
Comparison of the conductance of substituted benzenes

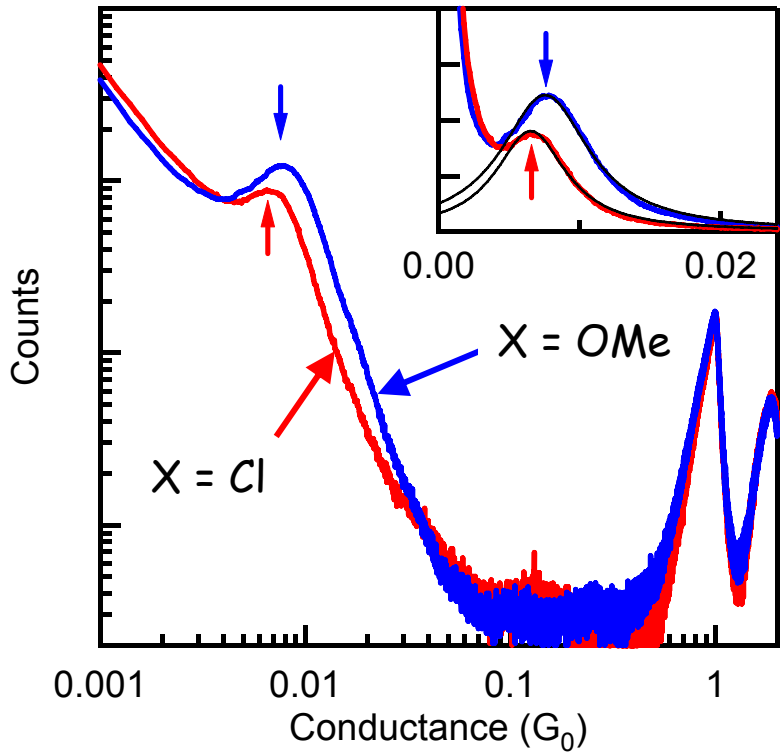


- Use a simple molecule - Diaminobenzene
- Add different substituents (X)
- Measure the low bias conductance

