Towards Molecular Spintronics: Different conductivity through open- and closed-shell molecules

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MOLECULAR-SPINTRONICS, where spin-polarized currents are carried through molecules, and in turn they can affect the state of the molecule.

The two possible spin states represent ‘0’ and ‘1’ in logical operations.

To develop this field, one major point is to find novel ways of both generation and conservation of spin polarized current.
Why organic molecules?

Due to their weak spin-orbit coupling and hyperfine interactions, organic molecules are considered to be ideal media for spin transport, in which spin coherence over time and distance could be preserved much longer than in inorganic materials.

*Theoretically:* Spin filters, i.e., as devices favoring transport of electrons with either spin up or spin down.

*Limitation:* only for situations in which spin flips can be neglected.

*Defined as a molecule with one or more unpaired electrons, and hence, it exhibits a magnetic moment.*

*Spin-polarization and its conservation.*

*J. Am. Chem. Soc. 2010, 132, 3682*
Some very appealing recent findings...

In the lower-T range: conductance of SPM network $<<$ SLM network.

Across NP of the SPM network:

Across NP of the SLM network:

This is the first experimental demonstration of the interaction between a single organic localized spin with an electron tunneling through the molecule.

Importance of studying the transport through the molecule
Polychlorotriphenylmethyl (PTMs) radicals as bistable and switchable multifunctional molecules

- Highly persistent
- Easily functionalized
- Magnetic
- Optical
- Fluorescent
- Electroactive

**Structure:**

- Closed-shell
- Open-shell $S=1/2$
SELF-ASSEMBLED MONOLAYERS (SAMs)

- Well-defined thickness
- Acts as a physical barrier
- Alters electronic conductivity and local optical properties

<table>
<thead>
<tr>
<th>Surface</th>
<th>Anchoring groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>Thiols</td>
</tr>
<tr>
<td></td>
<td>disulfides</td>
</tr>
<tr>
<td></td>
<td>Sulfinic acids</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silanes</td>
</tr>
<tr>
<td>ITO</td>
<td>Silanes</td>
</tr>
<tr>
<td></td>
<td>carboxylic or phosphonic acids</td>
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</tbody>
</table>
Preparation of PTM SAMs: Two different approaches

I) Two-step approach

- Terminal group that reacts with the PTM radical
- Binding group to the surface

II) One-step approach

- PTM unit
- Binding group to the surface

-Electrochemical properties
-Molecular wire
C-AFM: Three-dimensional Mode: 3D for transport measurements

At each tip-sample distance a voltage is applied between two fixed values and the current (I) as a function of the bias voltage (V) and the sample displacement distance towards the tip (z) are simultaneously measured.

Normal Force (F_n) and the current (I) as a function of the bias voltage (V) and the sample displacement distance towards the tip (z) are simultaneously measured.

In collaboration with Dr. Carmen Munuera, Marcos Paradinas and Prof. Carmen Ocal (ICMAB-CSIC)
At each $F_n$ is possible to obtain the $I/V$ curves. 

Voltage range: +2V
Piezo movement: 5nm

From C. Munuera
I) Two-step approach: non-conjugated PTM SAM on gold

![Diagram showing the two-step approach for non-conjugated PTM SAM on gold](image)

**Contact angle = 64°**

**Contact angle = 84°**

Transport properties through radical and non-radical SAMs

SAMs differ in their molecular structure but a large difference in the electronic structure:

\[ R(H) = 280 \, \text{M}\Omega \]
\[ R(r) = 35 \, \text{M}\Omega \]

\[ R(H) = 200 \, \text{M}\Omega \]
\[ R(r) = 12 \, \text{M} \, \Omega \]
Energylevels of non-radical and radical SAMs

DFT calculations on PTM-(CO)-NH-Ph

Non-resonant tunneling

Spin filter???

Radical SAM: LUMO assisted transport, contribution of resonant tunneling mechanism
II) One-step approach i.e., direct anchoring

Design and Synthesis:

\[
\begin{align*}
&\text{MeS} - \text{CHO} \\
&\quad \xrightarrow{1. \text{MeSNa}, \text{HMPA}} \text{AcS} - \text{CHO} \\
&\quad \xrightarrow{2. \text{AcCl}} \end{align*}
\]
Transport properties through conjugated PTM SAMs with C-SFM

Junction resistance (R) as a function of applied force

\[ R(H)/R(\text{rad}) \] is one order of magnitude higher than the non-conjugated SAM

Non-radical SAM: non-resonant tunneling
Radical SAM: resonant tunneling

(B3LYP\textsuperscript{13} hybrid functional and a 6-31G(d,p) basis set)

*ChemCommun.* 2011, 47, 4664
Negative differential resistance (NDR): decreasing current through a junction at increasing voltage.

*Attributed to resonant tunneling between molecular orbitals and the metal delocalized states.

*Junctions exhibiting nonlinear current-voltage properties such as NDR could serve as nanoscale analogues of multistate electronic switches (J. Am. Chem. Soc. 2004, 126, 295)

Different origins for NDR:

- Conformational changes.

- Charging of the molecule followed by the localization and delocalization of orbitals.

- Polaron formation in redox active molecules.
In these systems, the redox character does not determine the NDR.
Representative $I/V$ for both SAMs at different applied loads, at about 2nN higher for the non-radical.

$R(\alpha \text{H}) \sim 4000 \text{ M}\Omega$

$R(\text{rad}) \sim 100 \text{ M}\Omega$

Negative differential resistances (NDR) in both $I$-$V$ curves

$\alpha = \beta$

ChemCommun. 2011, 47, 4664
Proposed transport mechanism

<table>
<thead>
<tr>
<th>At low bias</th>
<th>Non-resonant tunneling</th>
<th>Resonant tunneling mediated by LUMO-β</th>
</tr>
</thead>
<tbody>
<tr>
<td>At higher bias</td>
<td>Some resonant tunneling with the unoccupied orbitals</td>
<td></td>
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</table>

α = β

LUMO

B-doped diamond

LUMO-β

Au

HOMO

SOMO
Conclusions

Open-shell form is significantly more conducting than the closed-shell derivative.

Larger conductivity is observed for the conjugated radical in agreement with a larger hybridization with the metal surface.

The redox character does not determine the NDR phenomena.

LUMO-β plays an important role in the transport which could be exploited for spintronics.

These type of comparatives measurements can help the fundamental understanding of the transport mechanism.
Acknowledgments

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