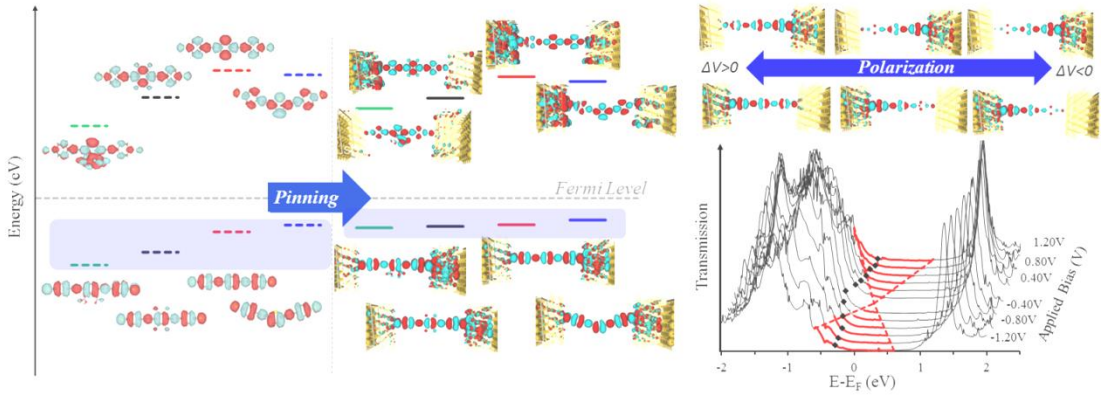

Fermi Level Pinning and Orbital Polarization Effects in Molecular Junctions

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Laboratory for Chemistry of Novel Materials

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Functional Molecular Junctions…

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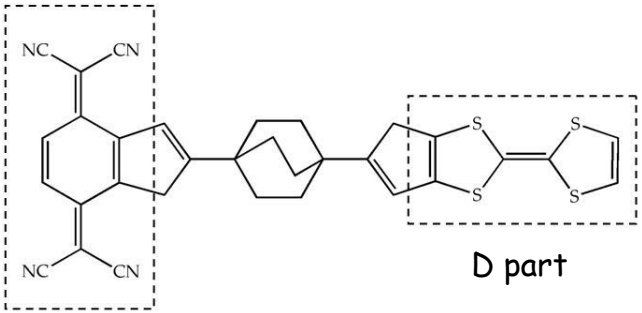
1974 : Aviram and Ratner



Can we develop all the basic functions of common electronic components at nanoscale

Angewandte Communications

VIP Self-Assembled Monolayers

DOI: 10.1002/anie.201201448

The Rate of Charge Tunneling through Self-Assembled Monolayers Is Insensitive to Many Functional Group Substitutions**

*Hyo Jae Yoon, Nathan D. Shapiro, Kyeng Min Park, Martin M. Thuo, Siowling Soh, and George M. Whitesides**

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Molecule–electrode interfaces in molecular electronic devices

Cite this: *Chem. Soc. Rev.*, 2013, **42**, 5642

Chuancheng Jia[a] and Xuefeng Guo*[ab]

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Cite this: *Nanoscale Horiz.*, 2016, 1, 399

Received 12th May 2016,
Accepted 31st May 2016

DOI: 10.1039/c6nh00088f

Dipole effects on the formation of molecular junctions†

Sachie Tanimoto, Makusu Tsutsui,* Kazumichi Yokota and Masateru Taniguchi

NanoSpain Conf 2017

Electronic processes in a SAM/metal interfaces

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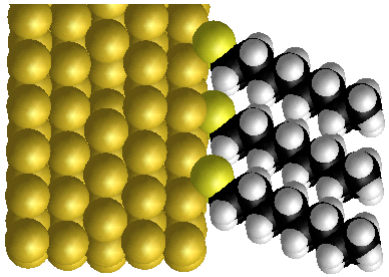