Substituent Effects

Comparison of the conductance of substituted benzenes

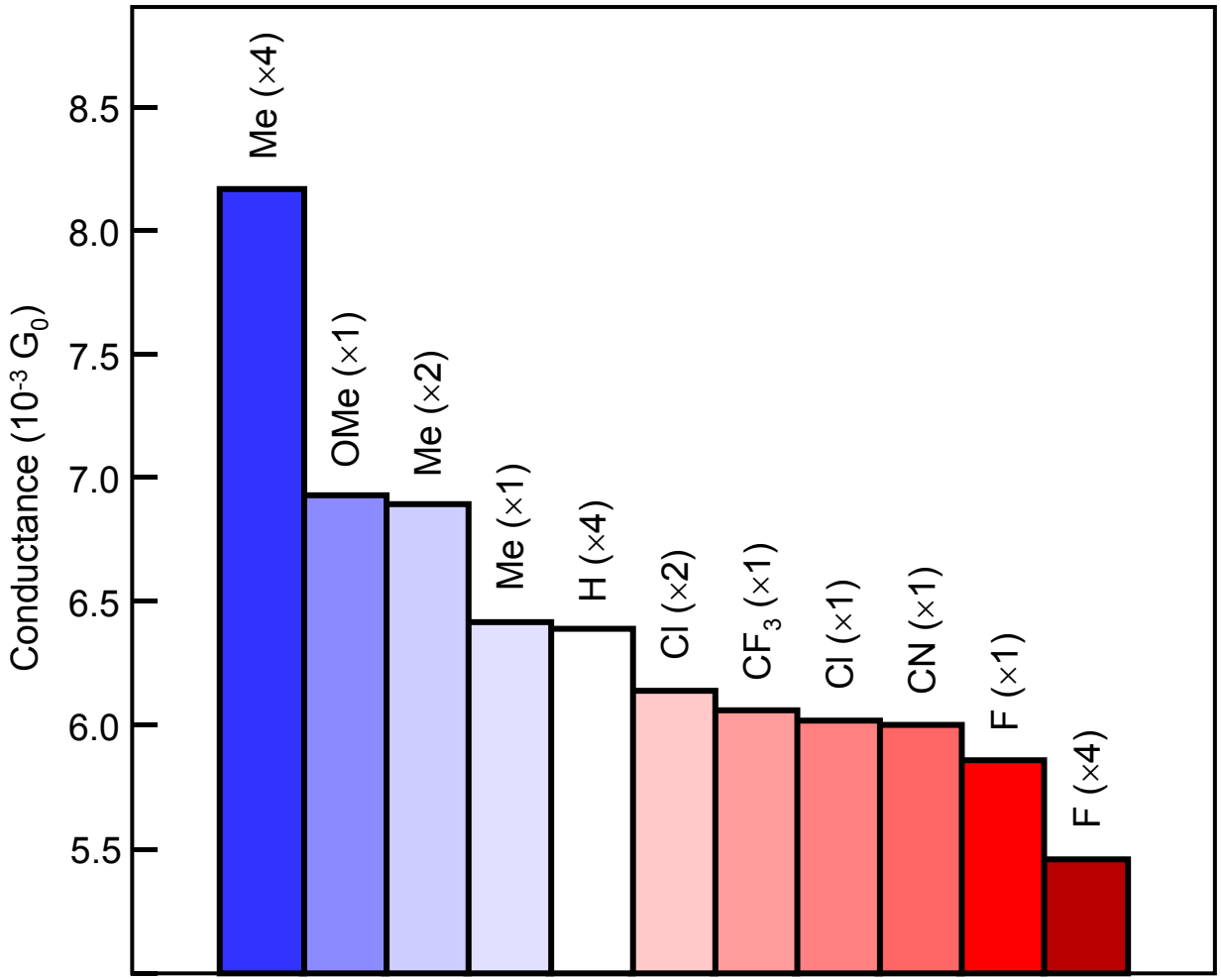


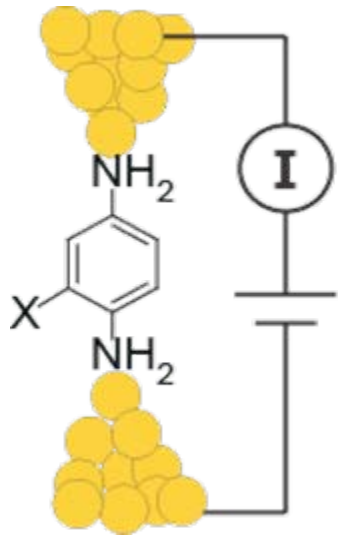


OMe → electron donating → increases conductance

Cl → electron withdrawing → decreases conductance

Trend: Conductance vs Substituents

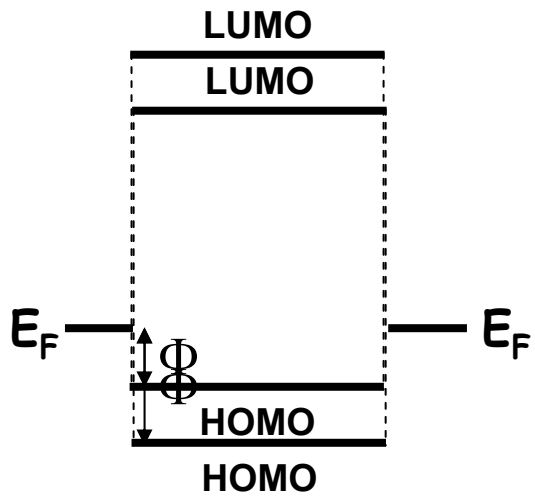




X used:
4, 2, or 1 Methyls,
1 Methoxy
2 or 1 Chlorine
4 or 1 Fluorine
1 Trifluoromethyl
1 Cyanide

