Impact of collective effects on charge transport through molecular monolayers

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11.12.2013
Outline

• Introduction
• Motivation
• Investigated Systems
• Methodology
• Results
Introduction

What is molecular electronics?

- single molecules as active elements in nanocircuits
- based on the bottom-up approach
- functional molecules add a unique ingredient of variability and structural control

http://www.asdn.net/asdn/electronics/molecular_electronics.shtml
A brief history of molecular electronics

1974 A. Aviram and M. Ratner - *molecular rectifiers*

1981 G. Binning and H. Rohrer - *STM*

1990 Mechanically Controllable Break-Junction *MCBJ*

1997 M. Reed and J. Tour - *first transport experiment* in single molecule junctions
Motivation

molecular junction
Motivation

single molecule vs. monolayer
Motivation

- two isomeric molecules
- same molecular IP

→ expect same charge transport characteristics

Motivation

single molecule vs. monolayer
Motivation

• different transport characteristics as monolayer

Motivation

- different charge transport polarity

Transmission and Current

- channel closest to Fermi Energy determines charge transport characteristics
Motivation

- thermocurrent of opposite sign
- Seebeck coefficient of opposite sign

Motivation

• two isomeric molecules behave very different in monolayer devices due to collective electrostatic effects

\( \text{N}_{\text{in}} \) local dipoles add up

\( \text{N}_{\text{out}} \) no local dipoles

Motivation

• fundamental difference in charge transport between single molecules and monolayers

• study collective effects through coverage dependent calculations in SAMs

• apply DFT combined with Green’s function approach

• investigate different docking groups
Investigated Systems

$\text{Au (111)}$  \hspace{5cm} \pi\text{- conjugated system} \hspace{5cm} \text{Au (111)}$

metal -- docking -- backbone -- docking -- metal
Investigated Systems

- internal

- docking

- reference
Methodology

- Coverage dependent calculations

  - DFT using VASP [1]
  - periodic boundary conditions
  - PBE exchange-correlation functional
  - 3 layers of Au acting as slab

Methodology

• Geometry optimization

- with VASP - conjugate gradient
- optimized structure and length in z direction
- relaxed innermost Au layers
Methodology

• Coverage dependence

\[ \theta = 1 \]

\[ \theta = 0.5 \]

\[ \theta = 0.0625 \]
Methodology

• Transport calculations

- DFT using SIESTA [1]
- periodic boundary conditions
- localized atomic orbitals
- semi-infinite lead

Transport calculations

Landauer - Büttiker formalism

\[ I(V) = \frac{2e}{h} \int T(E)[f_L(E + \mu_L) - f_R(E - \mu_R)]dE \]

\[ \mu_{L/R} = E_F \pm e \frac{V}{2} \]

\[ T = \text{trace} \left[ \Gamma_L G^R \Gamma_R (G^R)^t \right] \]

\[ T(E, V) \approx T(E, 0) \]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>current</td>
</tr>
<tr>
<td>V</td>
<td>voltage</td>
</tr>
<tr>
<td>T</td>
<td>transmission function</td>
</tr>
<tr>
<td>f_{L/R}</td>
<td>left/right electrode</td>
</tr>
<tr>
<td>\mu_{L/R}</td>
<td>chemical potential</td>
</tr>
<tr>
<td>G^R</td>
<td>ret. Greens function</td>
</tr>
<tr>
<td>\Gamma_{L/R}</td>
<td>broadening matrix</td>
</tr>
</tbody>
</table>
Coverage effect – molecules with internal dipoles

- internal

- docking

- reference
Coverage effect – molecules with internal dipoles

- two isomeric molecules
- same molecular IP (Ionisation Potential)
- same docking chemistry
\[ N_{\text{out}} \]

\[ \Delta E = 0.5 \text{eV} \]

DOS (a.u.) against \( E - E_F \) (eV) with different \( \Theta \) values.
$N_{in}$

![Molecular structure](image)

$\Delta E \leq 0.1\text{eV}$

![DOS plot](image)

- $\Theta = 1$
- $\Theta = 0.5$
- $\Theta = 0.25$
- $\Theta = 0.125$
- $\Theta = 0.0625$
Coverage effect – molecules with internal dipoles