$$\Delta\Phi = \Delta V_{SAM} + BD$$

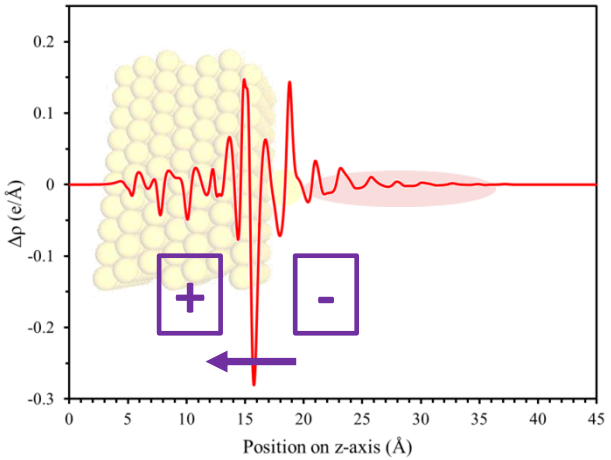
ΔΦ = Total Work Function Shift.

BD =Bond Dipole, interfacial electronic reorganization upon formation of the Au-S bond and surface reconstruction effects.

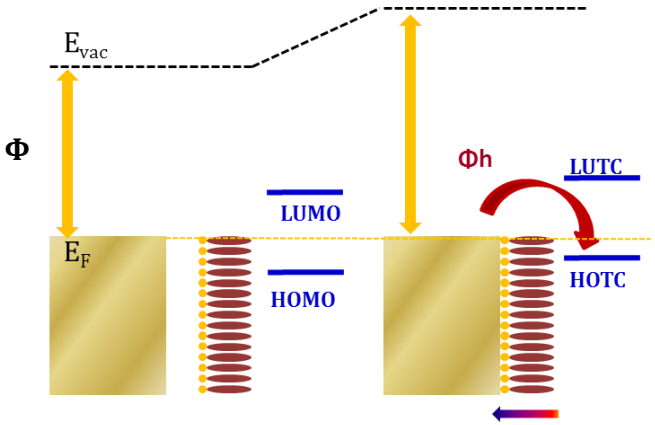
ΔV_{SAM} = molecular contribution from the dipole supported by the molecular backbone.

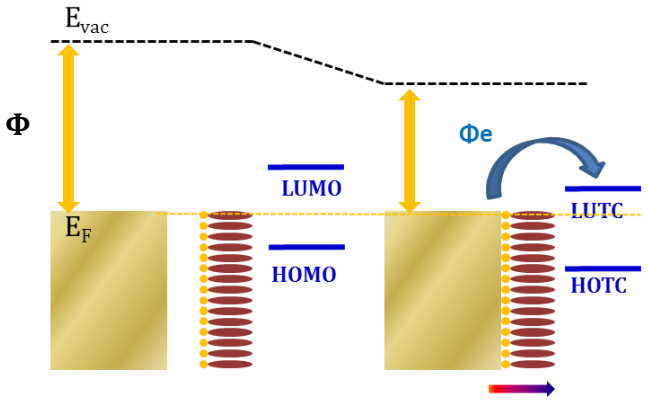
Electron Density Reorganization

$$\Delta\rho(z) = \rho_{Au(111)/mol}(z) - (\rho_{mol}(z) + \rho_{Au(111)}(z))$$

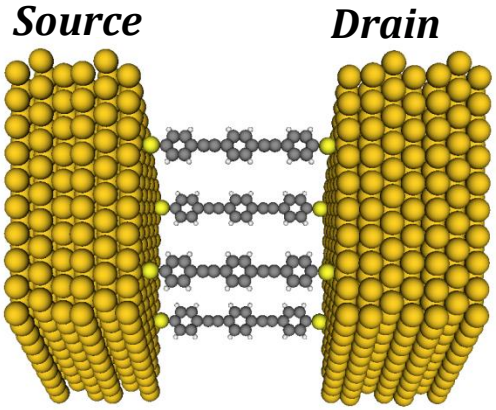


Interface Dipole (BD)

