On-Surface Synthesis and Characterization of Conjugated Oligomers Using Low Temperature Scanning Tunneling Microscopy and Spectroscopy

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Synthesis of molecular wires
- oligomers comprising porphyrins and phenyls

Characterization of molecular wires
i. resonant charge transport
ii. negative differential conductance
iii. spin-spin coupling
iv. spin crossover

Summary
Introduction: molecular electronics

Molecular electronics is the study and application of molecular building blocks for the fabrication of electronic components.

- **Advantages:**
  - Bottom-up fabrication
  - Multiple functionality
  - Mechanical flexibility
  - Environment-friendly

- **Challenges:**
  - Production?
    - Synthesize molecules with specific functionality
  - Visualization?
    - Probe structural details at atomic resolution
  - Characterization?
    - Measure electronic structure and charge transport property

http://www.asdn.net/asdn/electronics/molecular_electronics.shtml
Introduction: STM / STS

STM

Morphology

Electronic structure

Molecular orbital

STS

Transport property

Conductance

1 nm
Experimental setup

**Characterization:**
- STM: structural details
- STS: molecular orbital

**Sample preparation:**
- Organic molecule source
- Metal atom source

**Ultrahigh vacuum**
- Low-temperature
  - 77K @ LN₂
  - 4.8K @ LHe
Outline

- **Introduction**
  - molecular electronics
  - scanning tunneling microscopy and spectroscopy
  - experimental setup

- **Characterization of molecular wires**
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- **Summary**
Synthesis: introduction

On-surface synthesis

Oligomer 2

Oligomer 1

Oligomer 0
Synthesis: oligomer 2

**Br₂-TPP @ Au(111)**

**Ullmann coupling reaction @ 180°C annealing**

Oligomer 2
Synthesis: oligomer 1

Co-deposition and 180°C annealing

@ Au(111)
Synthesis: oligomer 0

On surface:

\[
\text{Br}_2-2\text{DPP}
\]

Steric hindrance

In solution:

Synthesize in solution then deposit on surface
Synthesis of $\text{Br}_2$-2DPP in solution
Synthesis: on-surface metalation

Metalation by Fe, Ni, Co, Zn, Mg, Mn, Ce ...

Oligomer 0, 1 and 2 can be *partially* or *fully* metalated by Fe
<table>
<thead>
<tr>
<th>Oligomer 0</th>
<th>Molecular wires</th>
<th>Metalation derivatives</th>
</tr>
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<tbody>
<tr>
<td><img src="image1" alt="Molecular wires" /></td>
<td><img src="image2" alt="Metalation derivatives" /></td>
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<tr>
<td>Oligomer 1</td>
<td><img src="image3" alt="Molecular wires" /></td>
<td><img src="image4" alt="Metalation derivatives" /></td>
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<tr>
<td>Oligomer 2</td>
<td><img src="image5" alt="Molecular wires" /></td>
<td><img src="image6" alt="Metalation derivatives" /></td>
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Synthesis: summary
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Charge transport: mechanism

Off-resonance tunneling

\[ G = G_0 \exp(-\beta z) \]
Saturated: 0.8 Å⁻¹
Conjugated: 0.2 Å⁻¹

Resonant transport: nearly length-independent

Delocalized molecular orbital

Charge transport: electronic property of oligomer 2

HOMO $\rightarrow$ localized

LUMO $\rightarrow$ delocalized

$-0.8 \text{ V}$

$1.6 \text{ V}$

HOMO $\rightarrow$ localized

LUMO $\rightarrow$ delocalized
Charge transport: conductance measurement

STM vertical manipulation

Before manipulation

After manipulation

2 nm

I (V) and \( \frac{dI}{dV} (V) \)

Before manipulation

After manipulation

2 nm

\( \Delta Z \)
Charge transport: different contacts

At lower tip height:

Z displacement: $> 5 \text{nm}$ (19 %)
$< 3 \text{nm}$ (81 %)

**Strong** contact vs. **weak** contact

ΔZ = 1.3nm
Charge transport: first-principle simulation

NEGF – simulation of transmission:

Weak:

Strong:

Conclusion: weak contact $\rightarrow$ physical adsorption

strong contact $\rightarrow$ covalent bonding

electrons transfer through delocalized LUMO
Charge transport: long-range resonant transport

At higher tip height:

Simulation:

- \( \Delta Z (\text{nm}) \):
  - 1.6
  - 2.6
  - 3.3
  - 4.3
  - 5.2

Graph showing differential conductance \( dI/dV \) against bias voltage. 

