

A Research Perspective on Molecular Electronics

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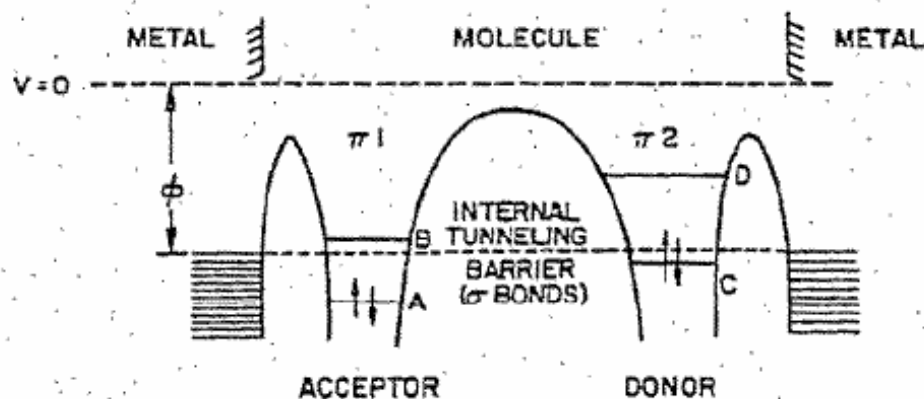
&

Center for Electron Transport in Molecular Nanostructures

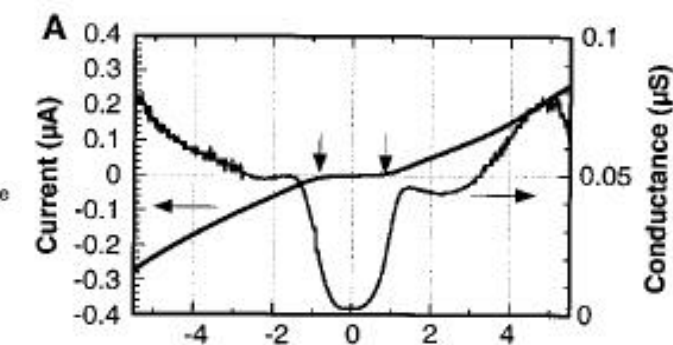
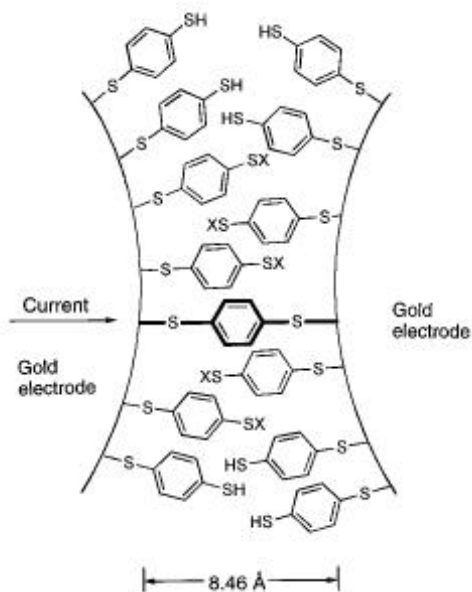
Columbia University



Vision: Functional Molecular Devices

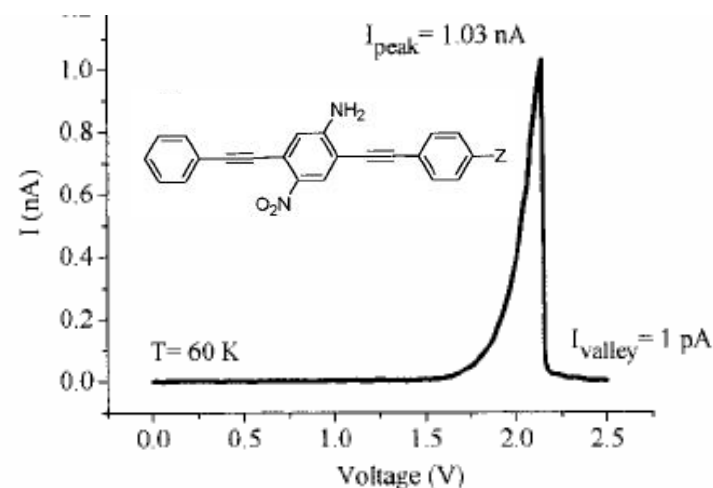
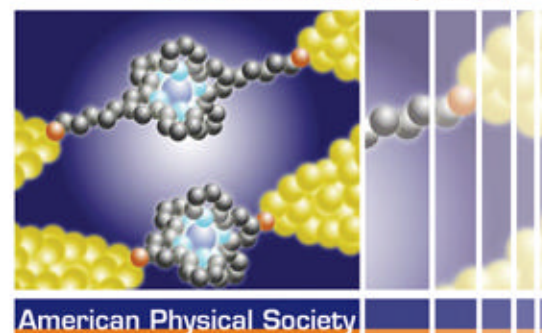


Aviram & Ratner, *Chem Phys Lett*, 1974



Reed et al, *Science*, 1997

2004
APS March Meeting
held in cooperation with the Canadian Association of Physicists
March 22-26 • Montreal, Canada



Chen, Reed, Rawlett & Tour,
Science, 1999



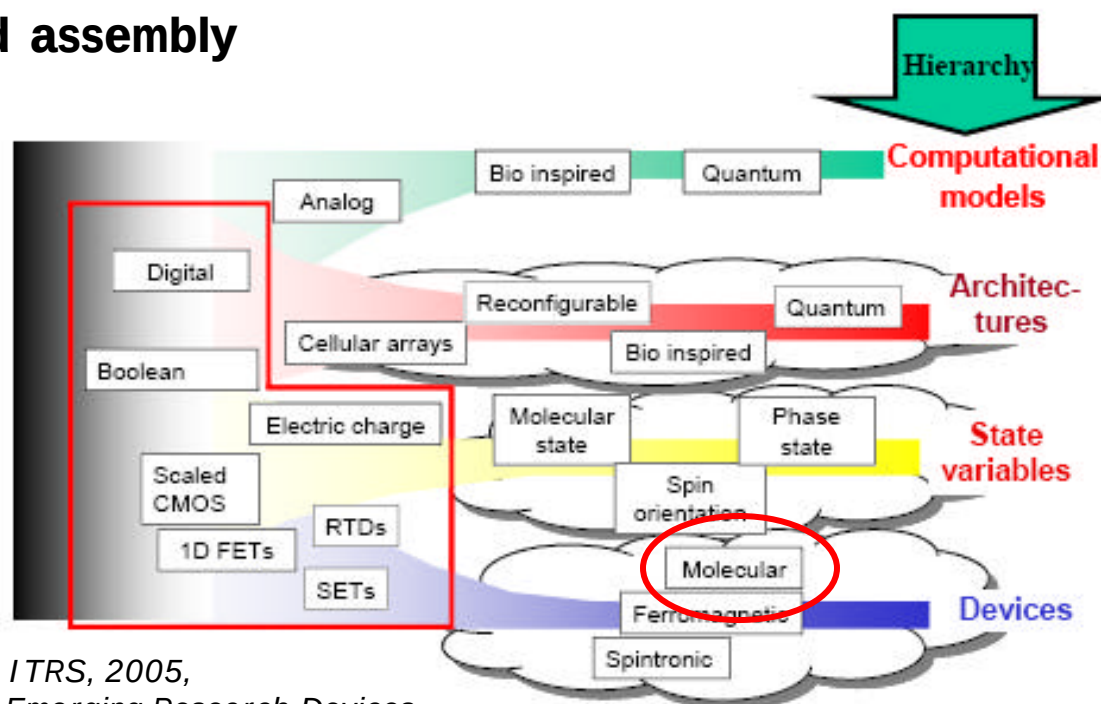
BROOKHAVEN
NATIONAL LABORATORY

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



Molecular Electronics: Post CMOS Technology ?

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

Narrow Assessment:

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

Broad Assessment:

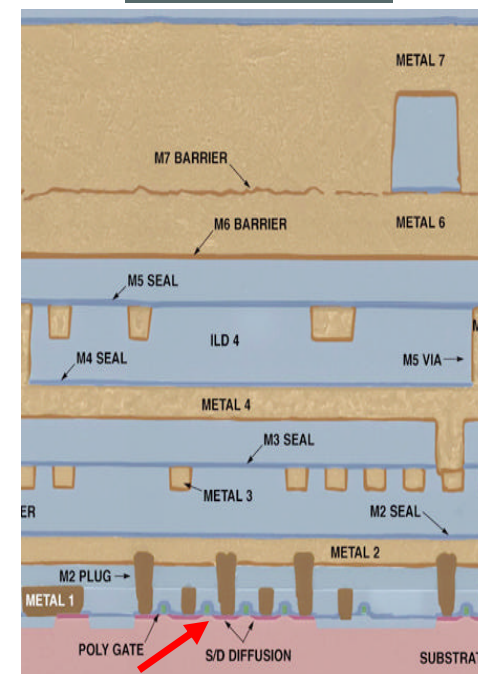
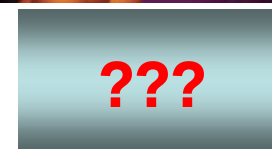
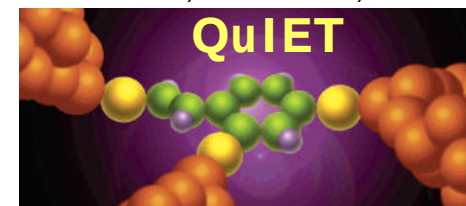
- Investment in fundamental understanding of heterogeneous molecular systems is critical:
electronics, sensors, energy, bio-interface,

“A knowledge gap exists between materials behaviors and device functions.”

