Molecular Electronics

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McGill University
Department of Chemistry
Outline

• Why use molecules?

• Making molecular measurements

• Conduction in molecules

• Molecular switches
Production Costs

Lithography Tool Price ($) vs. Year

- $100,000
- $1,000,000
- $10,000,000
- $100,000,000


Nano Imprint Litho

157nm

193nm
Technical Challenges

ITRS (International Technology Roadmap for Semiconductor) technology trends
Molecular Measurements
Elucidate the roles that “alligator clips”, metals and the molecular core play in defining I-V characteristics.
“Alligator Clips”

Attach molecules to surface and drive the self-assembly process

“Connect” molecular electronic structure to the metallic band structure

Reed and Tour Scientific American June 2000
Electronic Characterization Methods

Nanopore

Break Junction

Hg Drop

Crosswire Junction

Scanning Probes
Break Junction

QuickTime™ and a decompressor are needed to see this picture.

Advantages: Can measure single molecules
Electrical contact to device easy
Stable to T change (low T)

SAM in Nanopore

Advantages: SAM formation well understood
Stable once formed (T, V, molecular decomposition)
High yield of functional devices

Problems With the Top Electrode

Hot metal reacts with SAM (ex: Ti)

Hot metal doesn’t stick to SAM (ex: Au)

Crossed Wire Tunnel Junction

- Simple experimental apparatus
- Wide variety of wires available (Au, Pd, Pt, …)
- Junction contains $\sim 10^3$ molecules
- No metallization after SAM deposition
Thiolate-Metal Interaction

Higher conductivity corresponds to hole injection at the Pd-S interface.

Lower barrier for Pd-S compared to Au-S contact consistent with theoretical predictions.
SPM techniques
Conducting Probe AFM

C. Daniel Frisbie
University of Minnesota

- Molecular junctions made using metal coated AFM tips to contact self-assembled monolayers
- Junction resistance measured as a function of molecular length and contact type
Current vs. Voltage Measurements on Single Molecules

crystalline undecanethiol (C11) SAM

insert dithiol molecule at defect sites

bind 2 nm gold nanoparticles to inserted dithiols

Molecular Film vs. Isolated Molecule

• Intermolecular hopping does not contribute to conductance

Two Layer Tunnel Junction Model

Layer Transconductance:

\[ G = G_0 \exp(-\beta_i h_i) \]

Constant Current Imaging:

\[ G_{C11} G_{gap} = G_{OPV} G_{gap} \]

\[ \beta_2 = \left[ \beta_{C11} h_{c11} - \alpha(\Delta STM - \Delta h) \right] / h_2 \]

Determining $\beta$ via STM Imaging

Apparent height represents convolution of topography and electronic information.

## Molecular Decay Constants

<table>
<thead>
<tr>
<th>molecule</th>
<th>length (Å)</th>
<th>STM apparent height (Å)</th>
<th>$\beta$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C11</td>
<td>12.5</td>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>OPE</td>
<td>20.2</td>
<td>4.3</td>
<td>1.03±0.13</td>
</tr>
<tr>
<td>OPV</td>
<td>19.3</td>
<td>10.0</td>
<td>0.40±0.12</td>
</tr>
<tr>
<td>Ru-OPE (S to final C)</td>
<td>22.4</td>
<td>7.8</td>
<td>0.88±0.12</td>
</tr>
<tr>
<td>Ru-OPE (S to final Ru)</td>
<td>18.6</td>
<td>7.8</td>
<td>0.59±0.08</td>
</tr>
</tbody>
</table>

Multiple Break Junction Formation

Advantages: Good statistics
Probes local environment
Don’t need monolayer

We think about and model single-molecule junctions.
Measuring an Ensemble of Molecules

Are the properties of molecular wires in a metal-molecule-metal junction additive?

Does $G = nG_0$
Theoretical Predictions


Measurements on Alkanes

Scaling of Parallel Molecular Wires


<table>
<thead>
<tr>
<th>sample</th>
<th>molecular structure</th>
<th>length (nm)</th>
<th>crossed wire resistance</th>
<th>STM resistance</th>
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<tbody>
<tr>
<td>OPE</td>
<td><img src="image1" alt="Molecular Structure" /></td>
<td>2.02</td>
<td>$1.7 \pm 0.6 , \text{M} \Omega$</td>
<td>$1.7 \pm 0.4 , \text{G} \Omega$</td>
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<tr>
<td>OPV</td>
<td><img src="image2" alt="Molecular Structure" /></td>
<td>2.07</td>
<td>$0.5 \pm 0.2 , \text{M} \Omega$</td>
<td>$0.6 \pm 0.1 , \text{G} \Omega$</td>
</tr>
</tbody>
</table>
Molecular wires act as discrete non-interacting conductance channels (i.e. $G = nG_0$)
Possible Conduction Mechanisms

