ICMAB | INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA

CSIC CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

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

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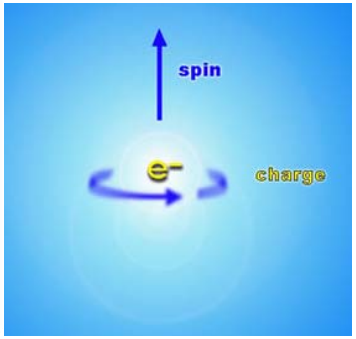
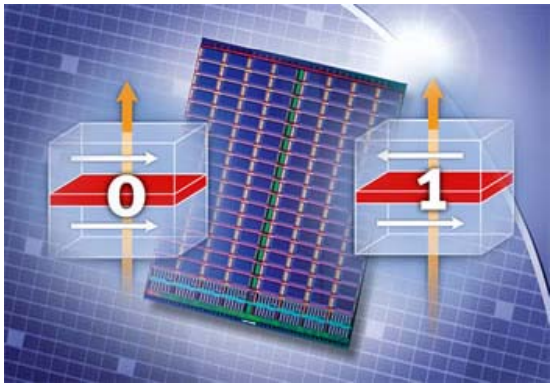
MOLECULAR-SPINTRONICS, where spin-polarized currents are carried through molecules, and in turn they can affect the state of the molecule.



Molecular-Spintronics: the art of driving spin through molecules by Stefano Sanvito and AlexandreReily Rocha



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.

ORGANIC RADICALS

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

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.

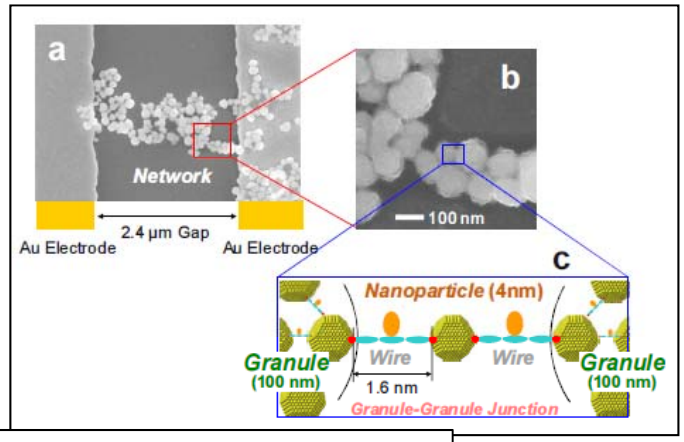
J. Am. Chem. Soc. **2010**, *132*, 3682

Spin-polarization and its conservation.

Some very appealing recent findings...

Spin-polarized wire molecules (**SPM**)

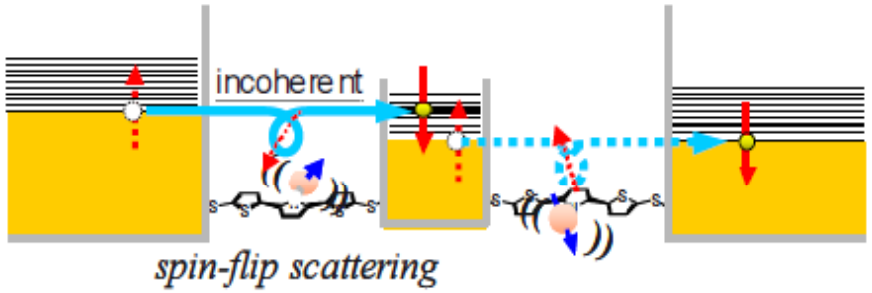
Spinless wire molecule **(SLM)**



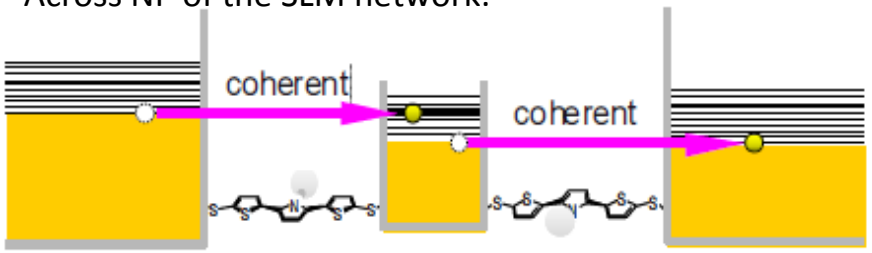
Phys. Rev. B. **2008**, *77*, 235316

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

Across NP of the SPM network:



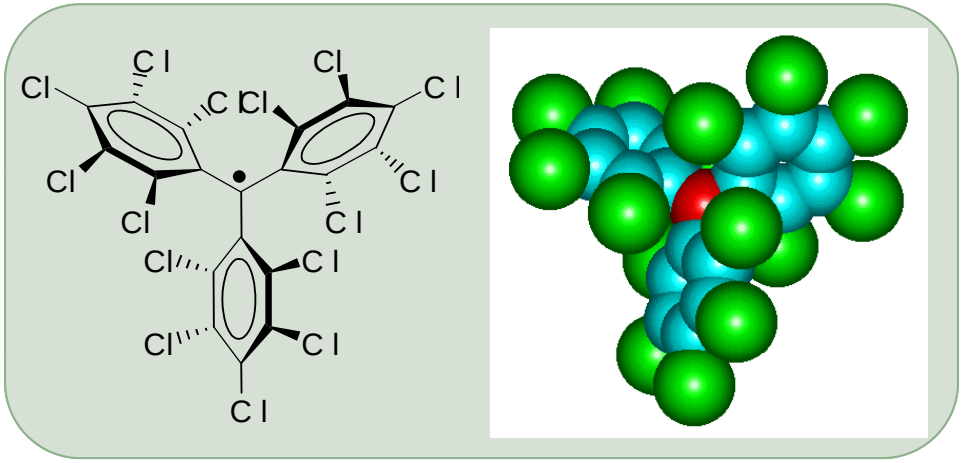
Across NP of the SLM network:

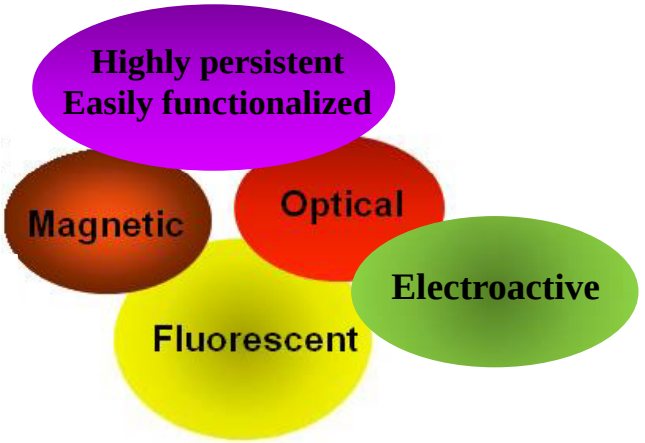


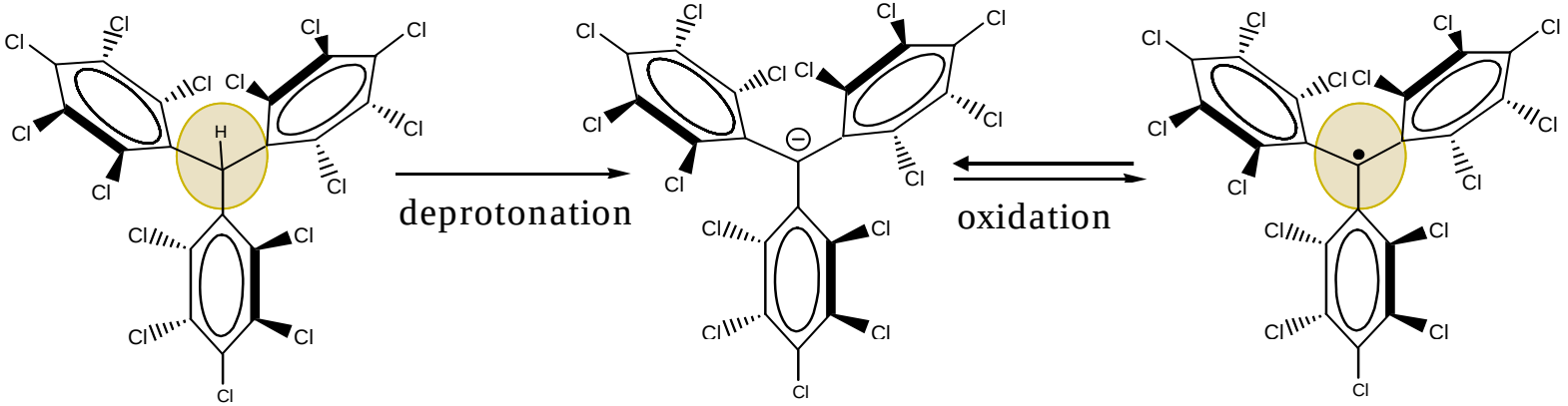
This is the **first experimental demonstration of the interaction between a single organic localized spin with an electron tunneling through the molecule.**

Importance of studying the transport through the molecule

Polychlorotriphenylmethyl (PTMs) radicals as bistable and switchablemutifunctionalmolecules



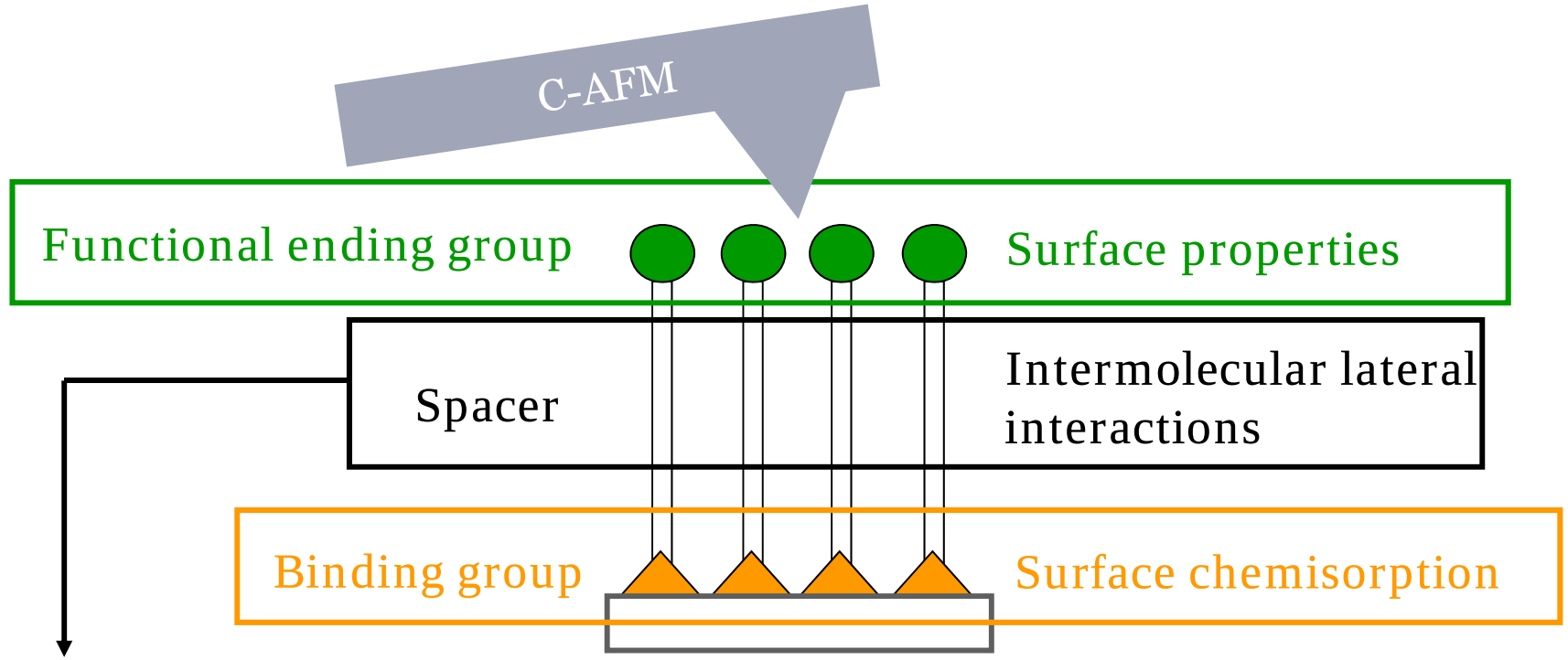




closed-shell

open-shell S=1/2

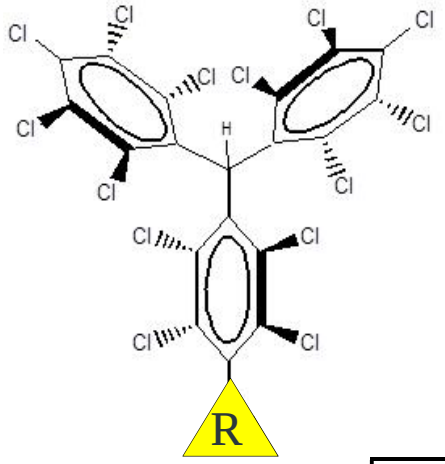
SELF-ASSEMBLED MONOLAYERS (SAMs)

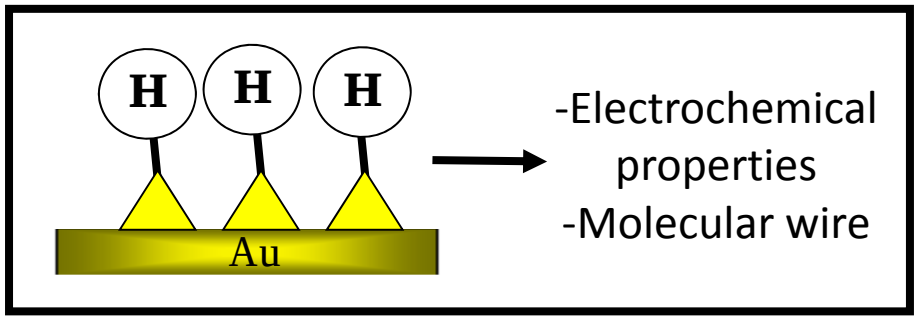


-Well-defined thickness
-Acts as a physical barrier
-Alters electronic conductivity and local optical properties