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

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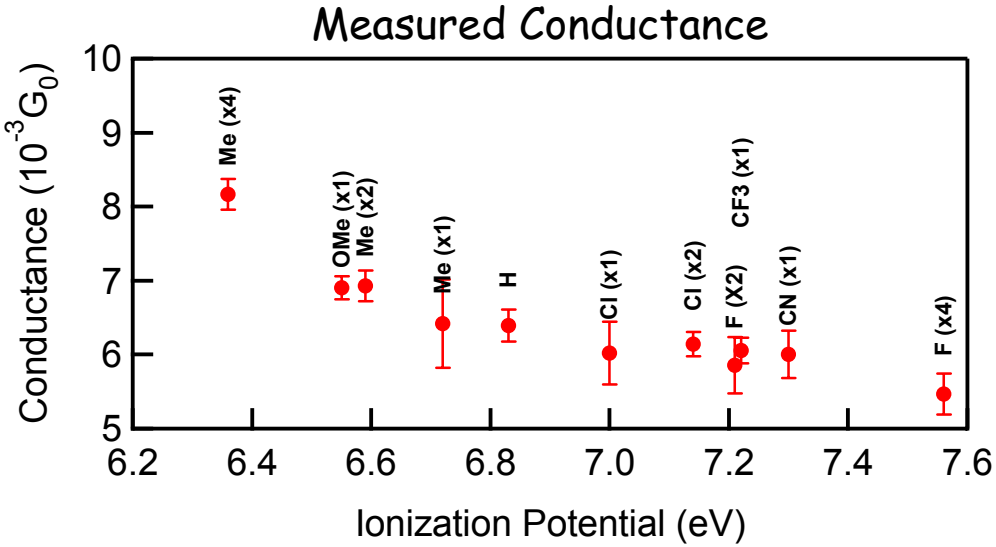

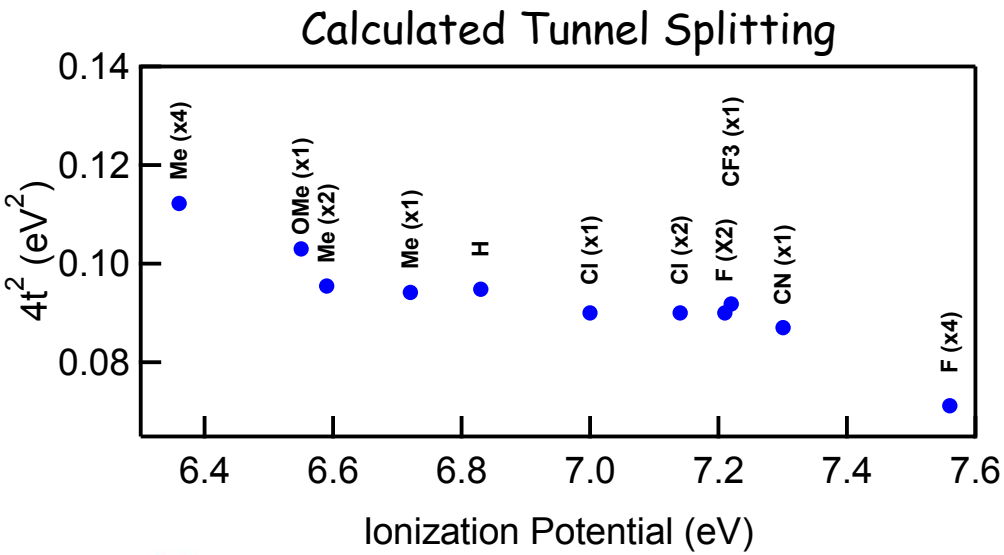

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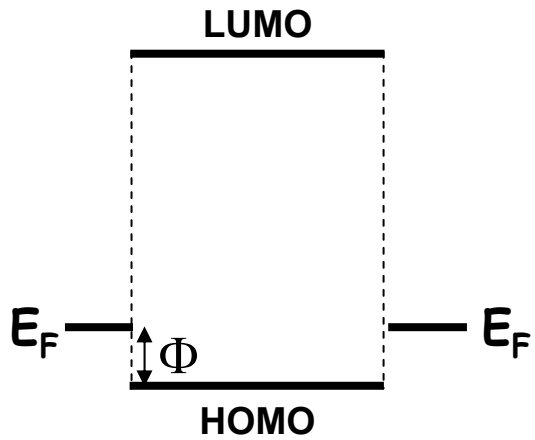

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Venkataraman, et al, Nano Letters, 2007