$N_{\text{in}}$ vs $N_{\text{out}}$
Coverage effect – molecules with internal dipoles

\[ N_{\text{in}} \quad \text{vs.} \quad N_{\text{out}} \]

\[ \Delta E = 0.8 \text{eV} \]

\[ \Delta E = 0.2 \text{eV} \]

\[ \text{DOS (a.u.)} \]

\[ E-E_F \text{ [eV]} \]
Coverage effect – molecules with internal dipoles

$N_{\text{in}}$  

$N_{\text{out}}$

\[ \Theta = 1 \]
\[ \Theta = 0.5 \]
\[ \Theta = 0.25 \]
\[ \Theta = 0.125 \]
\[ \Theta = 0.0625 \]

$\rightarrow$ two collective effects
Investigation

- molecule – metal bonding
Molecule - metal bonding

• charge rearrangements upon bond formation

\[ \Delta \rho = \rho_{\text{sys}} - (\rho_{\text{Au}} + \rho_{\text{mol}} - \rho_{\text{H}}) \]
Molecule - metal bonding

• electrostatic potential step due to $\Delta \rho$

\[ \nabla^2 V = -\frac{\Delta \rho}{\varepsilon_0} \]
SAM-substrate bonding

$N_{\text{out}}$

\[ \text{Au} \quad \text{S-C} \quad \text{N} \quad \text{H}_2 \quad \text{N} \quad \text{C-S} \quad \text{H}_2 \quad \text{Au} \]

\[ \Delta E_{BD}(\text{eV}) \]

$\Theta = 1$

$\Theta = 0.5$

$\Theta = 0.25$

$\Theta = 0.125$

$\Theta = 0.0625$
SAM - substrate bonding

$N_{in}$

![Graph showing $\Delta E_{BD}(eV)$ versus some parameter with different curves for different values of $\Theta$.]
Coverage effect – molecules with internal dipoles

$N_{\text{in}}$

$N_{\text{out}}$

→ coverage effect of Bond Dipole similar
Coverage effect – molecules with internal dipoles

\[ N_{\text{in}} \]

\[
\begin{array}{c}
\text{S} - \text{C} - \text{N} \\
\text{H}_2 - \text{C} - \text{N} - \text{C} - \text{H}_2 \\
\text{S}
\end{array}
\]

\[ N_{\text{out}} \]

\[
\begin{array}{c}
\text{S} - \text{C} - \text{N} - \text{N} - \text{C} - \text{N} - \text{C} - \text{H}_2 \\
\text{S}
\end{array}
\]

Graphs showing DOS (Density of States) for different coverages \( \Theta \):
- \( \Theta = 1 \)
- \( \Theta = 0.5 \)
- \( \Theta = 0.25 \)
- \( \Theta = 0.125 \)
- \( \Theta = 0.0625 \)

DOS is plotted against \( E - E_F \) (Energy relative to Fermi level) in eV.
Coverage effect – molecules with internal dipoles

Investigation

• molecule – metal bonding

• free monolayer
Free monolayer

coverage effect of local dipoles is different
Free monolayer

$N_{\text{in}}$

local dipoles add up

$N_{\text{out}}$

no local dipoles
Coverage effect – molecules with internal dipoles

\[ \text{\( N_{\text{in}} \)} \quad \text{local dipole and bond dipole effects cancel} \]

\[ \text{\( N_{\text{out}} \)} \quad \text{local dipole and bond dipole effects do not cancel} \]

\[ \rightarrow \text{two collective effects} \]
Coverage effect – molecules with internal dipoles

- two isomeric molecules act very different as monolayers due to collective effects

- ability of turning these collective effects off by tuning molecules with intramolecular dipoles
Transport calculations

**SIESTA** – localized atomic orbitals

**VASP** – plane waves

→ compare DOS

\[ N_{\text{out}} \]

![DOS graph](image_url)