– ITRS, 2005: Emerging Research Devices

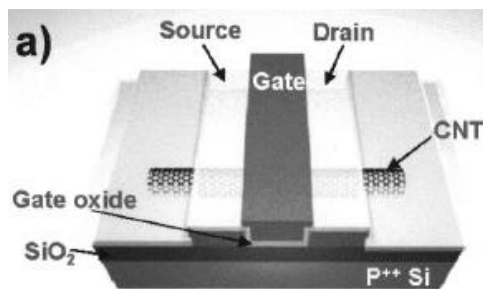
SSSC Meeting, Irvine
Mark S Hybertsen 10/19/2006 - 4

Cardamone, Stafford &
Mazumdar, Nano Lett, 2006



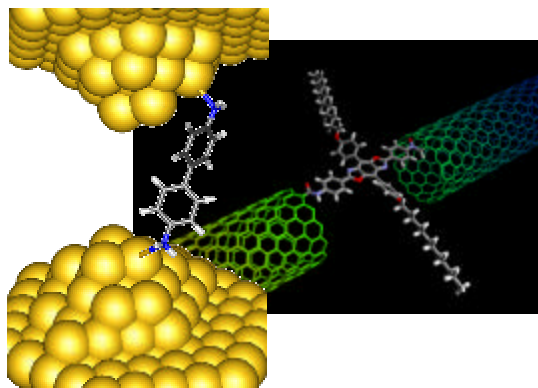
Scope of Materials

Carbon Nanotubes



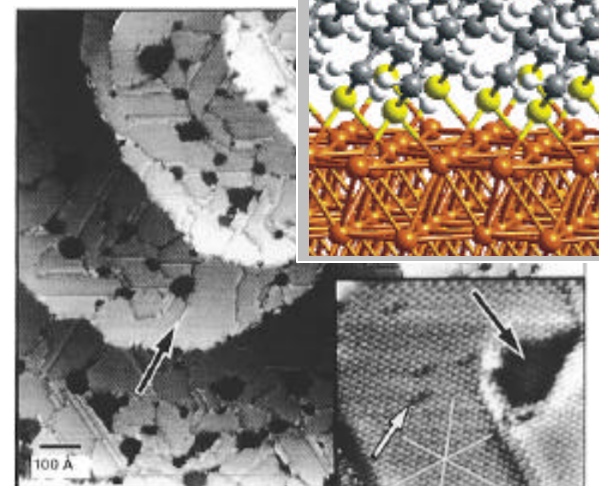
Avouris, et al, *Proc. IEEE*, 2003

Single Organic Molecule



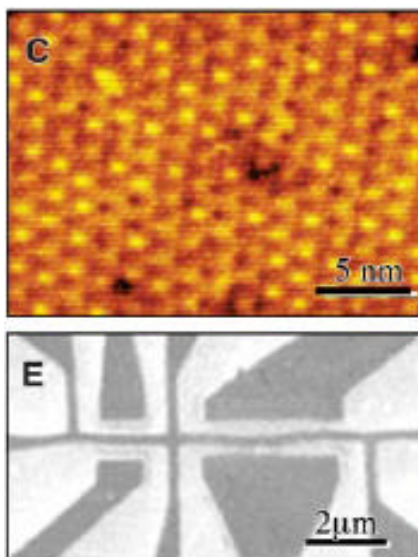
Venkataraman, et al, *Nature*, 2006
Guo, et al, *Science*, 2006

Self Assembled Monolayers: Thiol - Au



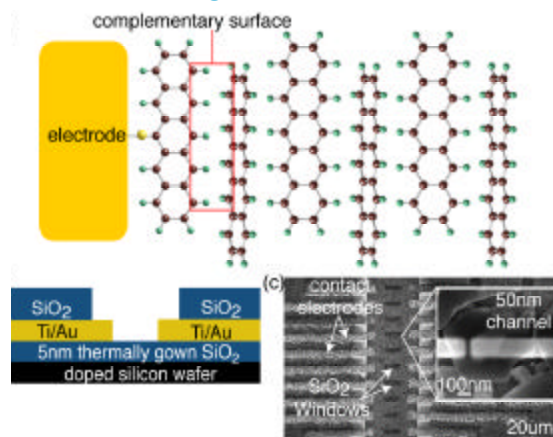
Poirier, *Chem Rev*, 1997
Fischer, et al., *Langmuir*, 2003

Ultrathin Graphite



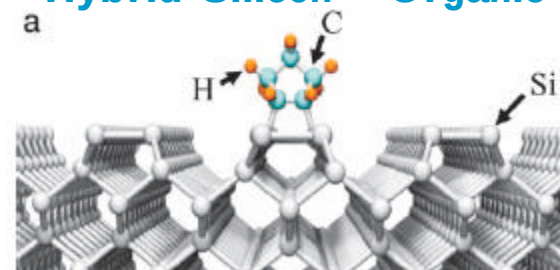
Berger, et al, *Science*, 2006

Organic Films



Tulevski, et al, *JACS* 2006

Hybrid Silicon - Organic

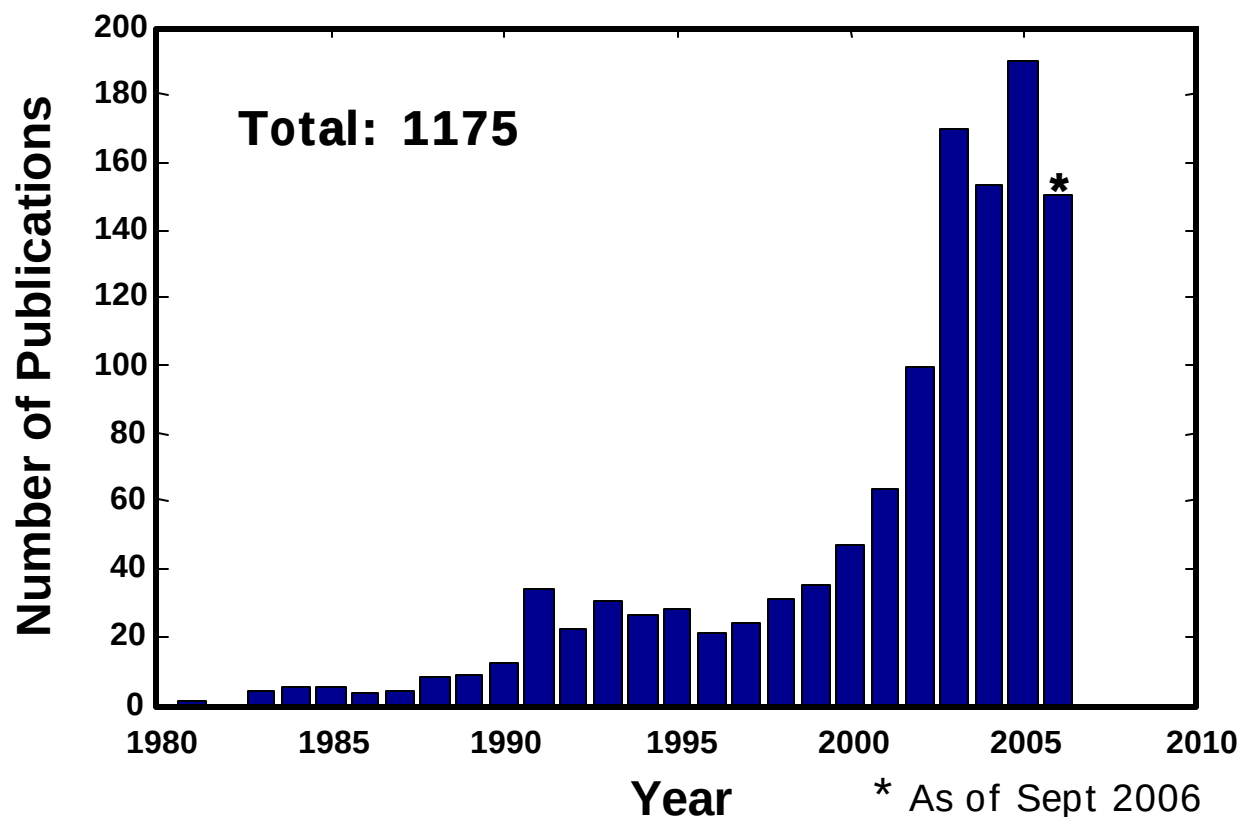


Guisinger, Yoder & Hersam, *PNAS* 2005



“Molecular Electronics” Research Activity

Web of Science search on “Molecular Electronics”