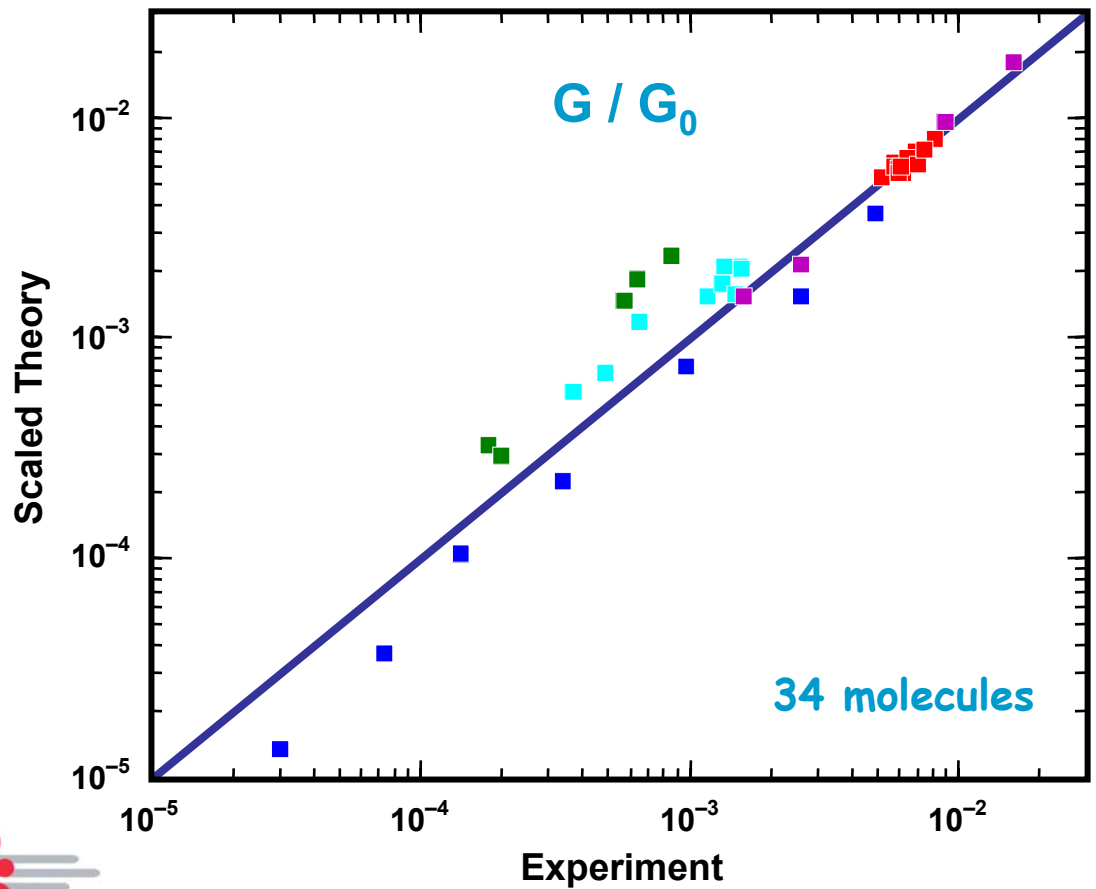
Summary: Tunneling Theory vs Experiment

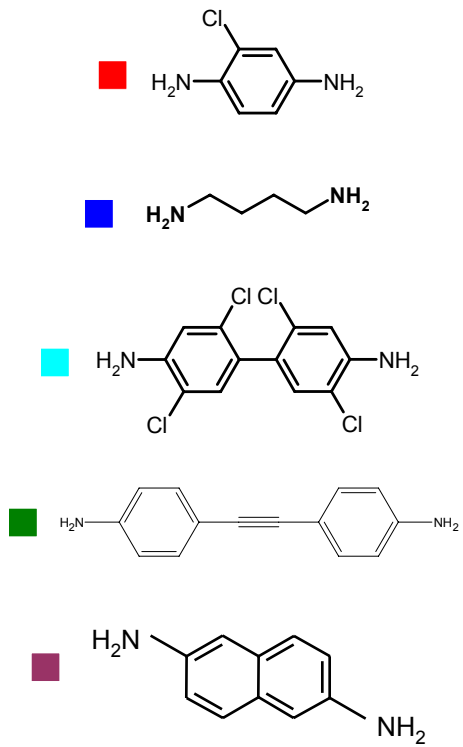
Reference Junction

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

Scaled Theory

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





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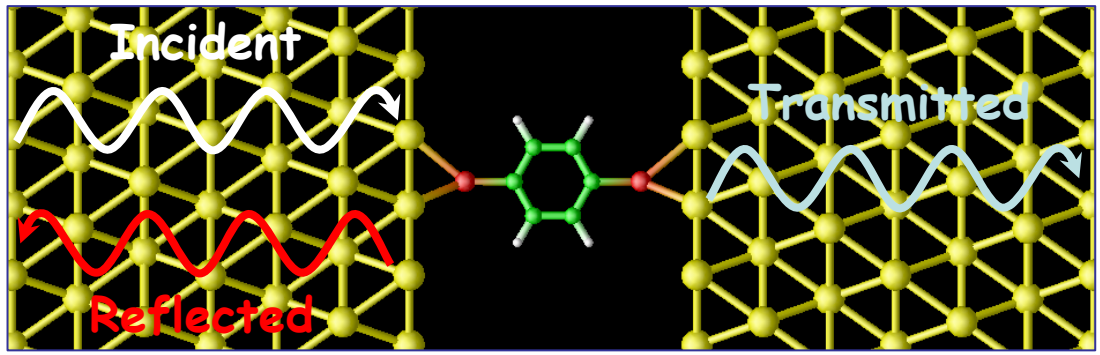
- Flexible & reproducible link for aliphatic & aromatic molecules
- Bonding hypothesis: donor-acceptor bond from amine lone pair into coordinatively unsaturated Au atoms on the electrodes

Trends: Impact of Molecular Properties on Conductance

- **Measured trends with clear physical interpretation**
  - **Molecule Conformation**