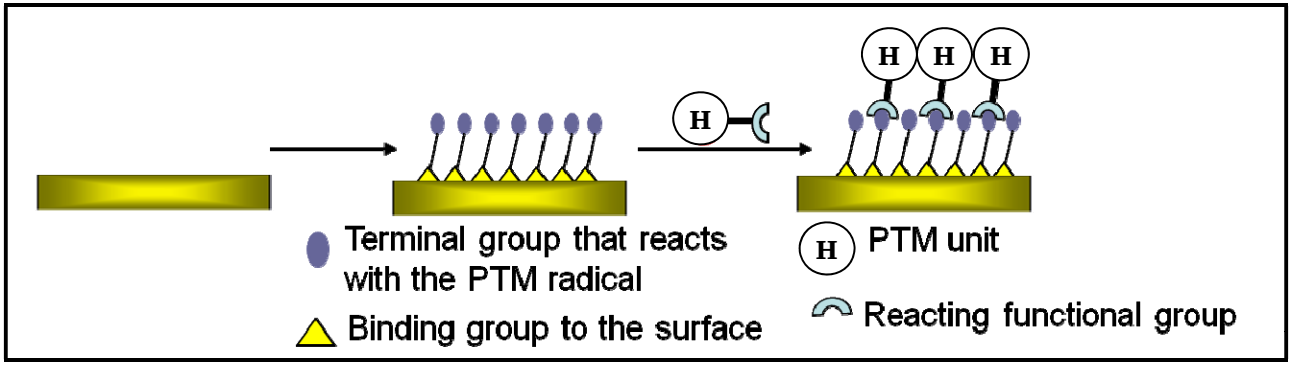
Surface	Anchoring groups
Gold	Thiols disulfides Sulfinic acids
SiO_2	Silanes
ITO	Silanes carboxylic or phosphonic acids

Preparation of PTM SAMs: Two different approaches

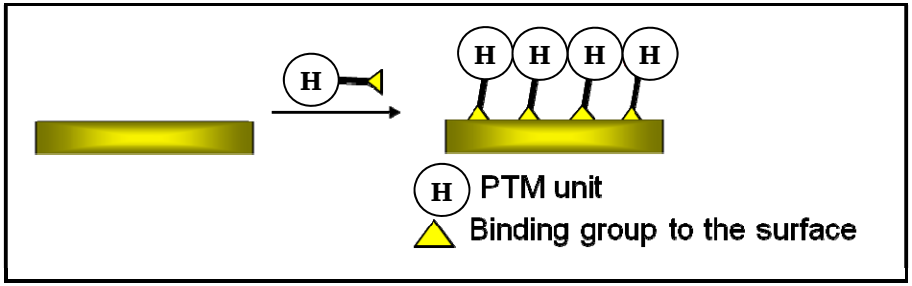




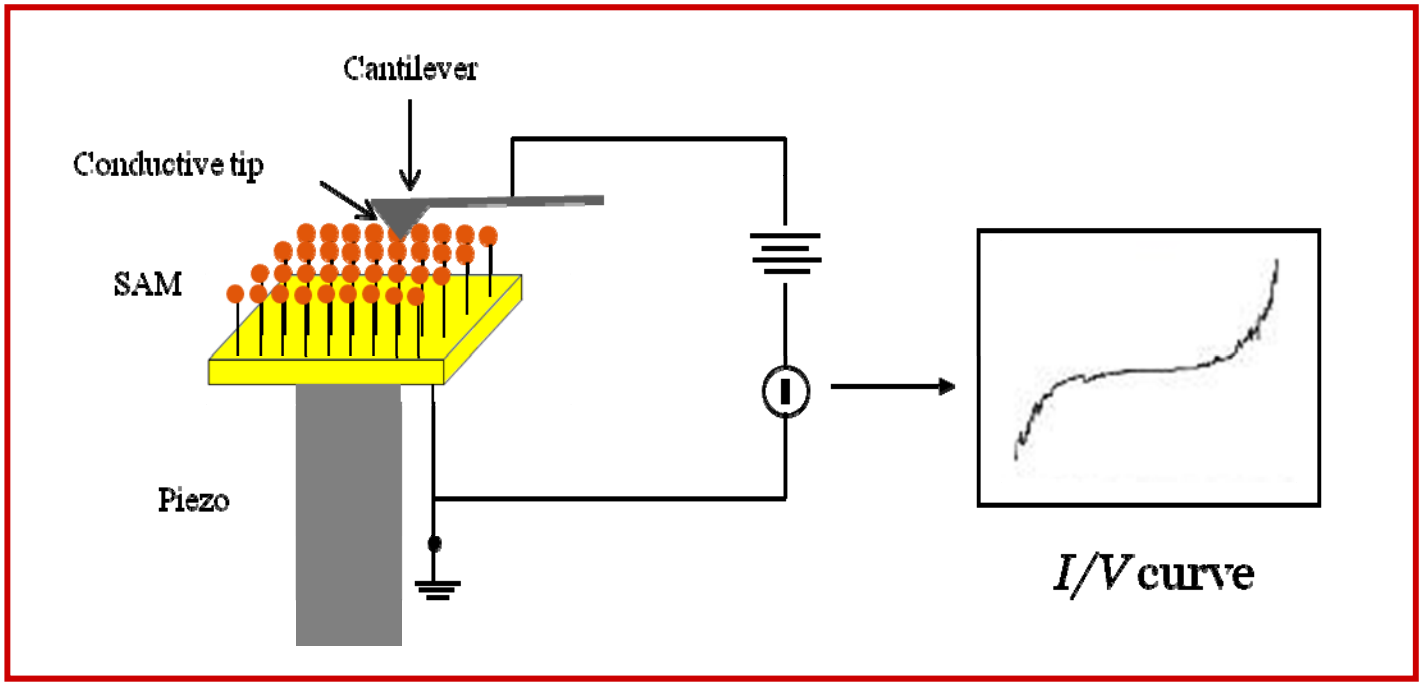
I) Two-step approach



II) One-step approach



C-AFM: Three-dimensional Mode:
3D for transport measurements

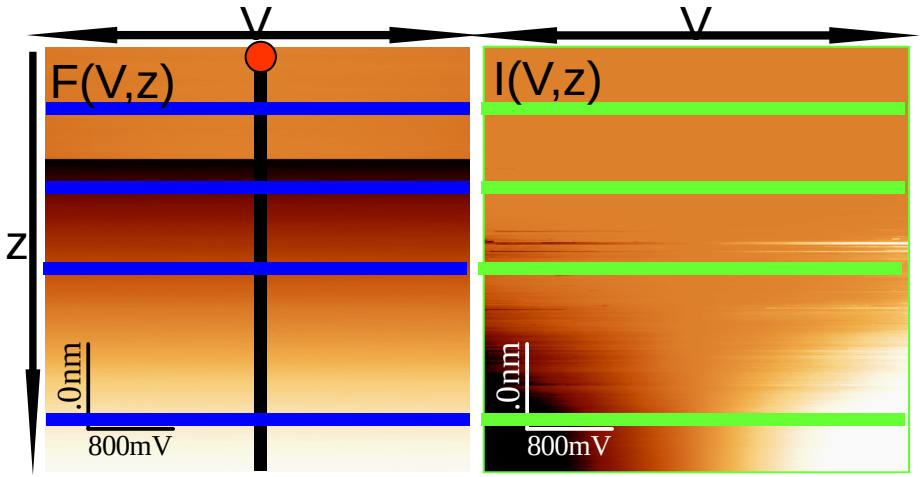


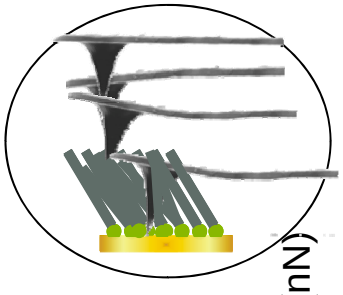
At each tip-sample distance a voltage is applied between two fixed values

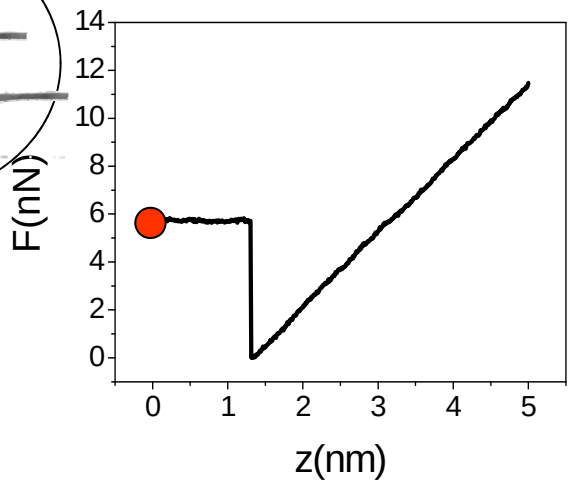
Normal Force (F_n) and the current (I) as a function of the bias voltage (V) and the sample displacement distance towards the tip (z) are simultaneously measured.