Note: Technical Digest, IEDM 2005
“Organic” 8 out of ~300



Outline

Introduction to “Single Molecule” Junctions

Examples of “Single Molecule” Conductance Phenomena

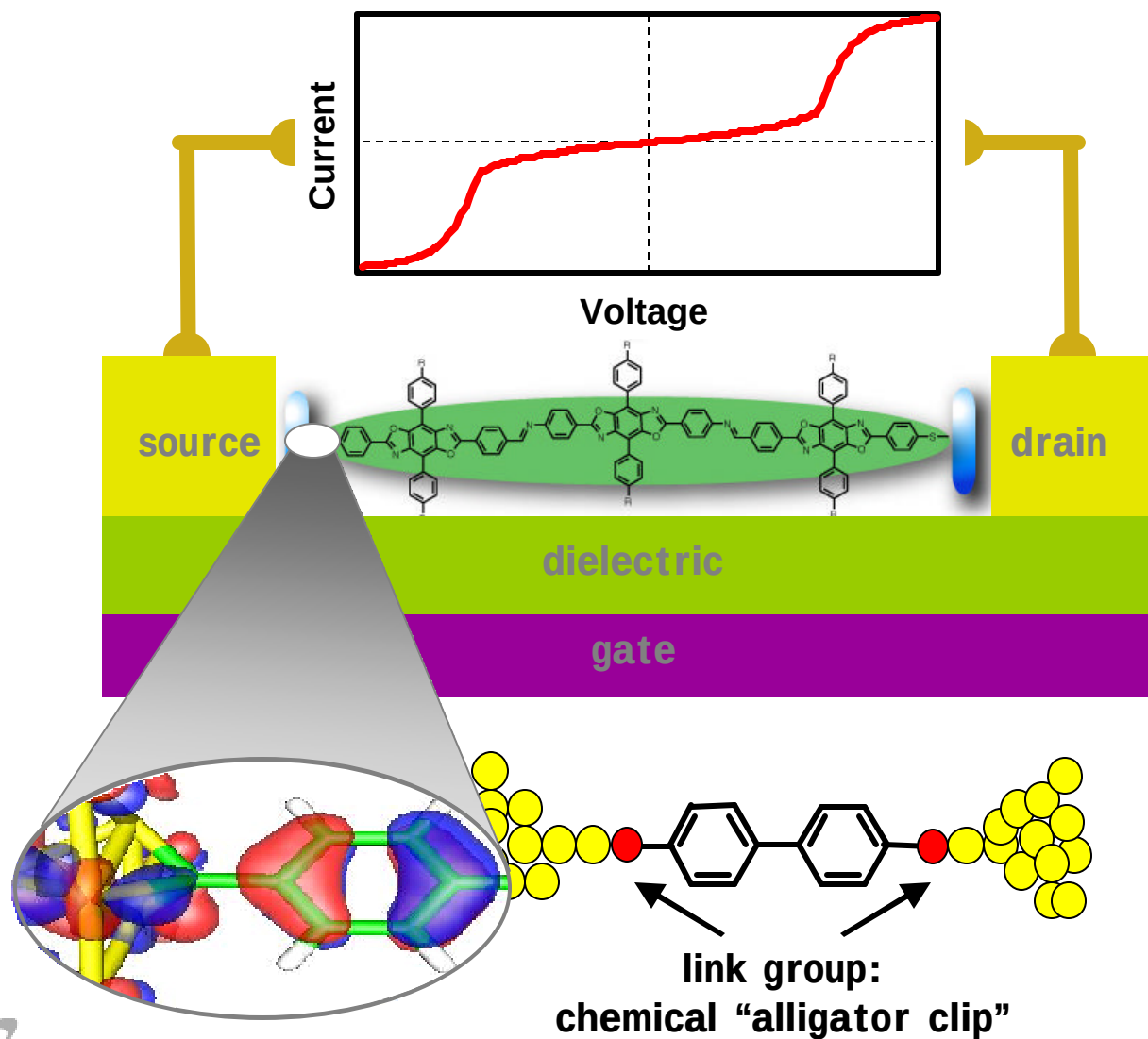
New Approach: Bonding in Single Molecule Junctions