  - **Substituent Effect**
- **Tunnel coupling from model molecular complexes: trends across all families**

DFT Based Conductance Calculations: How Wrong ?

Single Molecule Junctions: Scattering Theory



Conductance from transmission using the Landauer formula:

$$G = \frac{2e^2}{h} T(E_F) \quad \text{where} \quad T(E) = Tr(t^{\dagger}t),\ t = t_{sm}(E)$$

Solve Hamiltonian for scattering states at each energy E:

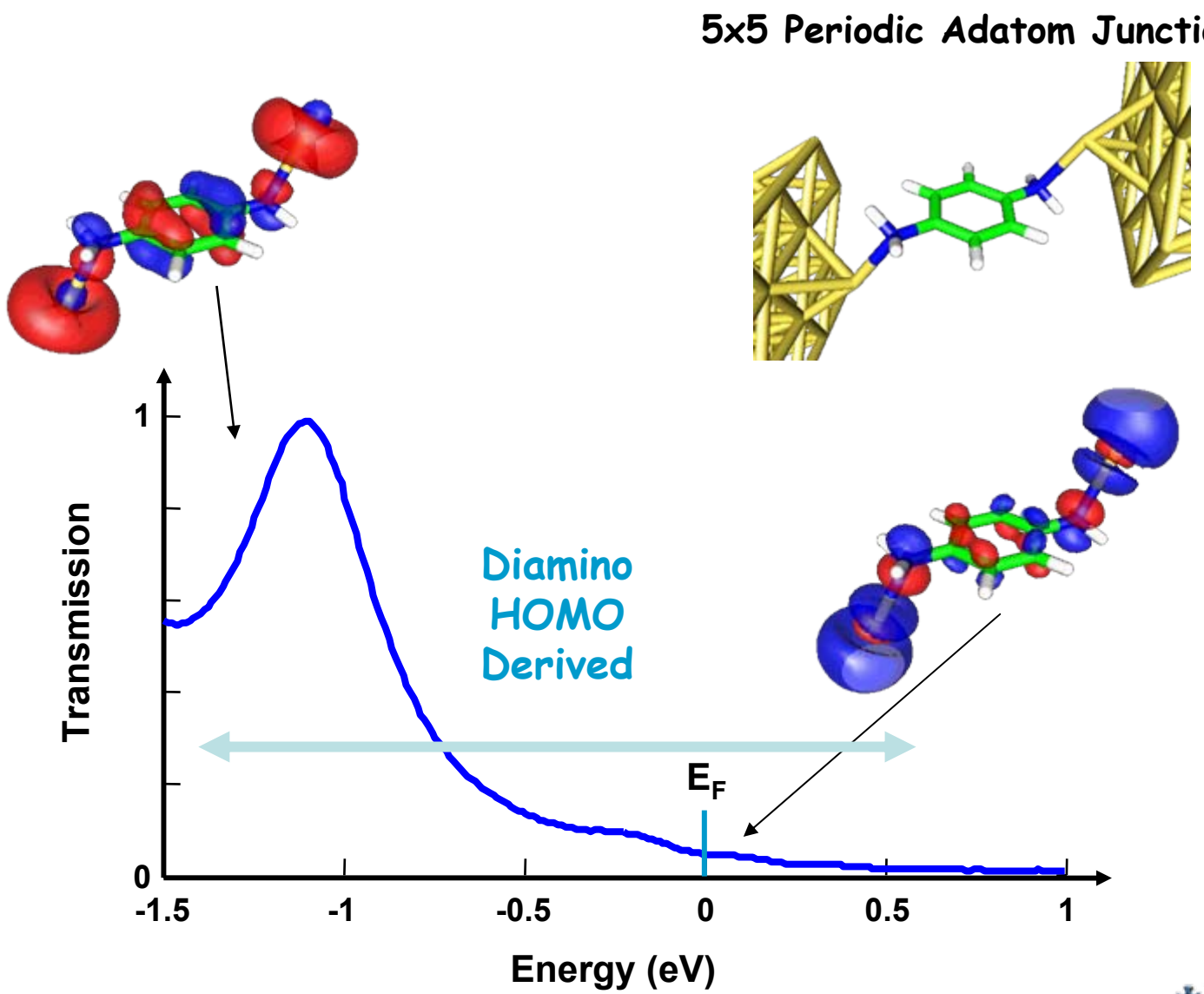
$$\left|\Psi_s^{\rightarrow}(E)\right\rangle = \left|\varphi_s(E)\right\rangle + \sum_l r_{sl}(E)\left|\varphi_l(E)\right\rangle + \sum_i c_{si}(E)\left|\phi_i\right\rangle + \sum_m t_{sm}(E)\left|\varphi_m(E)\right\rangle$$