In collaboration with Dr. Carmen Munuera, Marcos Paradinas and Prof. Carmen Ocal (ICMAB-CSIC)

At each *Fn* is possible to obtain the *I*/V

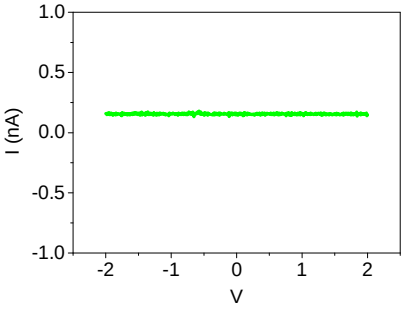


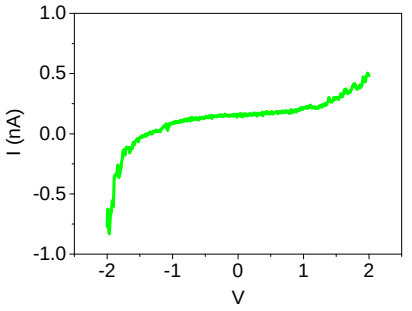


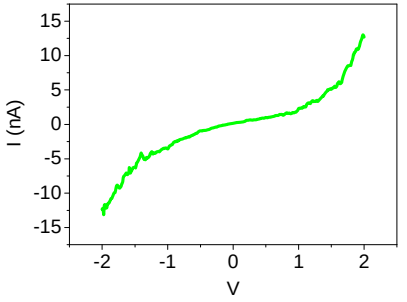


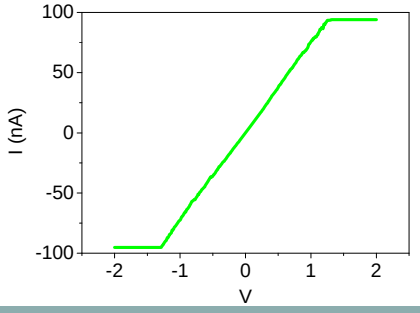
Voltage range: +2V

Piezo movement: 5nm



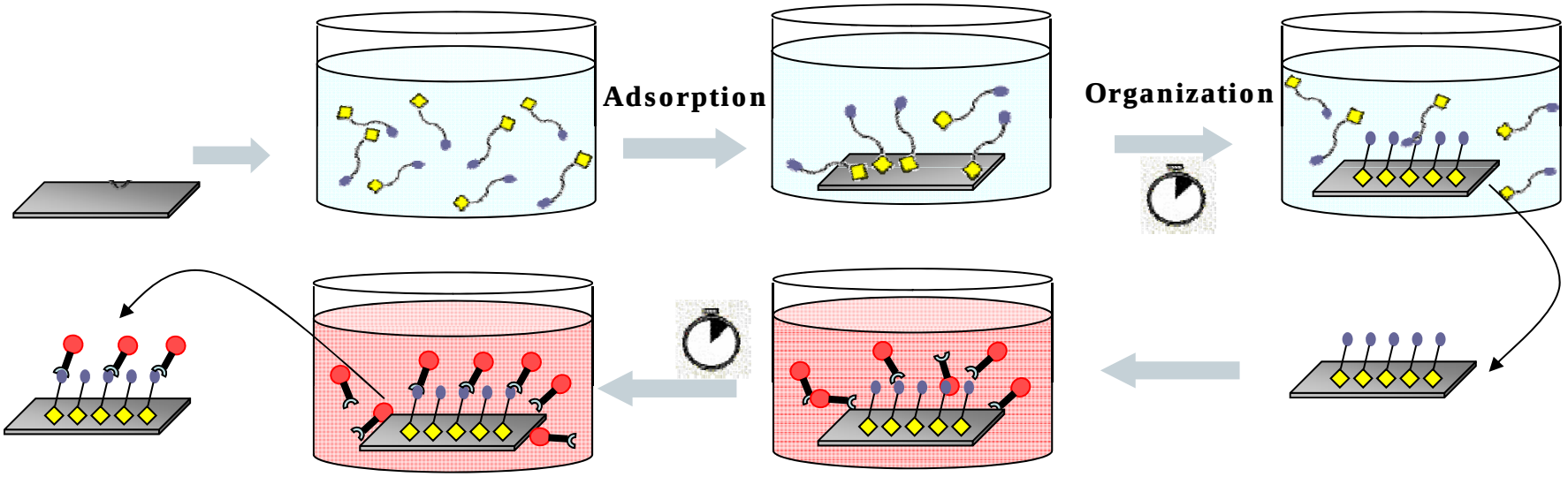


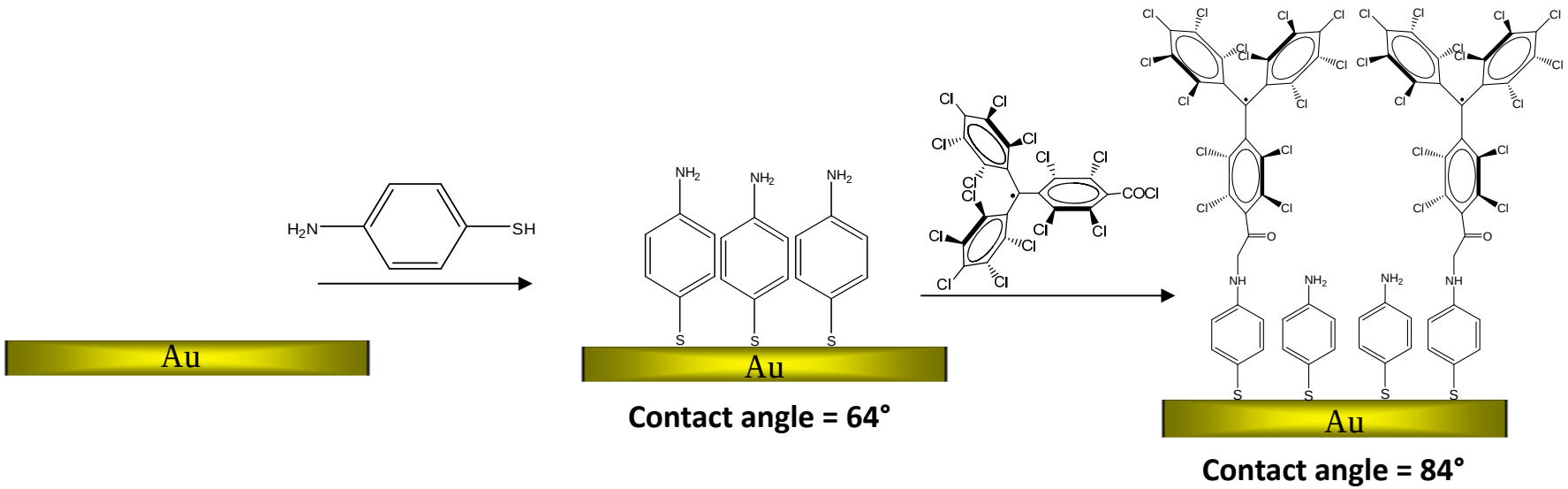




From C. Munuera

I) Two-step approach: non-conjugated PTM SAM on gold

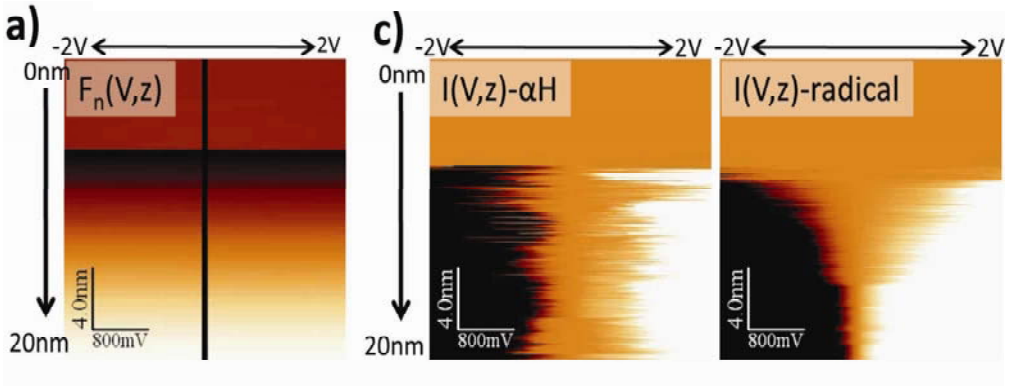


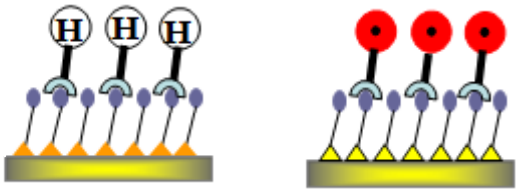


Contact angle = 64°

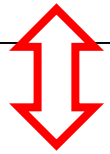
Contact angle = 84°

Transport properties through radical and non-radical SAMs





SAMLL difference in their molecular structure but LARGE difference in the electronic structure