Outlook

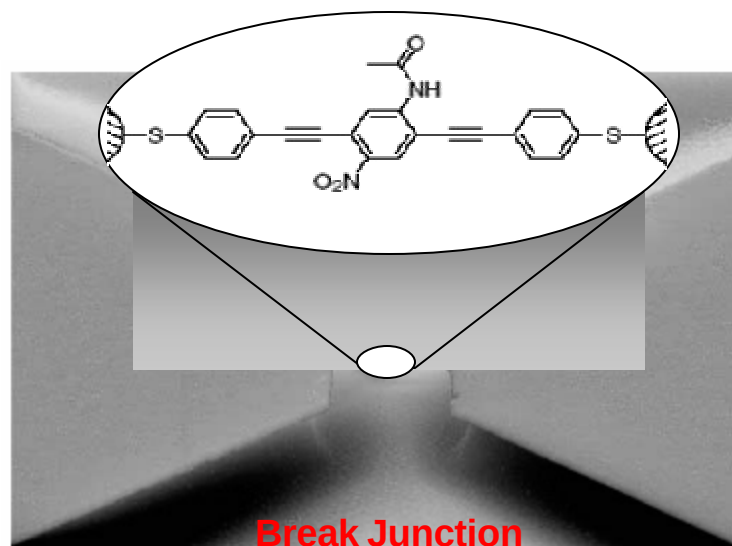


Probing Single Molecule Conductance

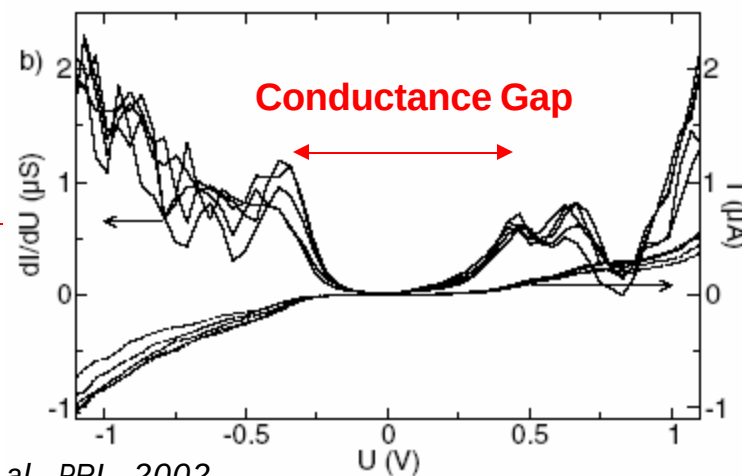
FET Paradigm



Molecular Scale Conduction

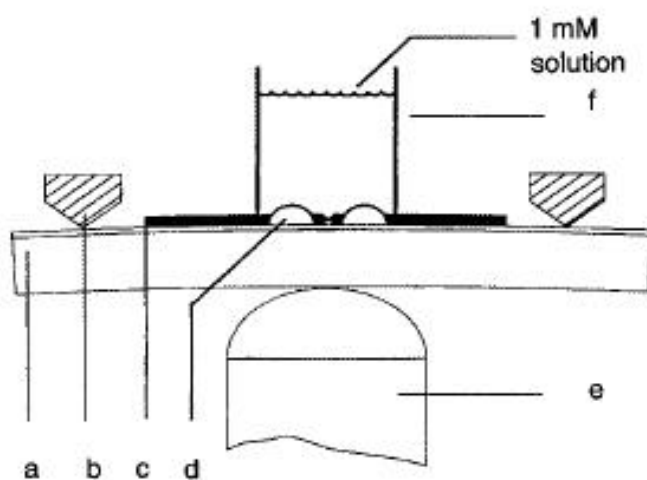


1 MW

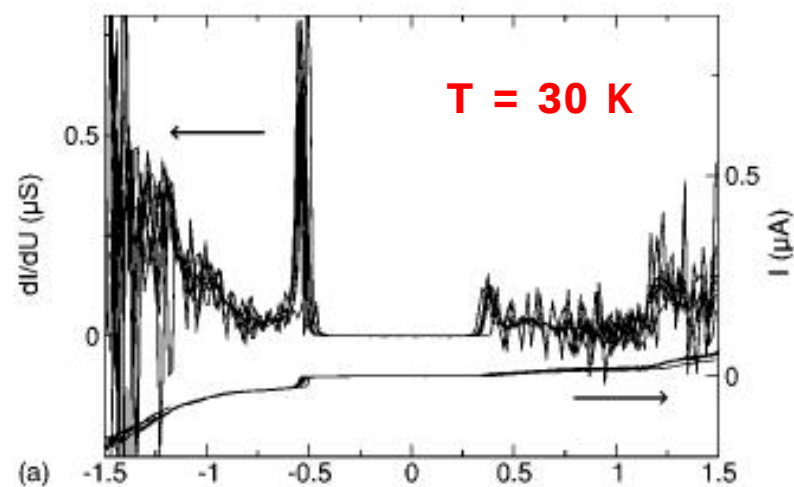


Reichart, et al., PRL, 2002

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



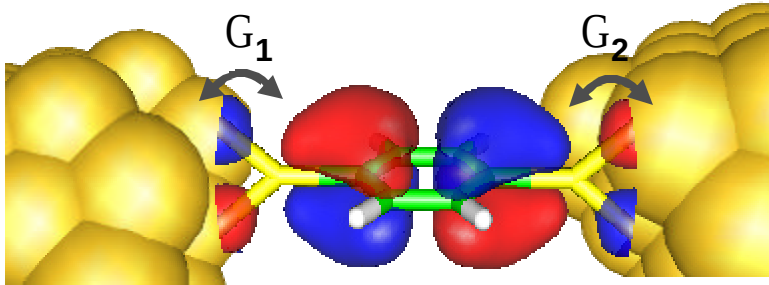
Reed, et al., Science, 1997



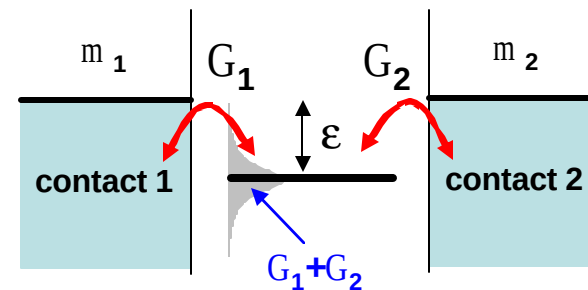
Reichart, et al., APL, 2003



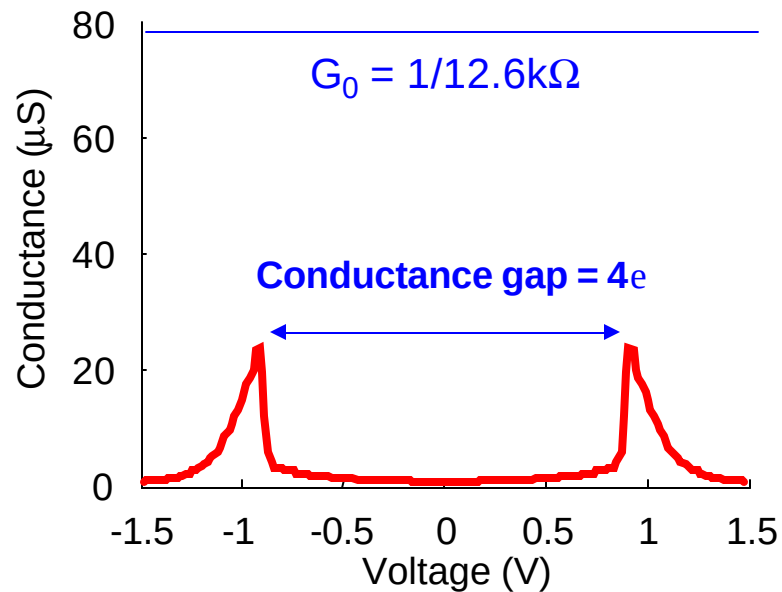
Resonant Tunneling Via Frontier States



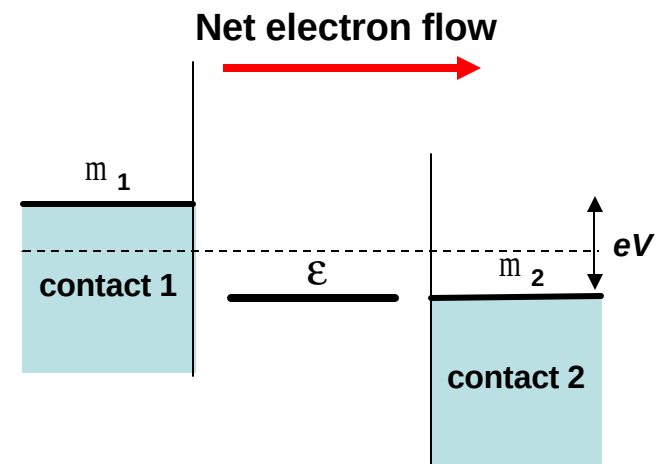
Zero Applied Bias



Weak Coupling: $\Gamma_{1,2} / \epsilon \ll 1$



Positive Applied Bias



Datta & coworkers



"Single Molecule" Measurement Techniques

Focus on fully bonded junctions

- STM: highly asymmetric junction

Mechanically controlled break junction

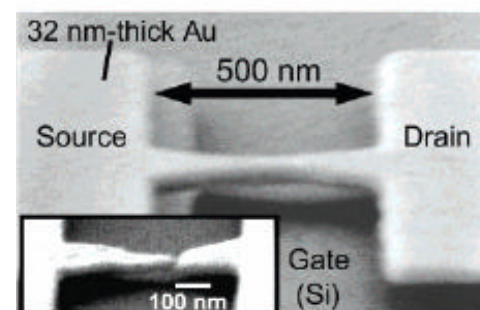
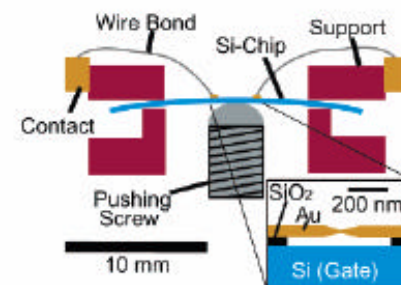
Electromigrated break junction

- Back gate
- Low T measurements
- ~20% success rate

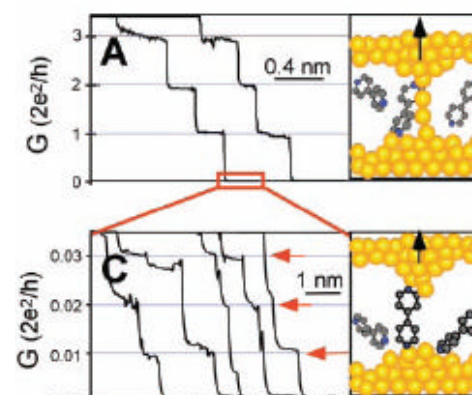
Repeated atomic scale Au junction

- Atomic wire calibration
- Statistical view from $\sim 10^4$ traces
- Electrochemical gate

Issue: bonding & structure



Champagne, Pasupathy & Ralph,
Nano Lett, 2005



Xu & Tao, *Science*, 2003



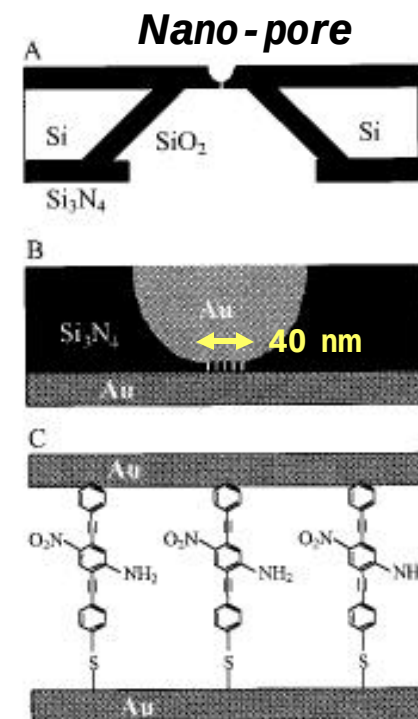
Small Area Molecular Junctions

Typically $10^3 - 10^4$ molecules

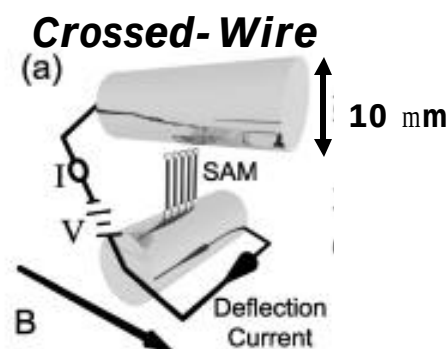
Advantage: exploit ordered SAM formation

Issues:

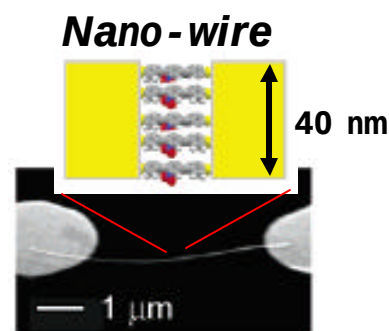
- Deposition of metal on molecules
- Symmetric vs asymmetric link chemistry
- Fraction of molecules carrying current



Chen, et al, Science, 1999



Kushmerick, et al,
PRL, 2002



Selzer, et al,
Nano Lett, 2004



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

Introduction to “Single Molecule” Junctions

Examples of “Single Molecule” Conductance Phenomena

New Approach: Bonding in Single Molecule Junctions

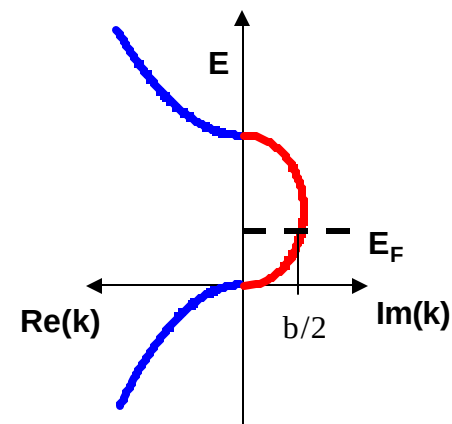
Outlook



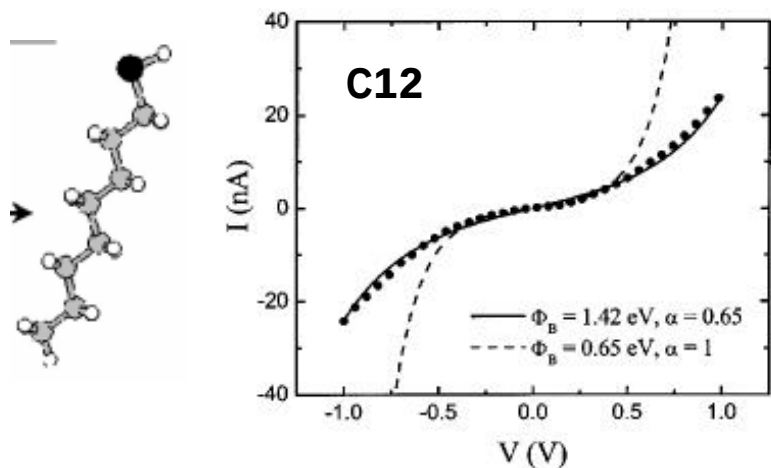
Molecular Conductance: Tunneling Regime

Evidence for tunneling regime:

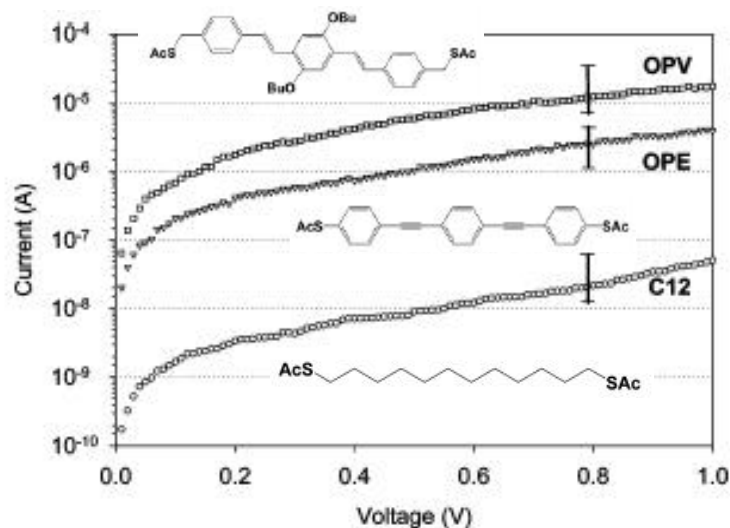
- Exponential length dependence: $G \sim e^{-bL}$
 - b typically $0.2 \text{ \AA}^{-1}$ (alkene) to $0.8 \text{ \AA}^{-1}$ (alkane)
 - Agrees with theory
- Fit to Simmons's model (M-I-M junction)
- T independent
- HOMO-LUMO gap dependence



Tomfohr & Sankey,
Phys Rev B, 2002



Wang, Lee & Reed, Phys Rev B, 2003



Cai, et al, J Phys Chem B, 2004



Molecular Conductance: Resonant Tunneling ?