incident reflected cluster transmitted

Self consistent junction potential: DFT (PBE)

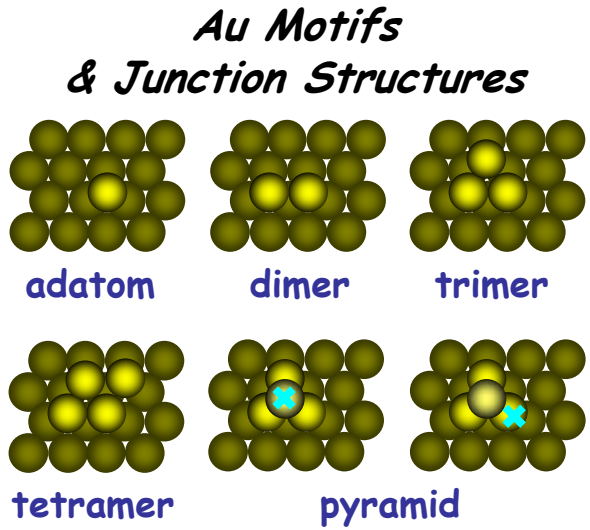
Choi, Cohen, Louie (2007)

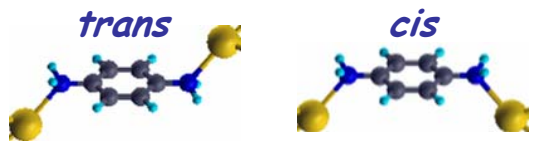
Example: Full Ballistic Transmission Calculation