- Resonant tunneling
- Non-resonant tunneling
- Non-coherent charge carrier hopping

Dominant Mechanisms for Short Molecules
Conduction via Tunneling

Arrhenius plot of current vs. 1/T at bias voltage 0.1 V to 1 V

Basic 2 Terminal Device
Structure Dependence of Charge Transport

![Graph showing current vs. voltage with molecular structures](image-url)
A molecular vibration can be stimulated when
\[ V \geq \frac{\hbar \omega}{e} \]
IETS of Alkane Thiol

Observation of both IR and Raman vibrational modes

Jason Lazorcik, James G. Kushmerick
IETS of Molecular Junctions

In Junction Optical Spectroscopy

Correlated Optical and Conduction Measurements

Outline

• Motivation
• Switching in Molecules
• Virus as a scaffold
• Making molecular circuits
• Molecular memory devices
Molecular Electronics

• How can we make molecular switches?

• Once we have switches, how can we make electrical contact?
Switching in Molecules
Previous Examples of Molecular Switching


Reed/Tour switch in nanopore voltage based switching

Weiss group (2001), Lindsay group (2003), others switch in STM stochastic switching

Current vs. Voltage Measurements on Single Molecules

crystalline undecanethiol (C11) SAM

25 nm x 25 nm

75 nm x 75 nm

insert dithiol molecule at defect sites

bind 2 nm gold nanoparticles to inserted dithiols

# Stochastic Switching

<table>
<thead>
<tr>
<th>molecule</th>
<th>matrix</th>
<th>reference</th>
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<tbody>
<tr>
<td><img src="image4" alt="molecule" /></td>
<td>decanethiol (C10)</td>
<td></td>
</tr>
</tbody>
</table>
Stochastic Switching

Measurements made at constant bias voltage (1V)

Stochastic switching is dynamic—molecules switch on and off
Molecular Film vs. Isolated Molecule

- Intermolecular hopping does not contribute to conductance

I/V Measurements on BPDN SAMs

Two-State Switching in BPDN

• Is it the same phenomenon as stochastic switching?

• Is it dependent on the experimental setup?

• Is it a molecular property?
Two-State Switching in BPDN

• Is it the same phenomenon as stochastic switching?

• Is it dependent on the experimental setup?

• Is it a molecular property?
Voltage Controlled Switching in STM

Bias history changes imaging properties of inserted molecules.

Change in molecule appearance is due to state change, NOT bias dependent imaging.
STM of a Non-switching Molecule

OPE shows no bias history dependent behavior

Stochastic, but no field based switching observed
Two-State Switching in BPDN

- Is it the same phenomenon as stochastic switching?
- Is it dependent on the experimental setup?
- Is it a molecular property?
Magnetic Entrapment of Metallized Silica Microspheres

SEM images of micromagnetic trap (MMT)
(a) Central region of MMT device.
(b) Image of magnetic proximal probe tips.

Crossed-Wire Test Bed

PRL 89, 086802 (2002)
JACS 124, 10654-10655 (2002)
JACS 125, 3202-3203 (2003)
Conductance Scaling

Molecular Memory Studied by Three Techniques

Consistent switch signature observed for same molecule in three independent test-beds.

Two-State Switching in BPDN

- Is it the same phenomenon as stochastic switching?
- Is it dependent on the experimental setup?
- Is it a molecular property?
In I/V curves, 2 states observed for BPDN molecule, but not for C11 alkane.
Controllable Switching

- Controlled switching between states induced by running bias through 0 V
- Conductance state can be controlled by the applied voltage
Switching between high conductivity state and low conductivity state is reproducible as long as tip stays over molecule
Reproducibility


Two-State Switching in BPDN

• Is it the same phenomenon as stochastic switching?

• Is it dependent on the experimental setup?

• Is it a molecular property?

• What is necessary for two-state behavior?
Switching Mechanisms

Bias offset demonstrates charging in molecule or film.
Two-State Switching in BPDN

• Is it the same phenomenon as stochastic switching?
  • No, independent phenomenon.
• Is it dependent on the experimental setup?
  • No, 3 different test beds show same qualitative behavior
• Is it a molecular property?
  • Yes, isolated BPDN molecules show two state switching
• What is necessary for two-state behavior?
  • Low lying redox states?
  • NO₂ functionality?
  • Pyridinyl functionality?
  • Biphenyl ring structure?
Redox Active Molecules as Switches

Designing a molecular switch:

Low-lying redox states

Conjugated system for conductance

Tong Ren, Purdue

Redox Active, No Switching!