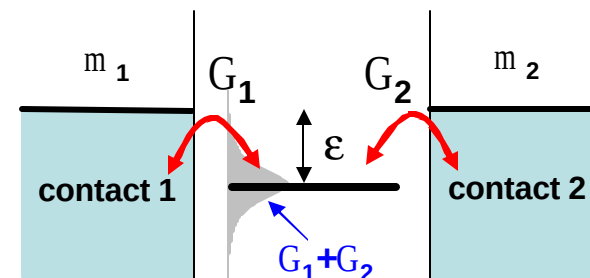
Near resonance: $G \rightarrow G_0$

Observed for Pt-H₂-Pt

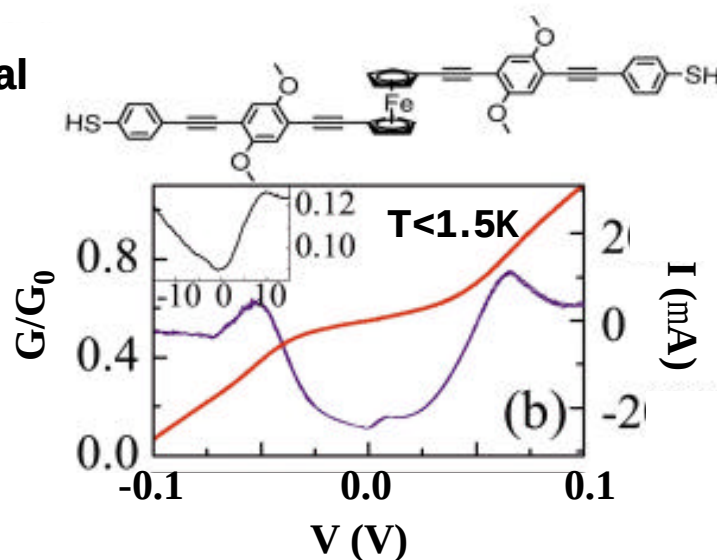
➤ Smit, et al, Nature, 2002

One molecular example

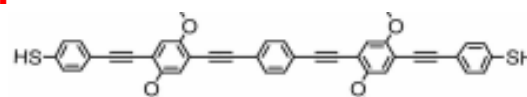
- Supported by detailed theory
 - Widely used ballistic conduction theory
 - DFT for 'realistic' atomic scale potential
- Control experiment:
 - OPE of the same length
 - $G < 0.01 \cdot G_0$
- Theory for OPE: $G_{\text{calc}} \gg G_{\text{expt}}$
 - Widely observed disconnect between theory and experiment
 - Atomic structure ...
 - ... or fundamental theory ??



$$\frac{G}{G_0} = \frac{4\Gamma_1\Gamma_2}{4\epsilon^2 + (\Gamma_1 + \Gamma_2)^2}$$



Getty, et al, Phys Rev B, 2005



Molecular Conductance: Gate Switching

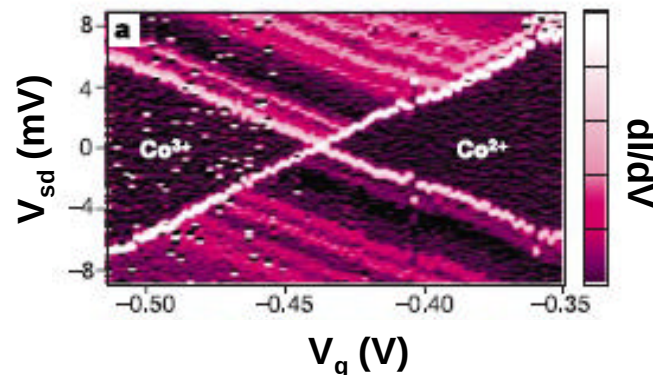
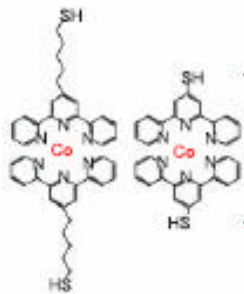
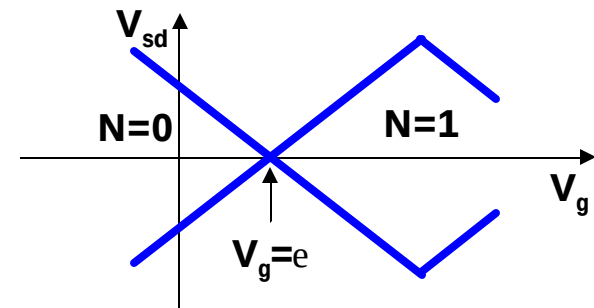
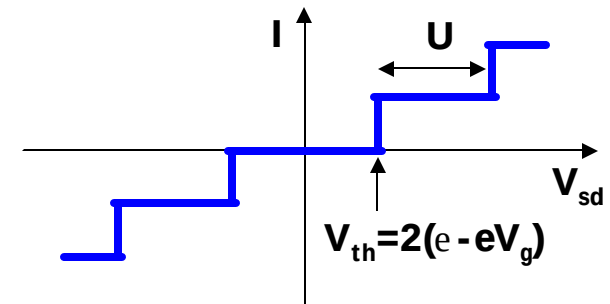
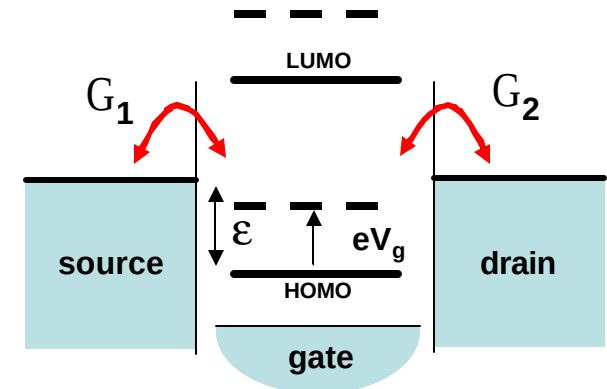
Conductance gap depends on gate bias

Coulomb blockade

- $U, DE \gg G_1, G_2 \gg kT$
- (few eV), ($< 1\text{eV}$), ($< 25\text{ meV}$)
- 1 or 2 charge states accessible

Single molecule transistor results

- C_{60} , transition metal complexes
- Kondo physics
- Vibrational excitations



Park, et al, Nature 2002

SSSC Meeting, Irvine
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Molecular Function: Electrochemical switching

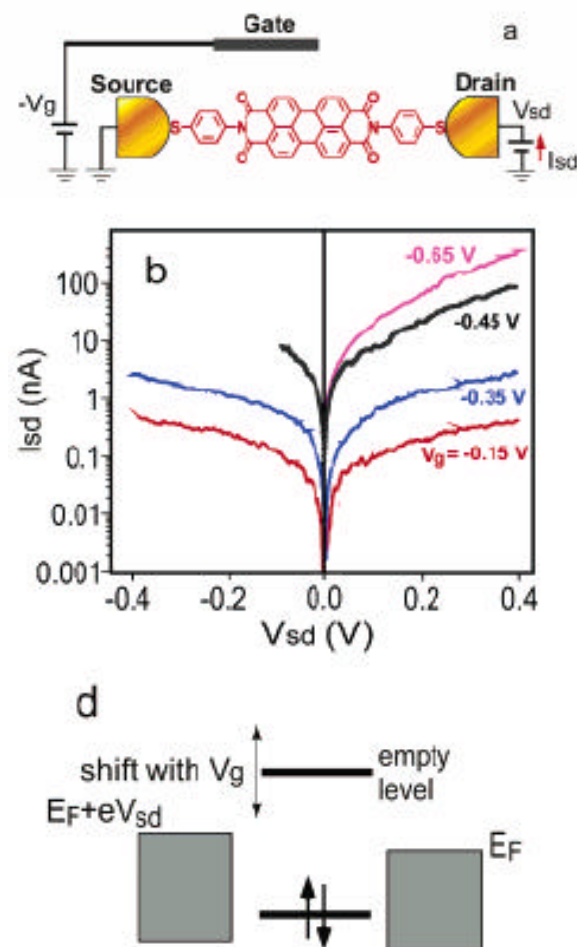
Electrochemical cell

- Counter electrode bias
- Electrolyte
- Thiol bonded junctions

Evidence oxidation/reduction driven changes in conductance

Electrochemical gating

- Repeated atomic scale Au junction formation
- PTCDI: used for n-channel thin film organic FETs
- Avoid reduction
- Observe 30x change in conductance



Xu, et al, JACS, 2005



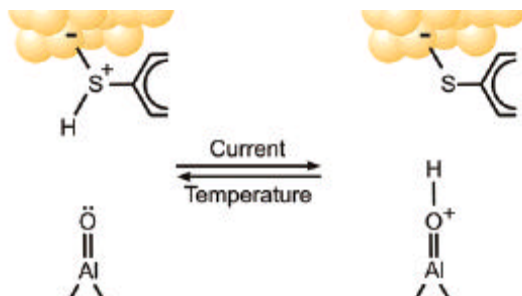
Molecular Function: Hysteresis

Voltage controlled conductance

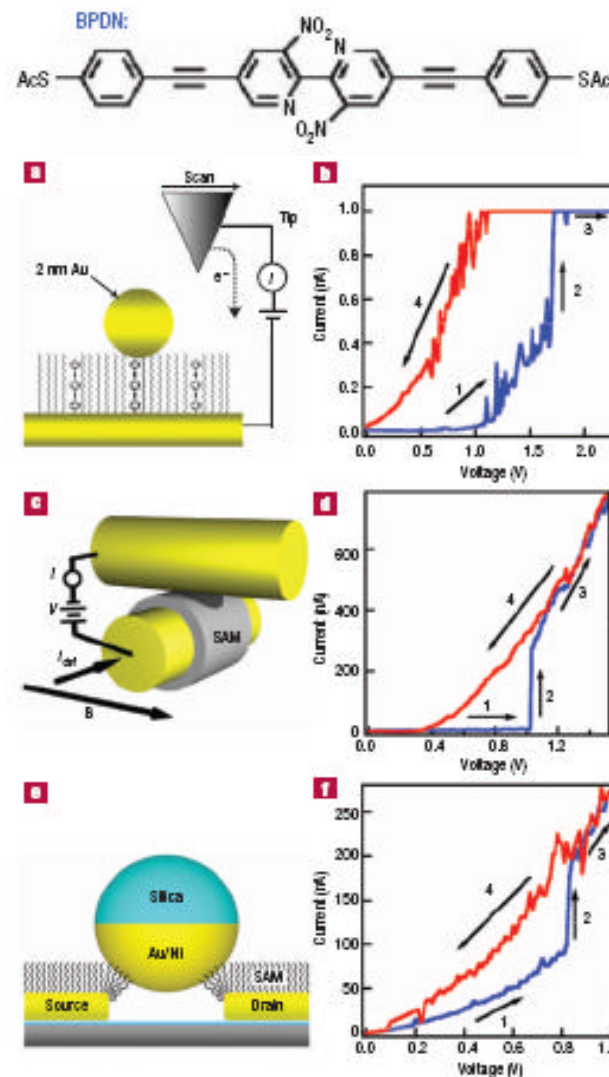
- Several examples in the literature
- Generally involves NO₂ group
- Details vary across literature
 - Blum et al show several cycles