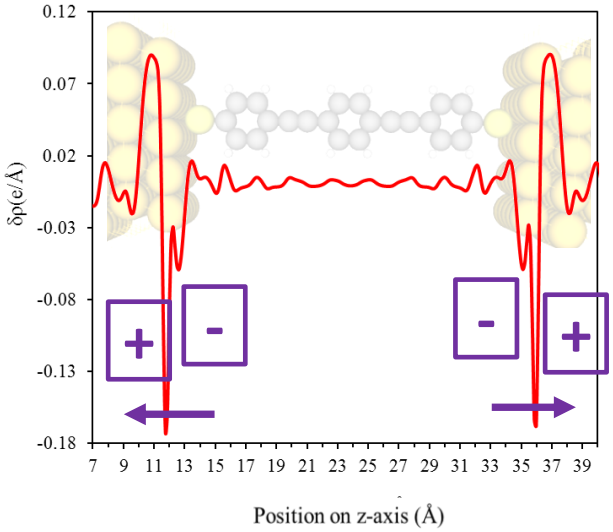




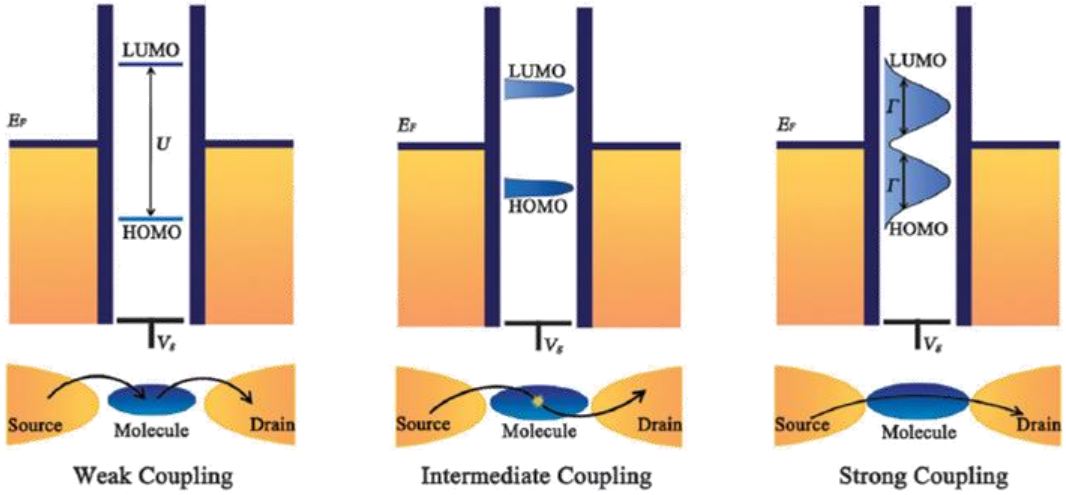
Molecular Junctions



Interface Dipoles



Voltage = 0V



Broadening

Energy shift

Transmission at 0 V

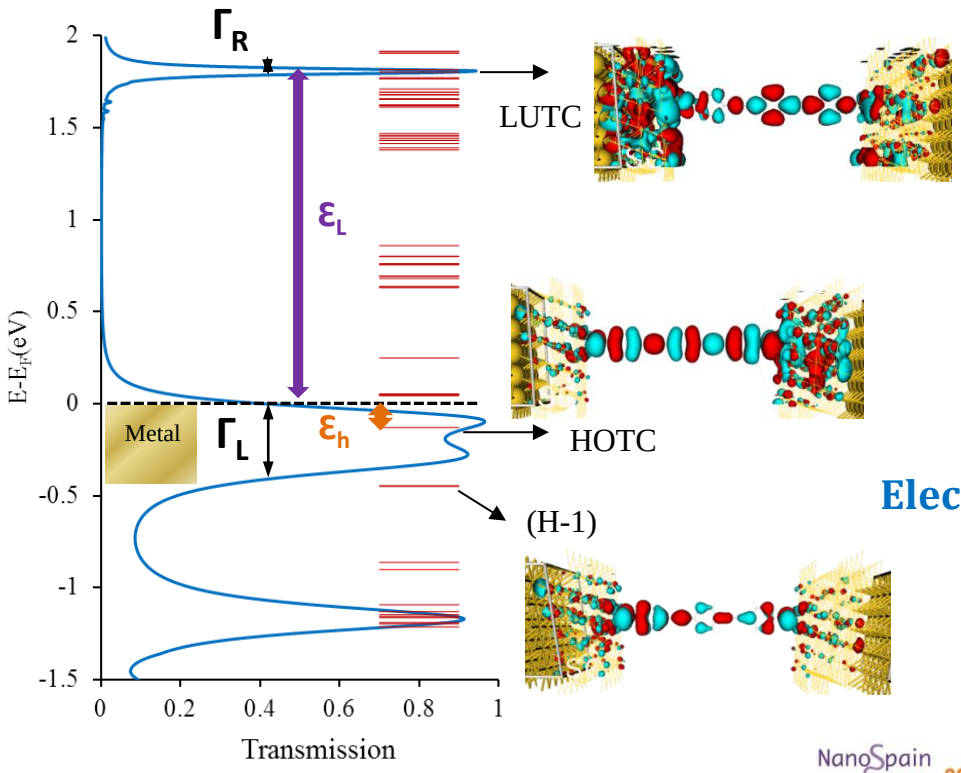
UMONS

- **Energy alignment of the molecular TC relative to the metal Fermi level: $\varepsilon_h/\varepsilon_L$**
- **Interplay between interfacial and intramolecular electronic couplings.**

*** Voltage = 0V**

Transmission Spectrum: gives the probability of one electron across the junction through the molecule in a coherent regime.

(MPSH) analysis



Interfacial coupling (Γ_L/Γ_R) → hybridization:
Strong hybridization ↔ Wide peak

Electronic Delocalization ↔ Intensity of the peak

Current Across Molecules

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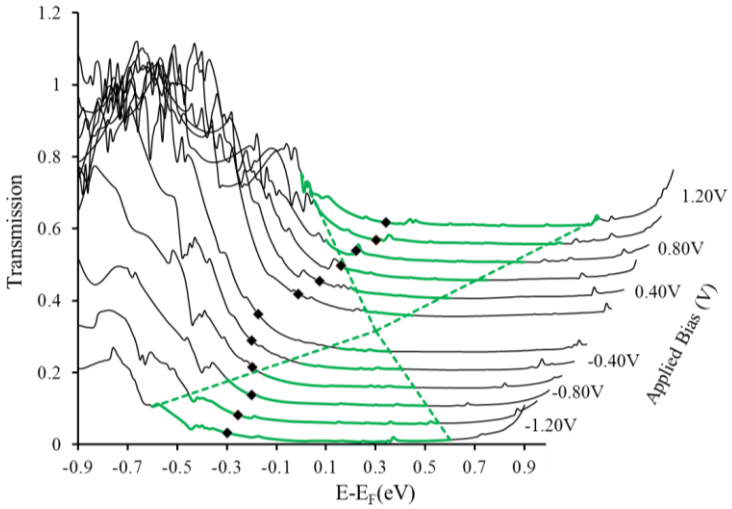
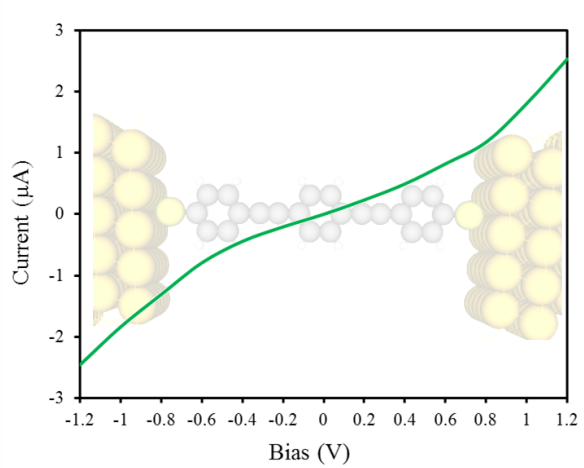
* **Voltage ≠ 0V**

Transmission Spectrum within a transmission window





$$I(V) = \frac{2e}{h}\int_{\mu_l}^{\mu_r} T(E,V)[f(E-\mu_l) - f(E-\mu_r)]dE$$

Landauer-Büttiker Formalism

- T(E,V): transmission probability at applied bias (V)
- $\mu_{l,r} = E_F \pm eV/2$: chemical potential of the electrodes.
- E_F: metal Fermi energy
- f (E-μ) : Fermi Dirac distribution function.