- **DOS** (a.u.)
- **E-E_F [eV]**

Legend:
- `vasp θ=1`
- `vasp θ=0.5`
- `vasp θ=0.25`
- `vasp θ=0.125`
- `vasp θ=0.0625`
- `siesta θ=1`
- `siesta θ=0.5`
- `siesta θ=0.25`
- `siesta θ=0.125`
- `siesta θ=0.0625`
Transport calculations

SIESTA  – localized atomic orbitals
VASP   – plane waves

$N_{\text{out}}$

$0.1 \text{ eV}$
Transport calculations

SIESTA – localized atomic orbitals

VASP – plane waves

\[ N_{in} \]

\[ \text{DOS (a.u.)} \]

\[ E-E_F [\text{eV}] \]
<table>
<thead>
<tr>
<th>SIESTA</th>
<th>vs.</th>
<th>VASP</th>
</tr>
</thead>
<tbody>
<tr>
<td>• reproduce the trends, but for low coverages we still have a mismatch of about 0.1 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• localized atomic orbitals cannot describe vacuum very well</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• introducing ghost atoms does not work so far</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Transmission and Current

- full coverage

\[ I(V) = \frac{2e}{h} \int T(E)[f_L(E + \mu_L) - f_R(E - \mu_R)]dE \]
Transmission and Current

- full coverage

\[ I(V) = \frac{2e}{h} \int T(E)[f_L(E + \mu_L) - f_R(E - \mu_R)]dE \]
Transmission and Current

• full coverage
Transport calculations - coverage

$N_{\text{out}}$
Transport calculations

Charge transport polarity

- change in charge polarity when going from monolayer to single molecule
- n-type $\rightarrow$ p-type
Transport calculations - coverage

$N_{in}$

![Molecule structure](image)

![Graphs](graphs)
Coverage effect – molecules with internal dipoles

First conclusion

\[ N_{in} \rightarrow N_{out} \]

- two molecules with same IP and docking chemistry result in two different monolayers due to collective effects
- ability of turning these collective effects off
- change in charge transport polarity when going from single molecule to monolayer due to collective effects
Results

- internal

- docking

- reference
Results – docking groups

• transport characteristics for full coverage

L. A. Zotti et al, small 2010, 6, No.14, 1529-1535
W. Hong et al, J.Am.Chem.Soc 2012, 134, 2292-2304
Results

- internal

- docking

- reference
Reference System

Tour$_{CH_2SH}$

- different molecular IP
- same docking chemistry
Reference System

Tour_{CH_2SH}
Reference System

Tour_{CH_2SH}
Results

- internal

- docking

- reference
Docking groups

\[ \text{Tour}_{\text{Pyr}} \]

- different molecular IP
- different docking chemistry
Docking groups

Tour$_{Pyr}$

- LUMO pinned at the Fermi Energy only for full coverage
Docking groups

**Tour\textsubscript{Pyr}**

- charge rearrangements extended along molecular backbone
- local polarization of the SAM
Docking groups

Tour_{Pyr}
Docking groups

Tour\textsubscript{Pyr}
Summary

- **collective effects** are very important in molecular electronics

![Molecular structures]

- two isomeric molecules result in two different monolayers with different charge transport polarity

- ability of turning collective effects off

- change in polarity when going from monolayer to single molecule
Summary

- **docking chemistry** strongly affects electrical transport

- collective effects can lead to **Fermi level pinning**
Outlook

Clusters of molecules

When do collective effects appear?
Acknowledgement

supervisor: Egbert Zojer

group: David, Iris, Gernot, Berni, Lisi and Elsi

financial support: Austrian Science Fund
Thank you for your attention!
“Length Dependence of Conductance in Aromatic Single-Molecule Junctions”
“Quantitative Current-Voltage Characteristics in Molecular Junctions from First Principles”
Isolated molecule vs. SAM

Experimental techniques

A) STM/cpAFM
B) Break junction
C) Liquid metal
D) Cross-wire
E) Cross-bar
F) Conducting Polymer

A. Gold wire

Add THF and benzene-1,4-dithiol

SAM

B. Gold wire

Wire stretched until breakage, resulting in tip formation

SAM

C. Gold electrode

Gold electrode

Solvent evaporates, then tips brought together until the onset of conductance

D. Gold electrode

Gold electrode