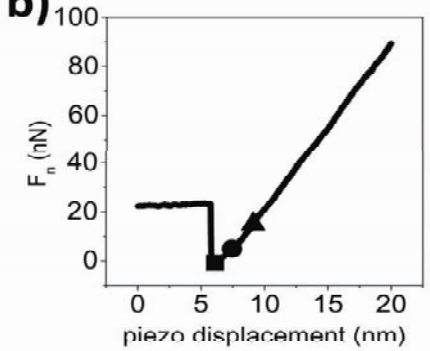


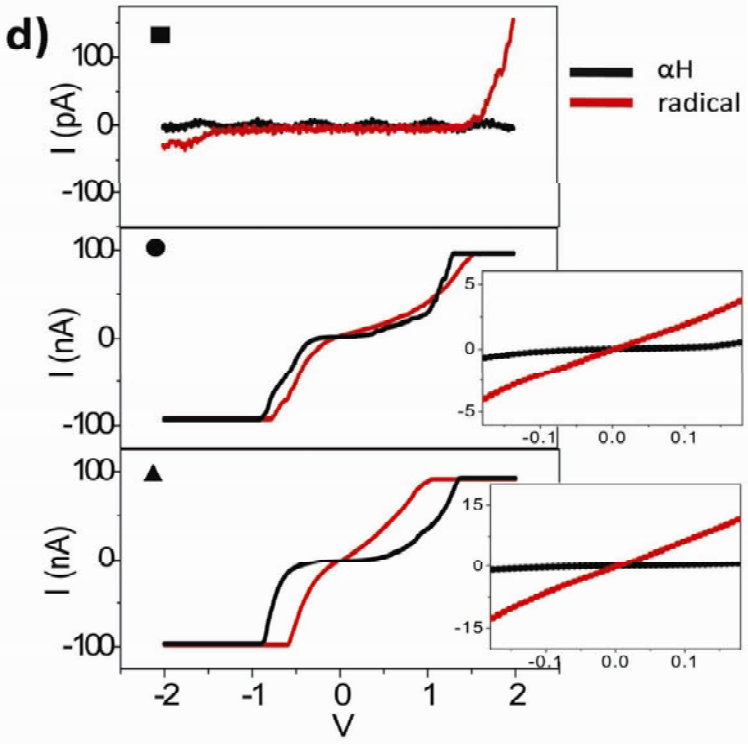
R(H) =280 MΩ

R(r) =35 MΩ

R(H) =200 MΩ

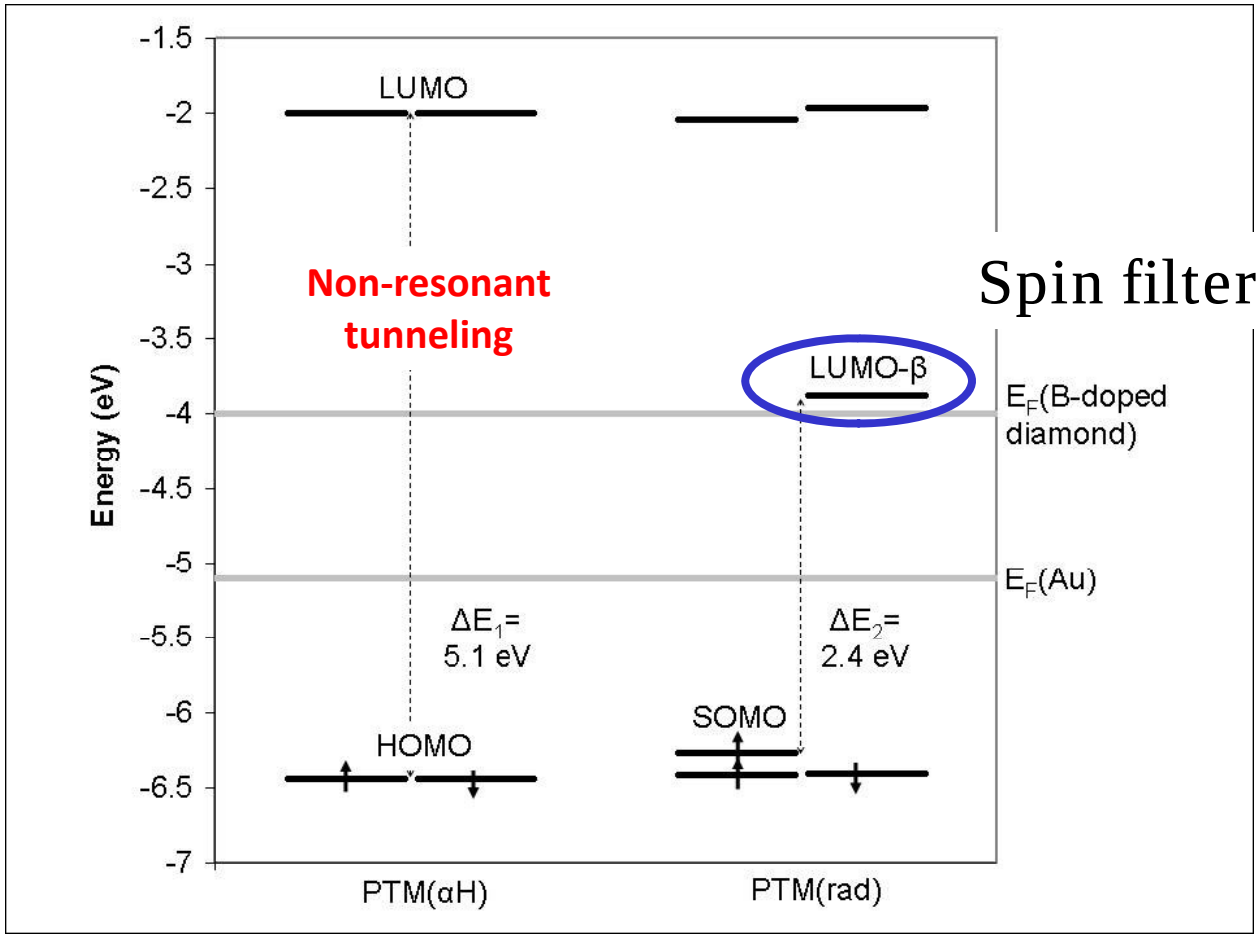
R(r) =12 M Ω





Energylevels of non-radical and radical SAMs

DFT calculationson PTM-(CO)-NH-Ph