Mechanism

- Change in charge state ?
 - No gate dependence (Keane, et al, Nano Lett, 2006)
- Conformation change ?
 - **Electrode - molecule link change ?**



Danilov, et al, Nano Lett, 2006

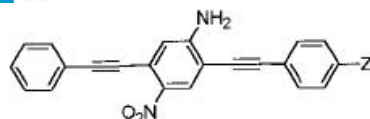


Blum, et al, Nat Mat, 2005



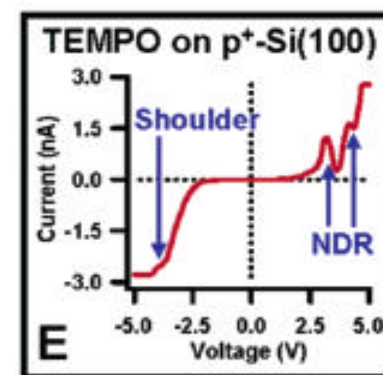
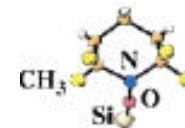
Molecular Function: Negative Diff. Resistance

Literature w/ NO₂ functionalized OPE mixed

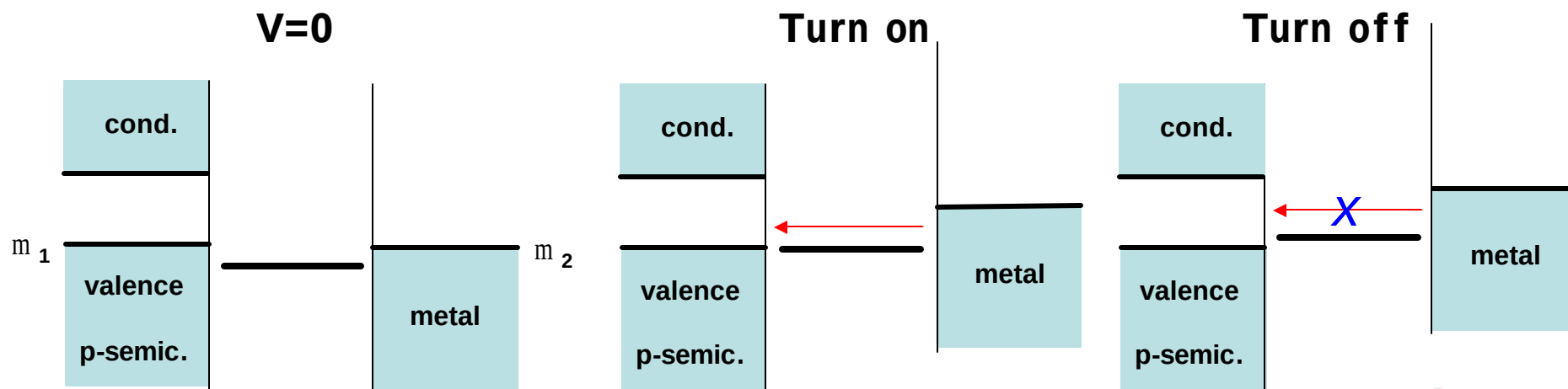


Proposal: One semiconducting electrode

- Intrinsic electronic mechanism
- Supported by simulations
- Initial observation w/ STM controversial
 - Structural switching ?



Guisinger, et al, Nano Lett 2004



Rakshit, et al, Nano Lett 2004



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Introduction to “Single Molecule” Junctions

Examples of “Single Molecule” Conductance Phenomena

New Approach: Bonding in Single Molecule Junctions

Outlook



Thiol – Gold Links: Pervasive, but ...

Large variations in
conductance measurements

Example - Benzenedithiol

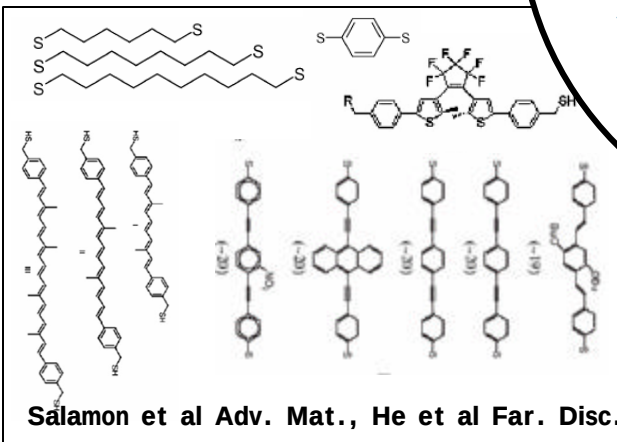
$1.1 \times 10^{-2} G_0 \rightarrow$ Xiao et al

$1.9 \times 10^{-5} G_0 \rightarrow$ Reed et al

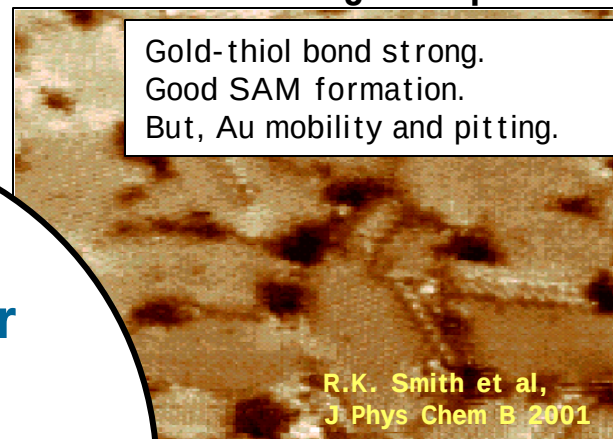
$1.9 \times 10^{-6} G_0 \rightarrow$ Tian et al

Range expected theoretically –
Basch, et al, Nano Lett, 2005

Limited conductance data
on dithiolated molecules



Thiol – Au binding not specific

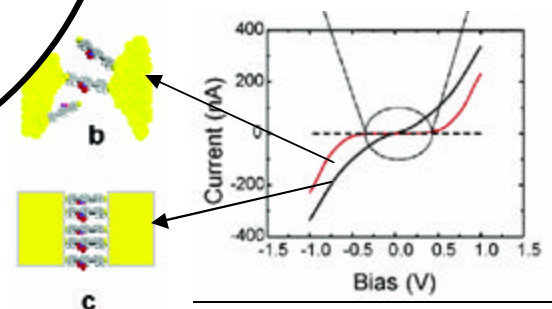


**Not reliable or
reproducible.**

**Limited studies of
systematic trends
for molecular
design**

Ensemble vs Individual

Large discrepancy



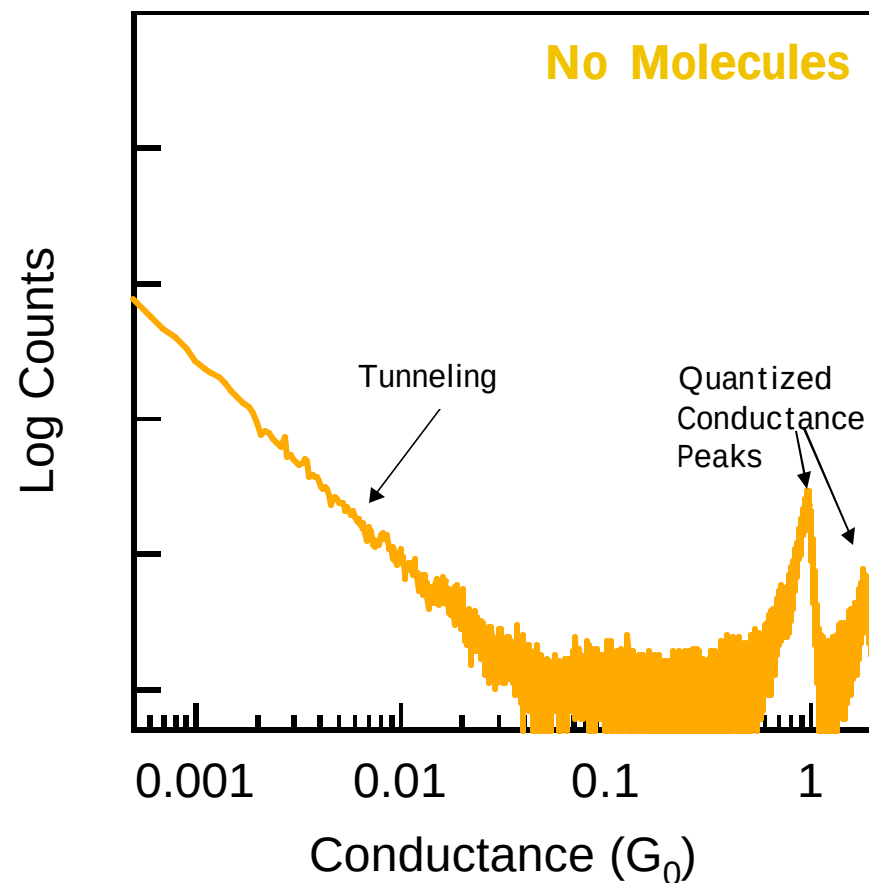
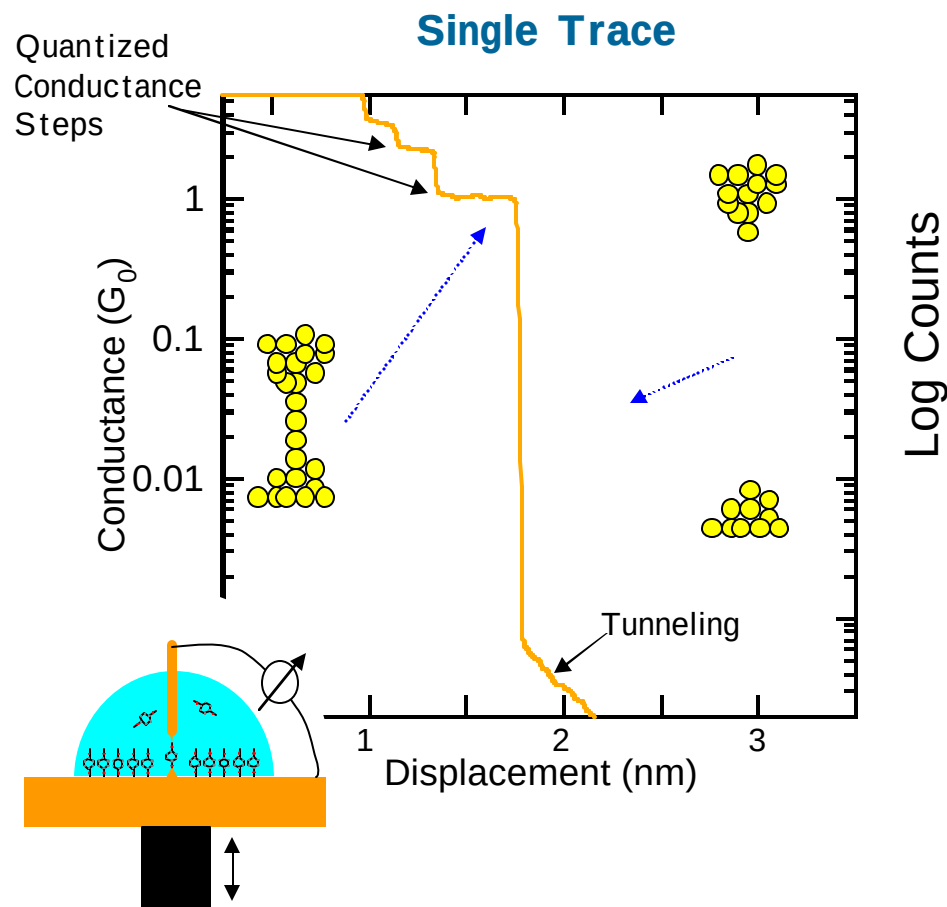
Selzer, et al, Nano Lett, 2005