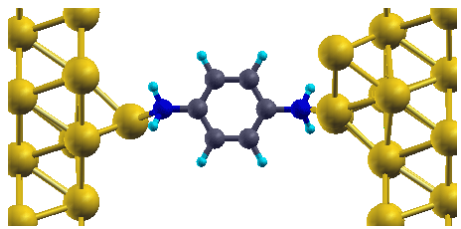


Quek, Neaton, Hybertsen, Choi & Louie

Status: Amine Linked Junction Conductance



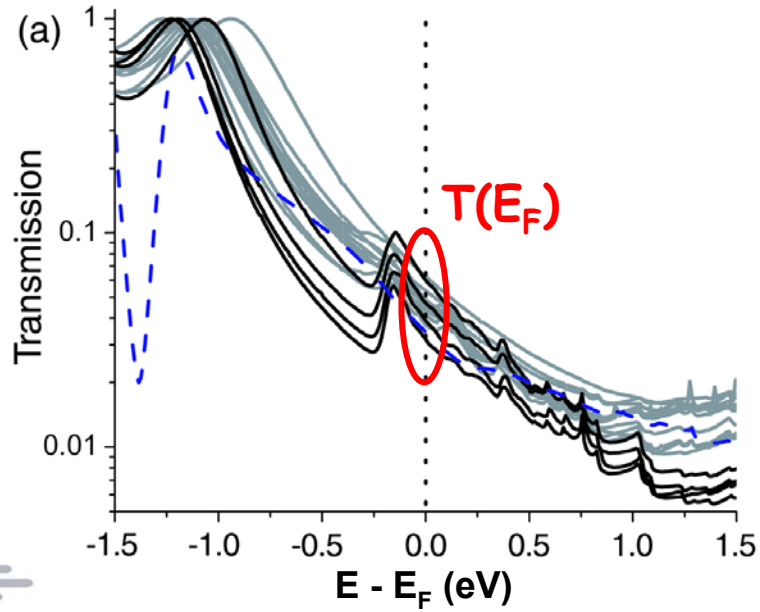


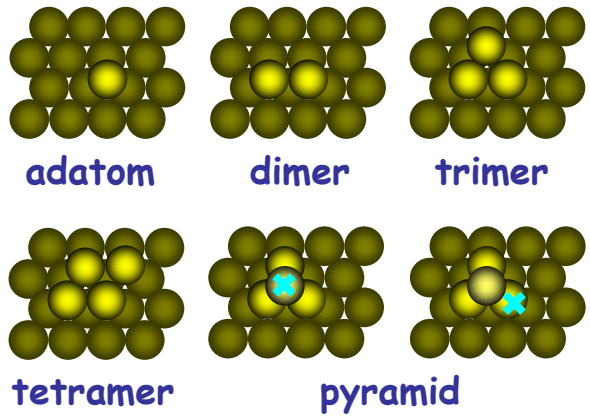


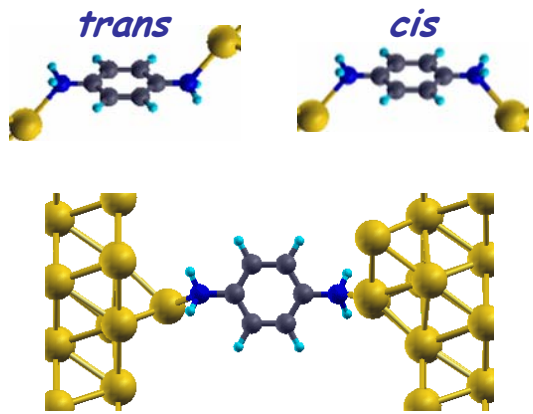
Status: Amine Linked Junction Conductance

16 junction structures analyzed –

- Calculated conductance: 0.04 G_0 ± 25%
  (Measured conductance: 0.0064 G_0 ± 40%)
  - Distribution similar
  - Magnitude too large by 6x
- Transmission dominated by a single channel: HOMO derived resonance
  - Agreement with substituent experiments







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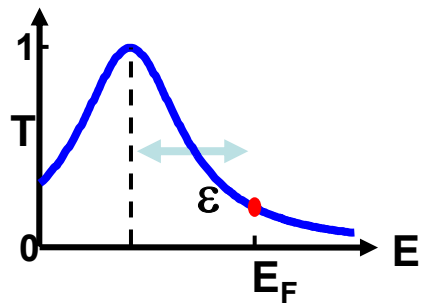
  - Substituent Effect
- Tunnel coupling from model molecular complexes: trends across all families



DFT Based Conductance Calculations: How Wrong ?

- **Qualitative picture: diamino HOMO dominates conductance**
- **Calculated conductance 6x measured conductance**
  - **Theory: beyond DFT orbital energies & independent electrons**

Molecular Electronics: Critical Challenges

Reproducible, controlled & robust electrode-molecule link

- Enable measurement of structure-conductance relations
  - Design rules for functional molecular devices
  - Theory & simulation validation
- Controlled bonding to complex molecules

In-situ characterization

- Heterogeneous nanosystems

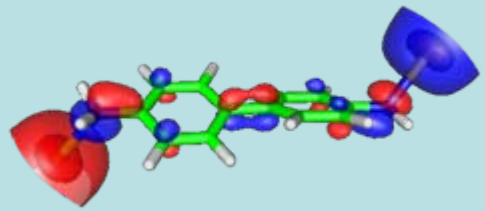
Demonstration of electronic functionality

- More control essential to test concepts

Functional device interconnection & isolation

- Large scale assembly of nanounits
- Control of variability of environment for each device

Amine-Gold Links:
Significant Progress



Question 1

Question 2