Materials , Objetives and Methodology

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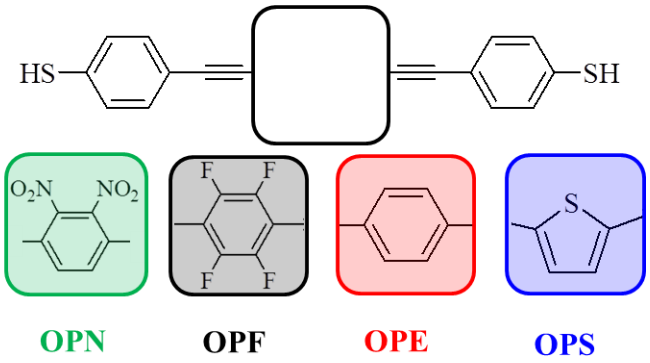
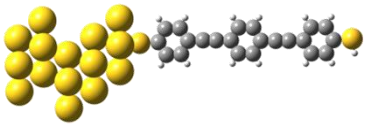
Molecular Wires

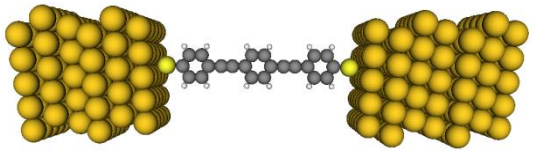


Objetives

1. Modulation of the Work Function of a metal substrate.



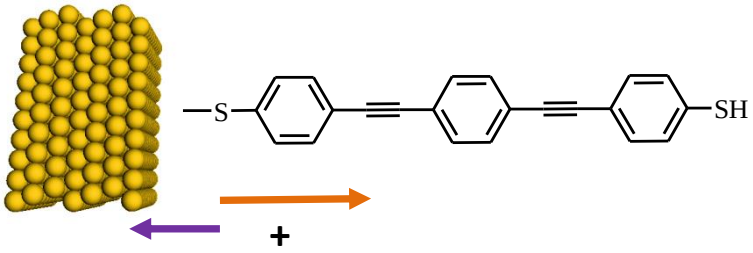
2. Energetic alignment of the molecular transport channels relative to the metallic Fermi level.
3. Conductivity , simulation the I-V curves and analyzing them from the evolution of the transmission spectra under bias.



- DFT
- GGA/PBE
- Troullier-Martin Pseudopotentials
- PBC
- SIESTA

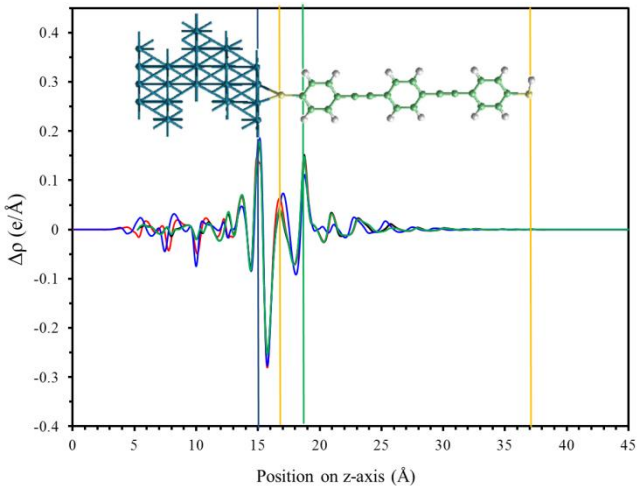
- DFT-NEGF
- GGA/revPBE
- Trouillier-Martin Pseudopotentials
- PBC
- ATK

Modulation of the Metal Work-Function



$$\Delta\Phi = \Delta V_{SAM} + BD$$

Electron Density Reorganization



eV	$\Delta\Phi_{theo}$	Φ_{theo}	ΔV_{SAM}	BD	$\Delta\Phi_{exp}$	Φ_{exp}
OPN	-0.969	3.862 *(0.001)*	-2.160	1.191	*	*
OPF	-1.051	3.780 *(0.081)*	-2.293	1.242	-1.025	4.175 *(0.005)*
OPE	-0.970	3.861 *(0.000)*	-2.306	1.336	-1.020	4.180 *(0.000)*
OPS	-1.071	3.760 *(0.101)*	-2.262	1.191	-0.926	4.274 *(0.094)*

↓Φ upon absorption with respect to the clean Au (111) surface

Substitution weakly modifies the Φ of Au (111)

* SKPM measurements (Not for OPN, yet)