Repeated Atomic Scale Junction Formation

Break Au point contacts in
solution: no target molecules

Histograms



Method: Xu and Tao, Science 2003

Venkataraman, et al, Nano Lett, 2006

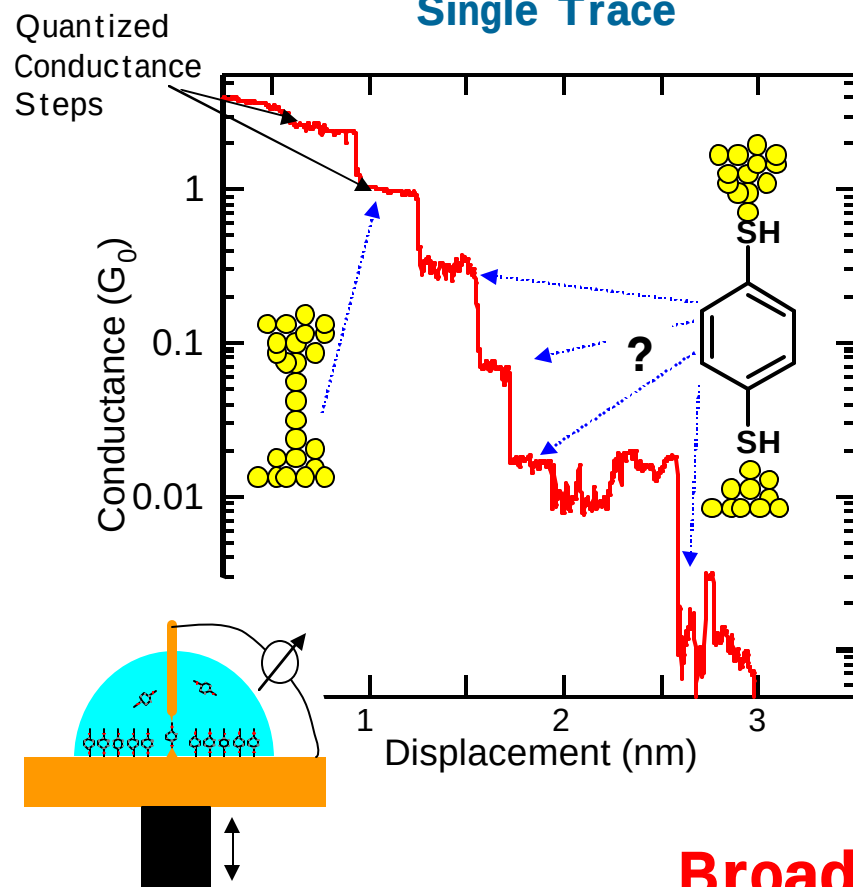
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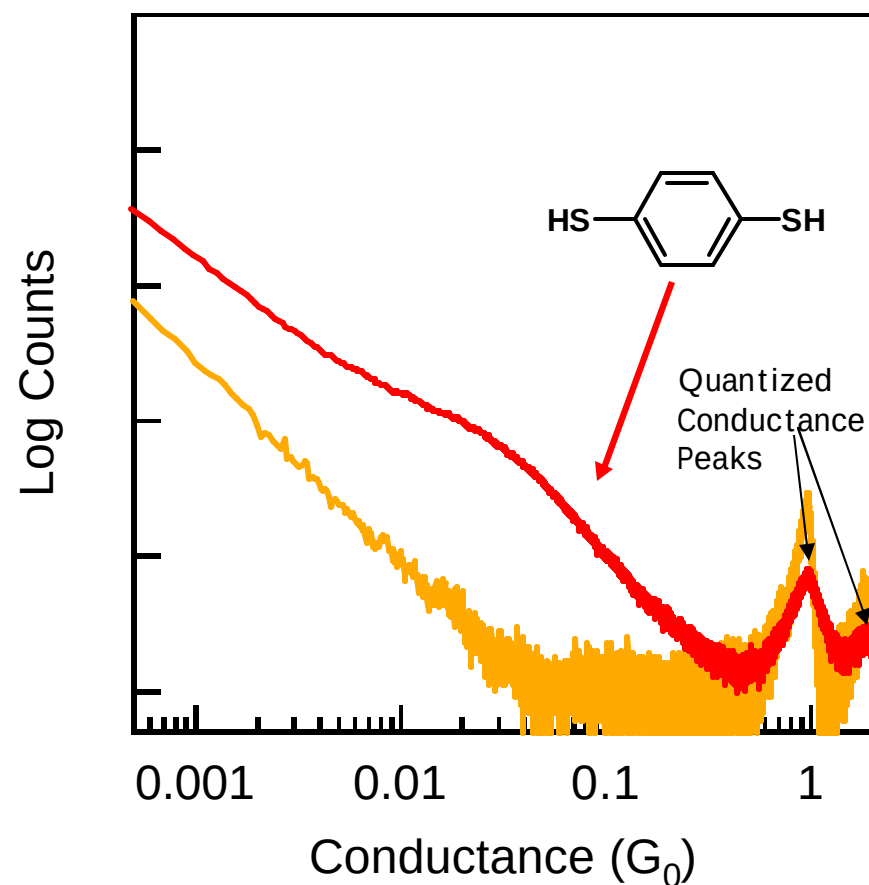
Link Chemistry: Thiol