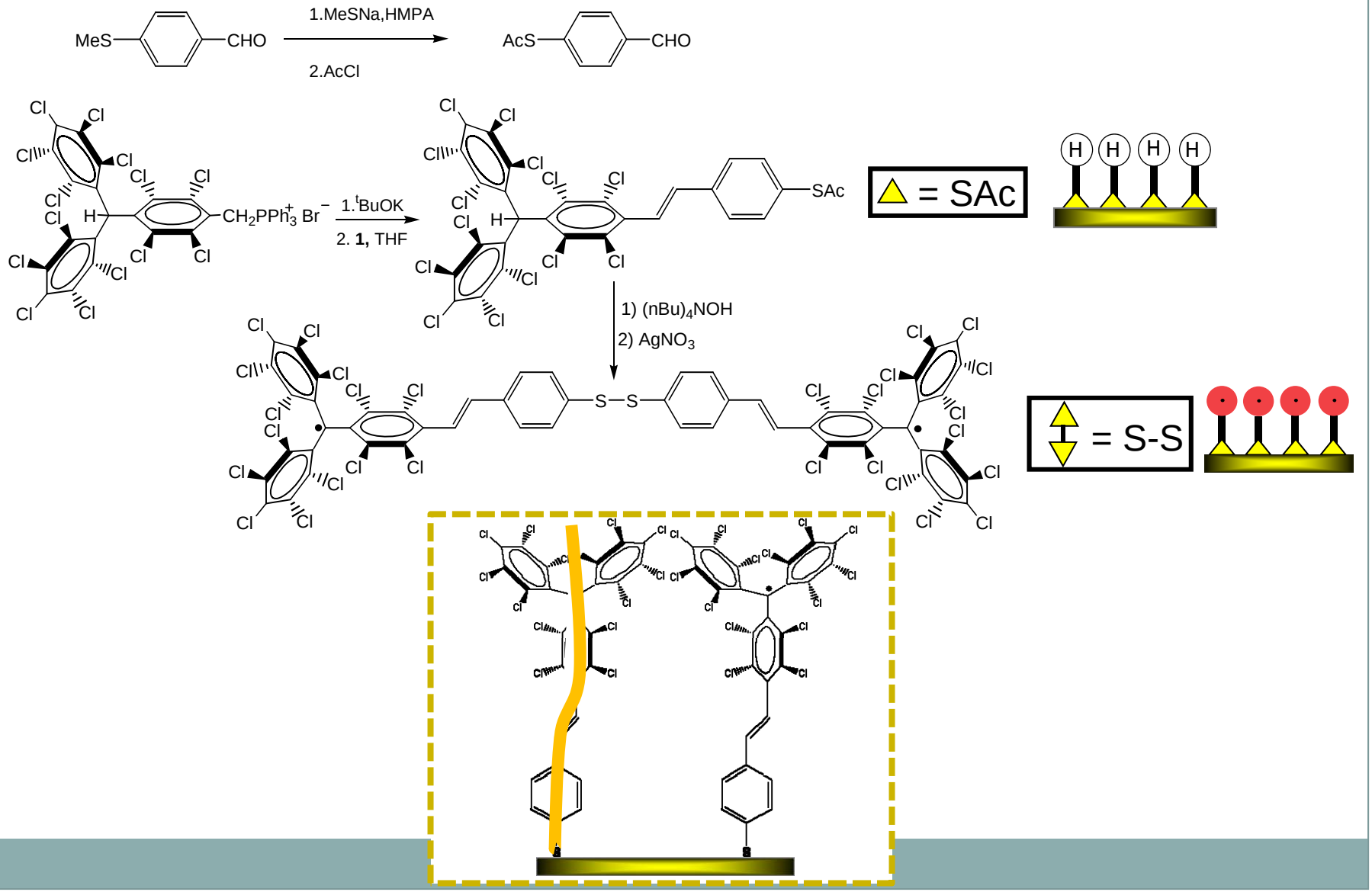


Spin filter???

Radical SAM: LUMO assistedtransport, contribution of resonant tunneling mechanism

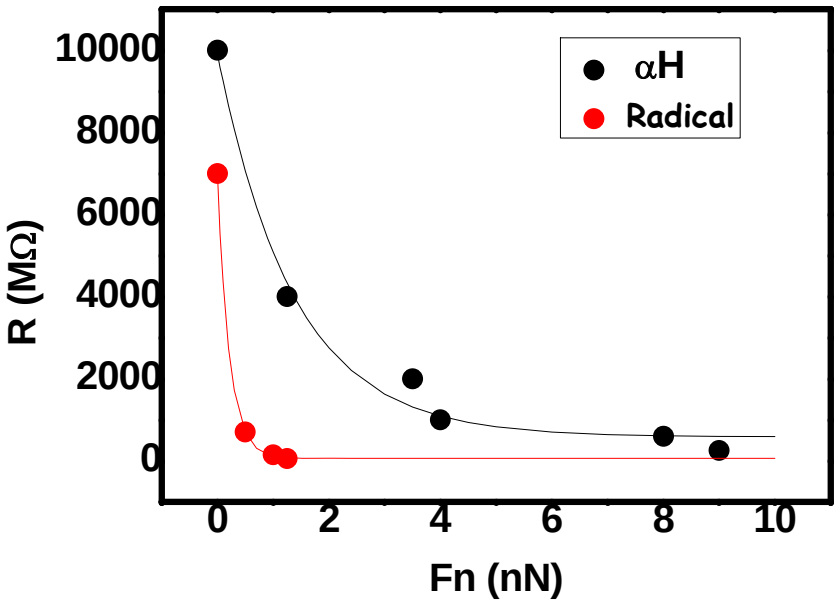
II) One-step approach i.e., direct anchoring

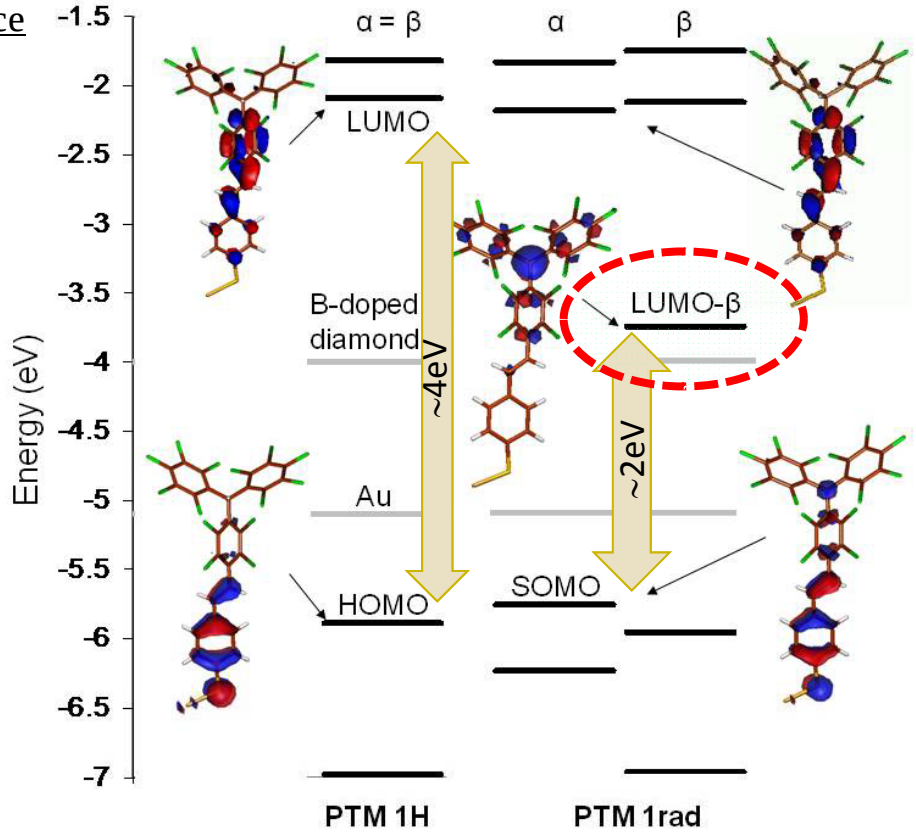
Design and Synthesis:



Transport properties through conjugated PTM SAMs with C-SFM

Junction resistance (R) as a function of applied force





R(H)/*R*(rad) is one order of magnitud higher than the non-conjugated SAM

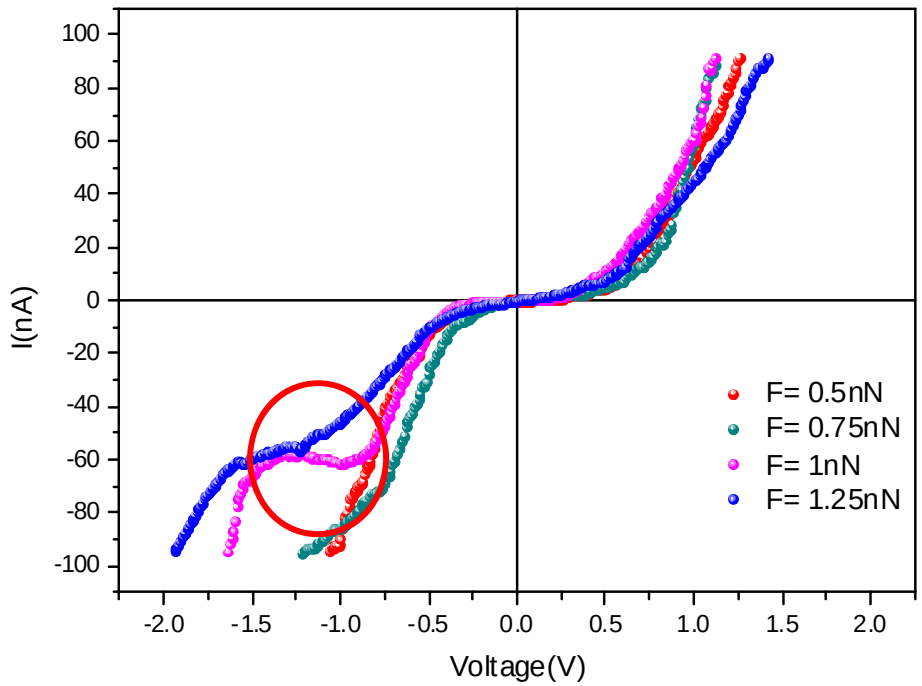
Non-radical SAM: non-resonanttunneling

Radical SAM:resonant tunneling

(B3LYP[13] hybrid functional and a 6-31G(d,p) basis set)

ChemCommun. 2011, *47,* 4664

I/*V* for radical PTM SAM:



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)

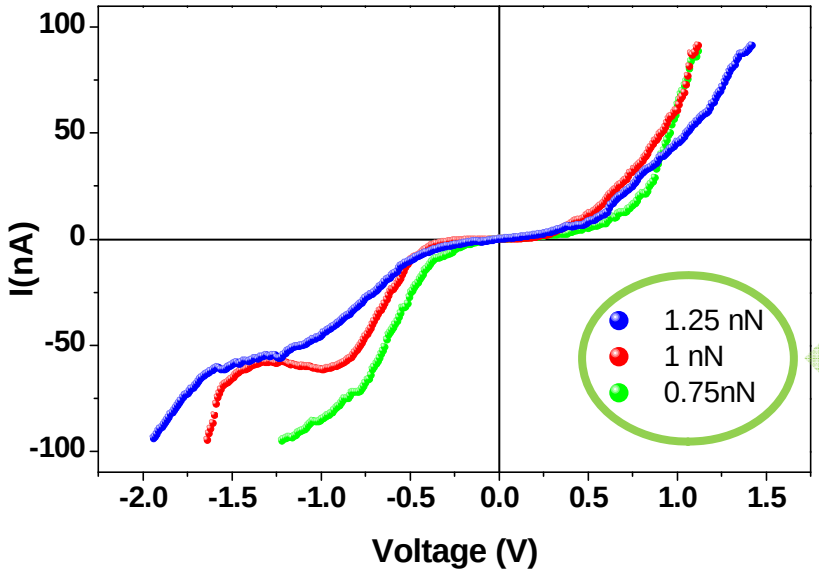
Different origins for NDR:

-Conformational changes.

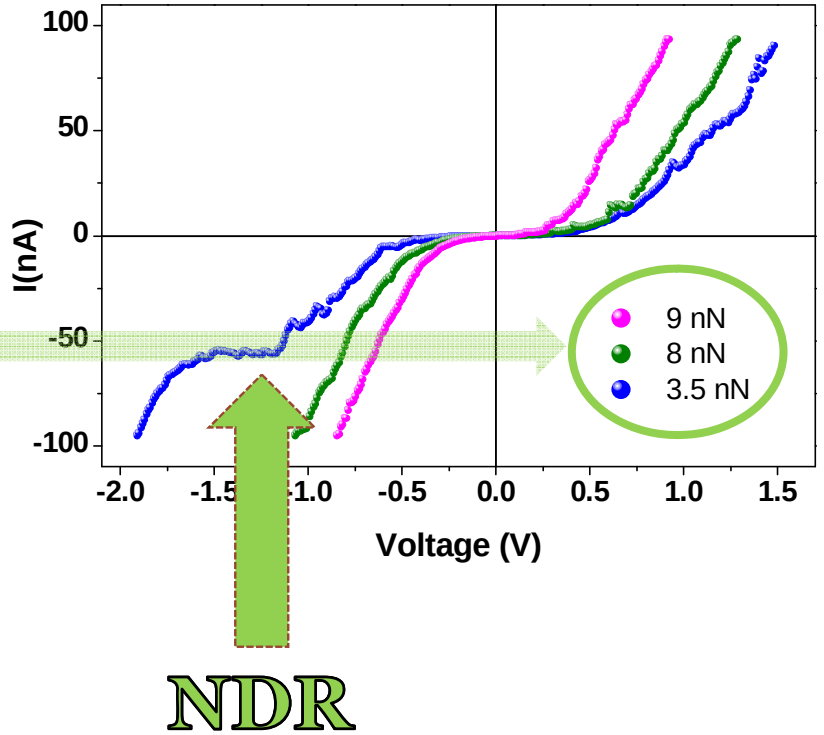
-Charging of the molecule followed by the localization and delocalization of orbitals.

-Polaron formation in redox active molecules.