Graph showing \( \Delta Z \) against bias voltage.
At higher tip height:

**Resonant** transport through **delocalized** molecular orbital magnetic impurities do not affect transport.
The magnitude of the **first** peak

**Oligomer 2**

**Fe-metalated oligomer 2**

Nearly length-independent
Charge transport: branched molecular wires

Br₂-TPP molecules @ Au(111) @ 250°C
Charge transport: T-wire exhibiting NDC

- Lift up T-wire by terminal S
- Stretched after manipulation
- Resonant charge transport
- Negative differential conductance
Charge transport: T-wire exhibiting NDC

- Lift up T-wire by terminal B
- Flipped after manipulation
- Resonant charge transport
- NDC
Charge transport: why NDC?

- Multi-pathway for current?
- Structural kink?
Charge transport: multi-pathway?

- 90°-kinked L-wire
- Lift up by terminal K
- No NDC

Multi-pathway
Charge transport: 90° kink?

- 90°-kinked L-wire
- Lift up by terminal T
- 67% with NDC
Charge transport: $120^\circ$ kink?
Charge transport: mechanism

Redox reaction and resonance transport

Polaron induced charge storage

Alignment and misalignment of delocalized molecular orbital

Changes in molecule-electrode coupling

M. L. Perrin et al., Nat. Nanotechnol. 9, 830 (2014)
Charge transport: first-principle simulation

HOMO-1 becomes *less delocalized* at high bias.
Charge transport: summary

Oligomer 2

- Resonant charge transport

- Negative differential conductance
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- **Summary**
Spin-spin coupling: introduction

Interaction between spins

- **Direct** coupling
  - overlap of orbitals with non-zero magnetic moment
  - dipole-dipole coupling

- **Indirect** coupling
  - interacting through a certain medium
  - RKKY – mediated by conduction electrons
  - exchange – mediated by organic molecule

[Diagrams showing distances 1.73 nm, 1.31 nm, and 0.89 nm]
Spin-spin coupling: Fe-TPP

Fe-TPP monomer

Spin-excitation spectroscopy @ 4.8K
Spin signature of individual atoms
Spin-spin coupling: Fe-metalated oligomer 2 and 1

Spins in the oligomers exhibit the same behavior as isolated spins: neighboring spins are \textit{decoupled}
Spin-spin coupling: Fe-metalated oligomer 0

Spin-excitation *quenched* \(\rightarrow\) neighboring spins are *coupled* 

*Exchange* interaction mediated by molecular backbone
Spin-spin **indirect** interaction mediated by molecular backbone
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Spin crossover: introduction

Spin crossover

External stimulus:
- Temperature
- Light
- Charge flow
- Pressure
- Electric field
- ... ...

Switches in Molecular electronics

Assemble of molecules

Single-molecule level?

Switching

Spin crossover: vertical manipulation + STS

Bottom to top: 1.2 to 3.4 nm

Kondo effect @ 4.8 K
Spin crossover: width of Fano resonance

\[ \Gamma_{\text{Fano, Res.}} \]
Spin crossover: DFT simulation

$d_{xy}$  
$d_{yz}$  
$d_{xz}$  
$d_{z^2}$  
$d_{x^2-y^2}$

PDOS (a.u.)

unpolarized  
unpolarized
Spin crossover: magnetic moment & Fe-N bond length

\[ T_K \approx \frac{\omega_0}{k_B} \exp\left(\frac{1}{J \rho}\right) \]

\( \rho J \rightarrow \text{spin density} \)

Porphyridium conformation:

**Saddle** ↔ **planar**

Graphs showing the relationship between magnetic moment and gap, and Fe-N bond length and gap.
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Thanks For Your Attention