Designing interfaces for Spin Injection into Organic Molecular Solids: A Surface Science Approach

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Office of Basic Energy Sciences
Serving the Present, Shaping the Future
Technological Motivation: Spintronics

Spintronics = “Spin-electronics”: Applications of spin-dependent charge transport

Already a huge industry:

Nobel Prize in Physics 2007

“For the discovery of Giant Magnetoresistance”

Large change in metallic sensor resistance due to the small magnetic field of a bit.


Recall Nobel Prizes in 2007

Nobel Prize in Physics 2007

Fert Grünberg

“For the discovery of Giant Magnetoresistance”

Nobel Prize in Chemistry 2007

Ertl

“For his studies of chemical processes on solid Surfaces”

Baibich et al.,

Ertl, Nobel Lecture.
Organic Semiconductors: New Mechanisms in Spintronics?

Organic Semiconductors: highly controllable optoelectronic properties by synthesis

1) Localized hopping transport – new “polaron” mechanisms of spin transport?

2) Synthetic tuning of molecular magnetism is very sophisticated

Mn_{12} : S = 10
Motivation: Magnetoresistance in Organic Semiconductors

“GMR” in an Organic Spin Valve:

Z. H. Xiong et al.

![Graph showing magnetoresistance](image)

No MR observed in thick Co/Alq3/Fe sandwiches?

Interface Effects: Spin Control with Molecular Orbitals?

300% “Tunneling GMR” in Alq₃ Nanojunctions


THE RISE OF SPINTERFACE SCIENCE

Little is known about the mechanisms that govern the injection of spins into organic molecules. A new study suggests that the metal/organic interface is key, paving the way for a new field in which interfaces are specifically designed for spin applications. This is this field of ‘spinterface’ science.

Stefano Sanvito

* Strong molecular coupling inverts effective interface polarization
Interface Effects: Spin Control with Molecular Orbitals?

Example: $p_z$-$d$ hybridization can control spin polarization at interfaces

DFT Calculations

Spin Polarized STM Imaging

Metal-Orgnic Interfaces in Spintronics: A Chemistry View


I learned about the beauty of these ideas as a Post-Doc with John Yates at Pitt
Scanning Tunneling Microscopy

Quantum tunneling from a sharp tip allows atomic-resolution images:

Scanning Tunneling Spectroscopy (STS)

**Tunneling Current:**

\[
I(z, V) = \frac{\pi e \hbar^3 A}{2m^2} \int_0^{eV} \rho_s(eV)\rho_t(E-eV)T(z, V, E)dE
\]

\[\exp(-f(E, V)z)\]

**Density of States:**

\[
\rho \propto \frac{V}{I} \left[ \frac{dI}{dV} \right] z = z_0
\]
Spin Polarized STM: High Resolution TMR on Clean Surfaces

R. Wiesendanger, Rev. Mod. Phys. 81, 1409 (2011)

Spin-polarized conductance:

\[ G = G_{SA} + G_{SA} m_s m_t \cos \theta \]

Spin polarized DOS and spin asymmetry A:

\[ m_s = \frac{\rho^\uparrow - \rho^\downarrow}{\rho^\uparrow + \rho^\downarrow} \propto \frac{G_P - G_{AP}}{G_P + G_{AP}} \equiv A \]

Fe-coated Tungsten tips often give Spontaneous spin contrast on Cr(001):

We use this to make “model” spin valves!
Surface Electronic Structure of Cr(001) at T = 130 K

Clean Cr(001) Topographic STM image

Tunneling Spectrum of Cr(001)

Surface state peak is due to $d_{z^2}$ orbitals on Cr(001)
Spin Polarized Interface States For Spintronics

Alq3

Cr(001)
Decomposing the Spin Polarized Interface States for Alq2/Cr(001)

\[ \text{Enhances Fermi level spin polarization at the interface!} \]

Similar to the interaction mechanism in our previous study of PTCDA/Cr(001):

Hybridization Mechanism: Alq3 on Cr(001)

Charge transfer

Alq3 vs. Crq3: Changing d-orbital content

S = 0

Alq3: $\pi$ frontier orbitals

Crq3: $\pi$+d frontier orbitals

S = 3/2

DFT Calculations from W. Jiang and F. Liu, University of Utah MSE
SS is gone!

Crq3

Cr(001)
Hybridization Mechanism for Crq3 on Cr(001): Orbital Mixing

Something like a conventional covalent bond forms here.

Cr(001) $d_{z^2}$ surface state

$dd\sigma$ $dd\sigma^*$

LUMO $d$ orbital of Cr
Comparative Density Functional Theory Studies of Alq3, Crq3 on Cr(001)

**Crq3**

$E_b = 9.35 \text{ eV}$

$z_b = 0.262 \text{ nm}$

**Alq3**

$E_b = 7.72 \text{ eV}$

$z_b = 0.282 \text{ nm}$
Connecting DFT Trends with SPSTM Spectroscopy

**Substrate PDOS**

- **Craq3**: No surface state, antibonding, bonding
- **Alq3**: Surface state, former LUMO, antiparallel

**Molecule PDOS**

- **Craq3**: antibonding
- **Alq3**: bonding
Summary: Tuning from Metallic to Resistive Spin Filters

Spin polarized interface states form at Alq3 and Crq2 interfaces with Cr(001)

The nature of the interfaces is surprisingly sensitive to details of orbitals

We can tune from a metallic to a resistive interface within a single

See e.g. Raman Applied Physics Reviews 1, 031101 (2014).
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The Organic and Carbon Electronics Lab (ORaCEL)

A new interdisciplinary center supporting collaborative efforts in organic semiconductors, conjugated polymers, graphene, carbon nanotubes and hybrid carbon materials

https://oracel.wordpress.ncsu.edu/

Shared instrumentation, seminar series, proposal and course development

Funded by the NC Carbon Materials Initiative

Director: Prof. Harald Ade

Science Collaborations?

Broader Impact support network?
These calculations show evidence of a $d_{z^2}$-derived surface state near the Fermi Level. While not in perfect agreement with experiment, it is at least qualitatively reproducing the symmetry, spin polarization, and existence of the surface state.
**Traditional Semiconductors:** highly controllable electronic properties by doping

1) Band transport with challenging spin injection:

   *Appelbaum et al., Nature 447, (2007).*

2) Magnetic doping is a difficult materials science problem...