I/*V* for radical PTM SAM:

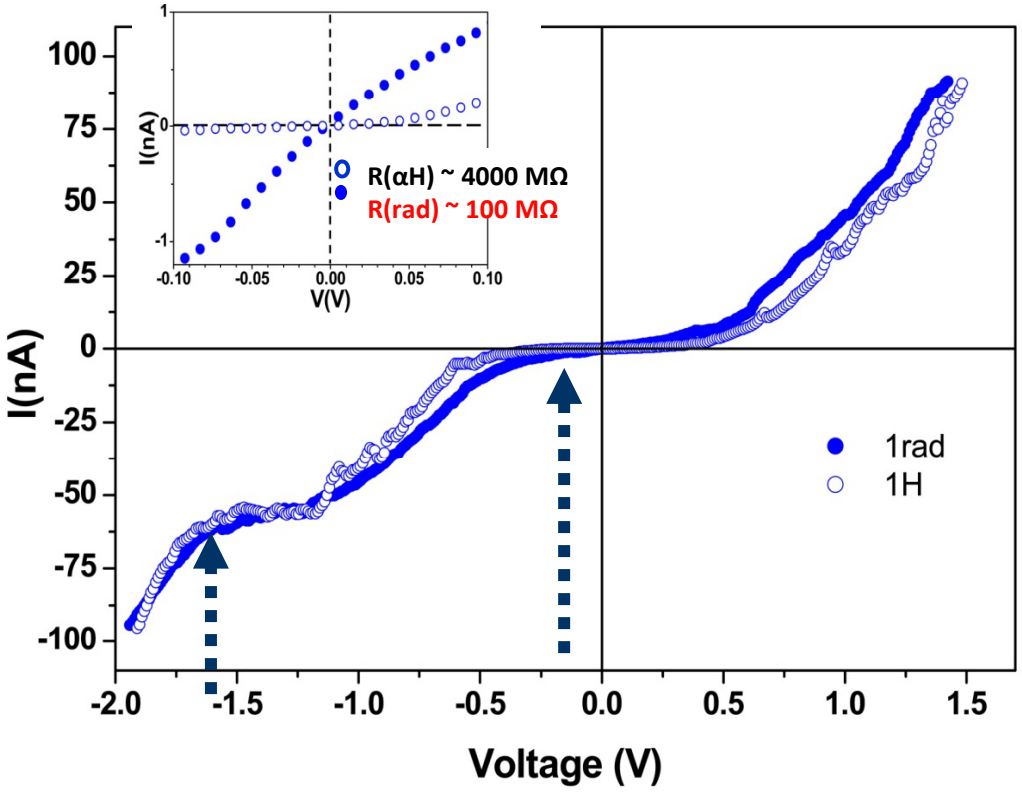


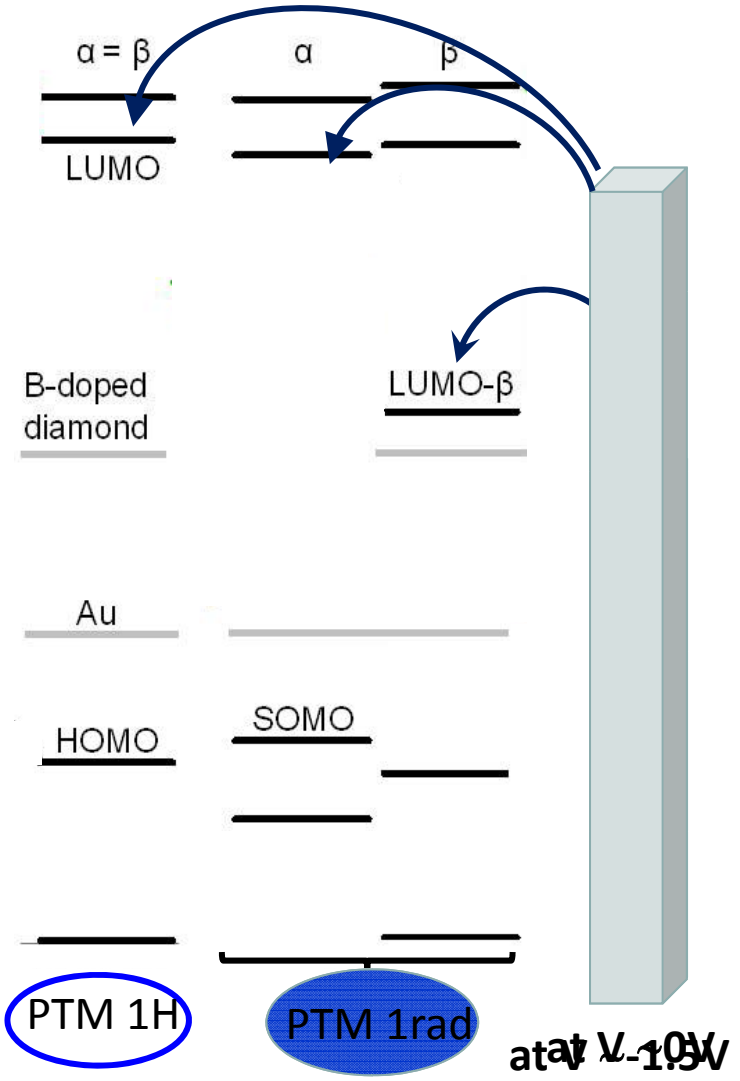
I/*V* for non-radical PTM SAM:



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.

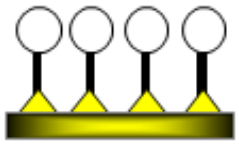
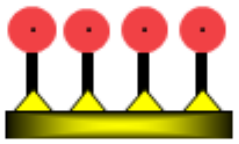


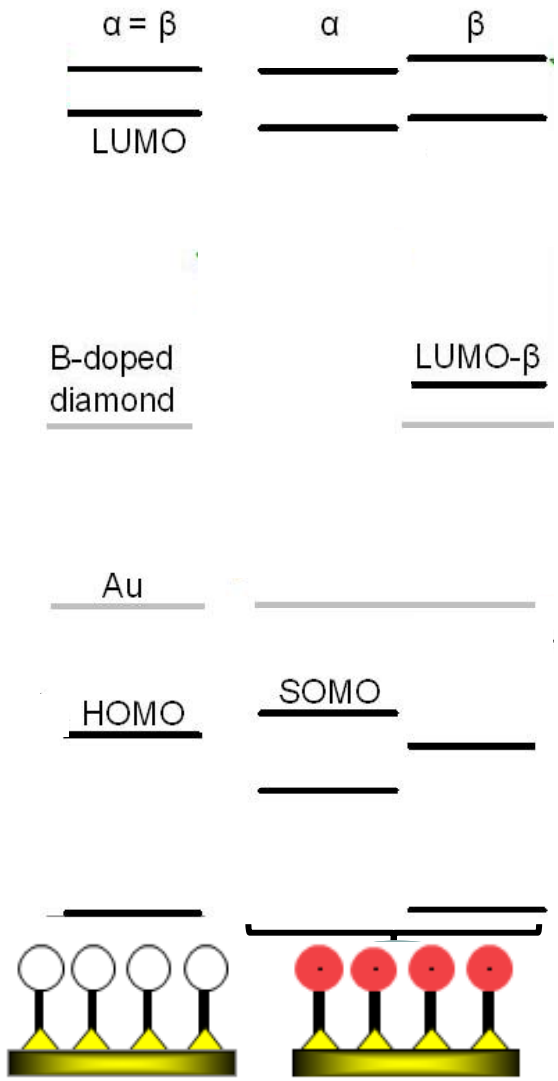


Negative differential resistances (NDR) in both *I-V* curves

ChemCommun. 2011, *47,* 4664

Proposed transport mechanism

		
At low bias	Non-resonant tunneling	Resonant tunneling mediated by LUMO-β
At higher bias	Some resonant tunneling with the unoccupied orbitals	



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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- Prof. Concepció Rovira
- Prof. Jaume Veciana

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Prof. Stefan Bromley (ICREA, U. Barcelona)