Single redox wave with a formal potential (vs. Ag/AgCl/KCl) of $E^\circ = 0.40$ V

Stochastic switching, but no two state behavior in $I/V$.

Scott Trammel, NRL
Two-State Switching in BPDN

• Is it the same phenomenon as stochastic switching?
  • No, independent phenomenon.

• Is it dependent on the experimental setup?
  • No, 3 different test beds show same qualitative behavior

• Is it a molecular property?
  • Yes, isolated BPDN molecules show two state switching

• What is necessary for two-state behavior?
  • Low lying redox states? NO!
  • NO₂ functionality?
  • Pyridinyl functionality?
  • Biphenyl ring structure?
What is needed for switching?

<table>
<thead>
<tr>
<th></th>
<th>BPDN</th>
<th>trans-DN</th>
<th>cis-DN</th>
<th>BP</th>
<th>Biphen</th>
<th>OPE</th>
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Molecules courtesy Jim Tour
Biphenyl-Dinitro

95% of all molecules probed show 2-state behavior.

For any given molecule, 90% of the I/V traces show 2-state behavior.

Large change in conductance: high to low ratio is $30 \pm 10$. 
Biphenyl

No two-state behavior observed
Cis-Dinitro

85% of all molecules probed show 2-state behavior

For any given molecule, 80% of the I/V traces show 2-state behavior

Large change in conductance: high to low ratio is $15 \pm 8$

Bias offset seen for high conductive state, as in BPDN
Bipyridyl

83% of all molecules probed show 2-state behavior.

For any given molecule, 20% of the I/V traces show 2-state behavior.

Small change in conductance: high to low ratio is $3.5 \pm 2$. 
BP Bias Offset

BPDN

Bias offset opposite in direction?
Polaron Model

### Conductance and Switching

<table>
<thead>
<tr>
<th>molecule</th>
<th>length (Å)</th>
<th>STM apparent height (Å)</th>
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<td>20.2</td>
<td>4.3</td>
<td>1.03±0.13</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>24.1</td>
<td>5.1</td>
<td>1.16±0.31</td>
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<tr>
<td>Bipyridyl</td>
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<tr>
<td>Bipyridyl-Dinitro</td>
<td>24.1</td>
<td>9.3</td>
<td>0.73±0.18</td>
</tr>
</tbody>
</table>

Biphenyl and substituted biphenyls in the low state show the same measured current at 1 V.
What is needed for switching?

• Molecules with NO$_2$ groups have “strong” switching signatures.

• Smaller switching signature still present for pyridyl molecule without NO$_2$ groups!

• No switching for molecule lacking both NO$_2$ and pyridyl groups.
### What is Needed for Switching?

<table>
<thead>
<tr>
<th>Molecular Structure</th>
<th>Switching</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Molecular Structure 1" /></td>
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<tr>
<td><img src="image2.png" alt="Molecular Structure 2" /></td>
<td>Yes</td>
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<tr>
<td><img src="image3.png" alt="Molecular Structure 3" /></td>
<td>Yes</td>
</tr>
<tr>
<td><img src="image4.png" alt="Molecular Structure 4" /></td>
<td>Yes (Minimal)</td>
</tr>
<tr>
<td><img src="image5.png" alt="Molecular Structure 5" /></td>
<td>No</td>
</tr>
<tr>
<td><img src="image6.png" alt="Molecular Structure 6" /></td>
<td>No</td>
</tr>
</tbody>
</table>
Conclusions

• BPDN exhibits bias controlled switching between two conductance states independent of measurement technique

• Redox activity is not enough to produce switching

• NO₂ groups produce a large difference between high and low states, but not required for conductance switching

• $\beta$ for high conductance state significantly enhanced vs. low conductance state (and unsubstituted biphenyl)

• Switching mechanism possibly related to charging, but still unknown—IETS is a good probe
Acknowledgements

NRL
John C. Yang
Charles M. Patterson
Banahalli R. Ratna
Martin H. Moore
Scott Trammell

Rice University
James M. Tour
Yuxing Yao
Jay C. Henderson

SAIC
Ranganathan Shashidhar
David P. Long

Purdue University
Tong Ren

NIST
James G. Kushmerick

Funding
DARPA, ONR