Break Au point contacts in solution: benzenedithiol

Single Trace



Histograms

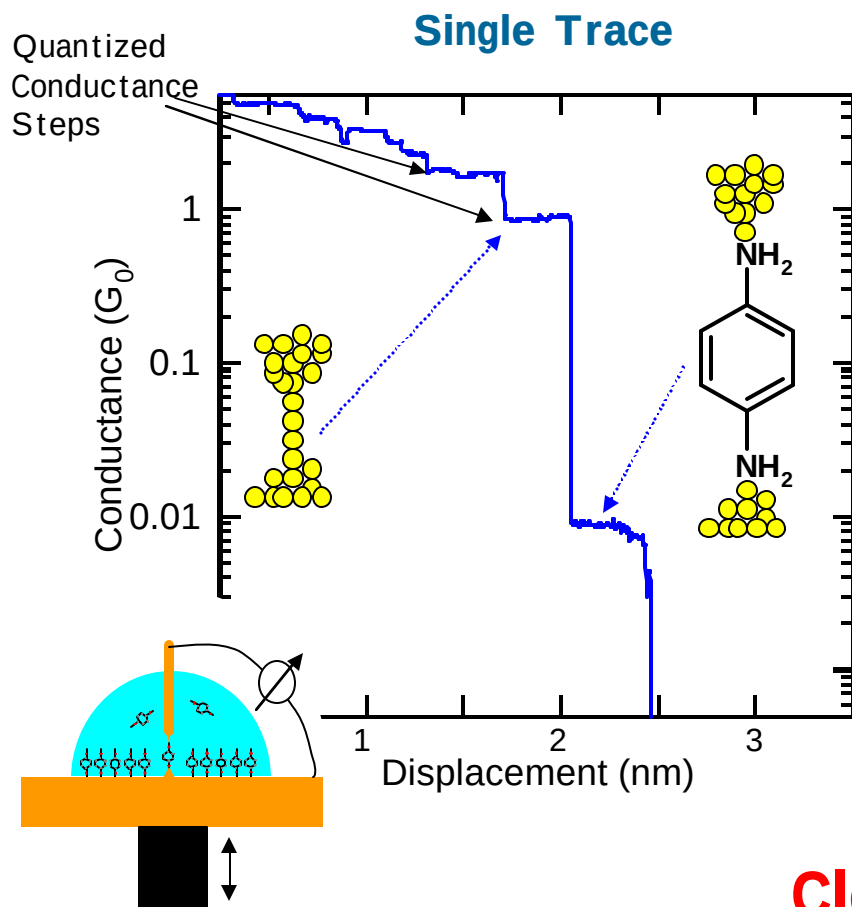


Broad distribution

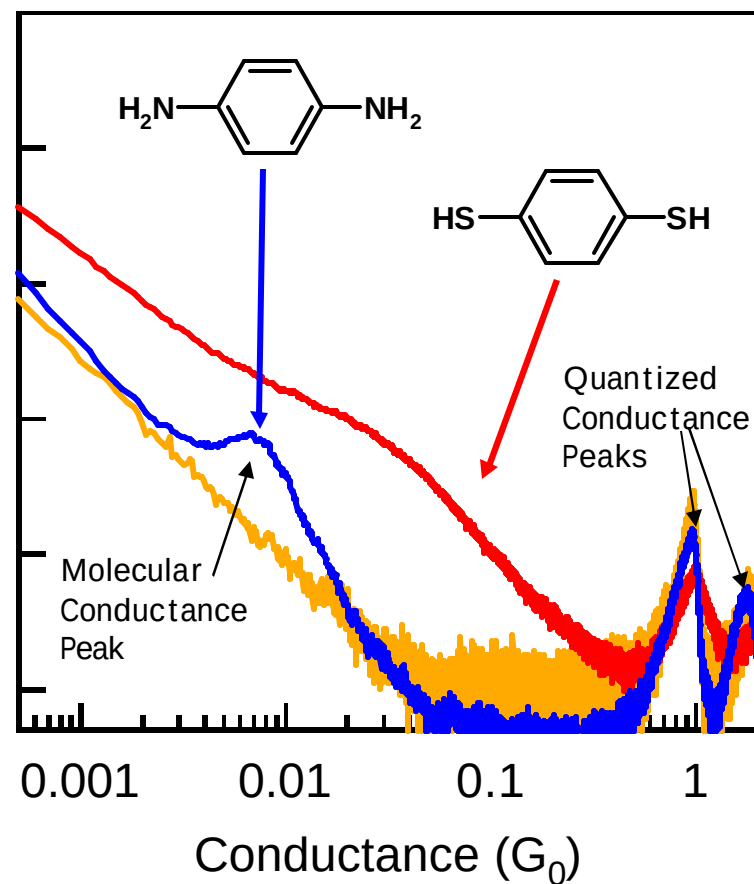


Link Chemistry: Amine

Break Au point contacts in solution: benzenediamine



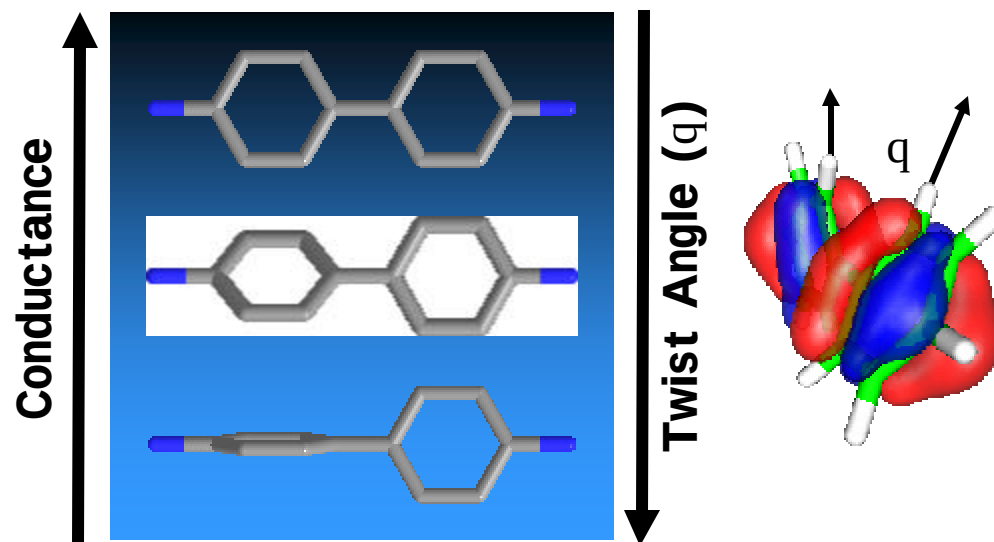
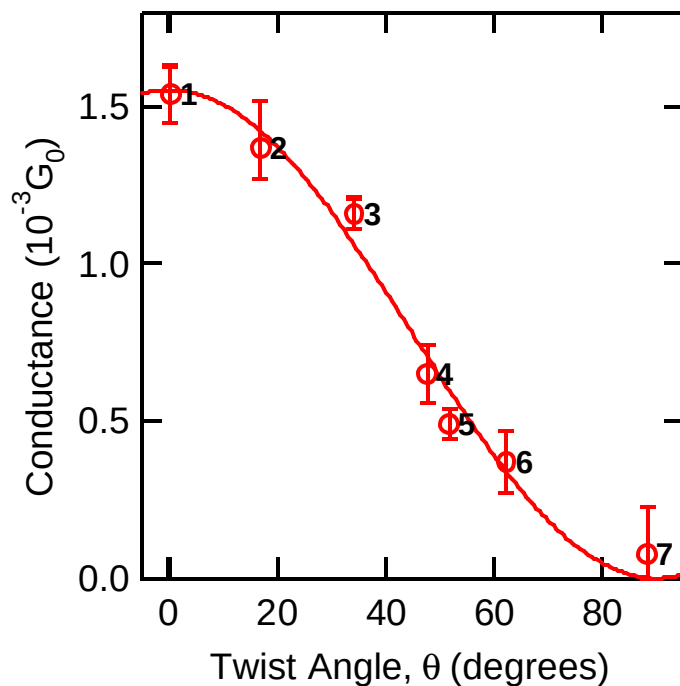
Histograms



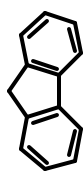
Clear peak



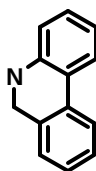
Conductance vs Molecular Conformation



Amine link
not shown



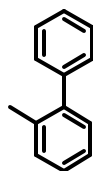
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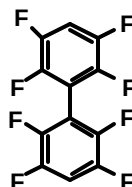
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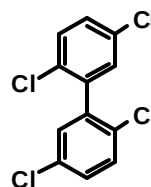
3



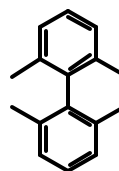
4



5



6



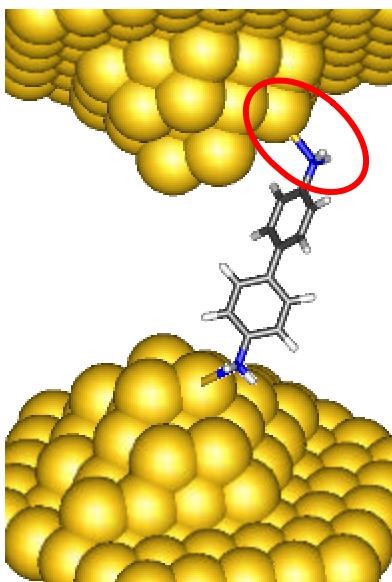
7

Structure - Function:
Cosine square
dependence measured



Why do Amine-Gold Linkages Work ?

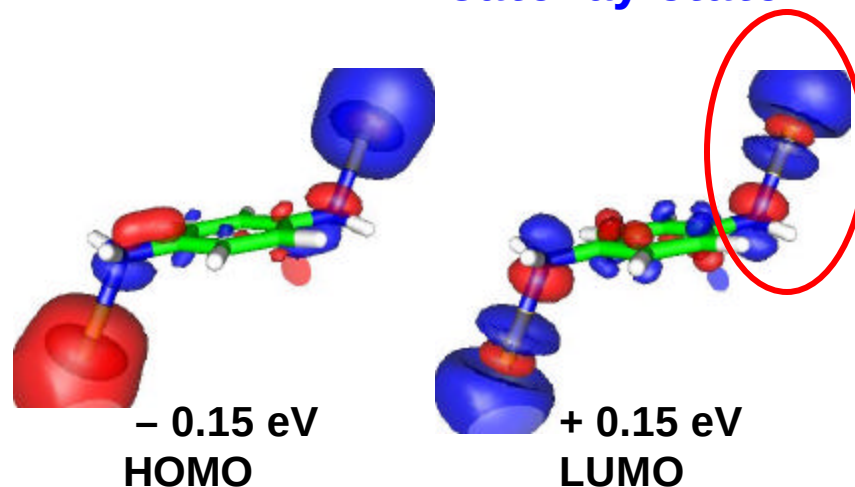
Donor-Acceptor Bond:
N lone pair –
Undercoordinated Au sites



Prototype: ad-atom
Binding energy: ~ 0.5 eV

Frontier Link Orbitals

Gateway state



Au s – N lone pair orbital
Tunnel coupled through p system

Selective bonding motif that
directs a single local orbital
for electronic coupling



Outline

Introduction to “Single Molecule” Junctions

Examples of “Single Molecule” Conductance Phenomena

New Approach: Bonding in Single Molecule Junctions

Outlook



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, ...)



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 more 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
 - Single electron transistors: electrostatic variations



Molecular Electronics: Outlook

Near Term:

- Progress on controlled junction formation
- Establishment of basic “design rules”
- Progress on Nanoelectronics Research Initiative vectors will come with better controlled materials platforms
- Development of hybrid technologies (e.g. CNTs)

Intermediate Term:

- Evaluation of functional molecular device metrics against emerging architectures
- Progress on heterogeneous assembly strategies

Long Term:

- Disruptive materials & process technology change:
 - How far will the electronics industry go ?
 - Key driver will be managing complexity



Molecular Electronics: Post CMOS Technology ?

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

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

SSSC Meeting, Irvine
Mark S Hybertsen 10/19/2006 - 32

Cardamone, Stafford &
Mazumdar, Nano Lett, 2006