Transmission and MPSH analysis at equilibrium

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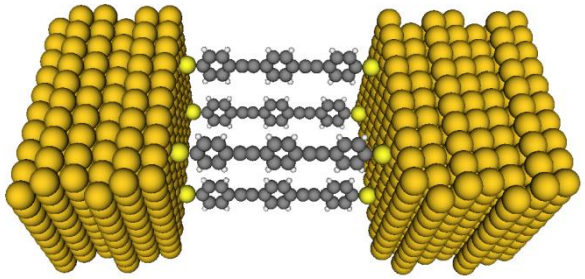
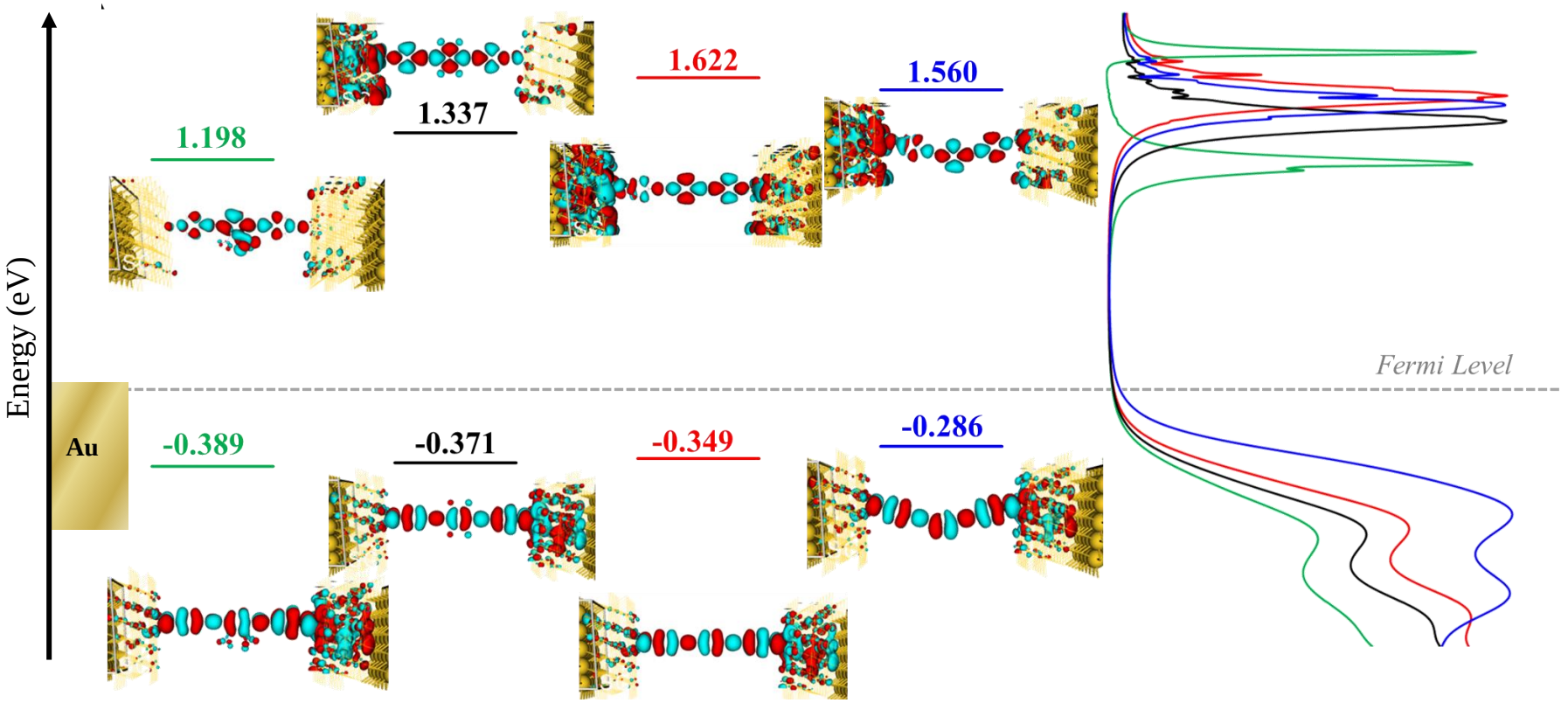


	T 0 V	L(Å)	ε_h (eV)
OPN	0.016	20.29	0.389
OPF	0.019	20.29	0.371
OPE	0.021	20.29	0.349
OPS	0.039	19.30	0.286



Energy-Level Alignment at equlibrium

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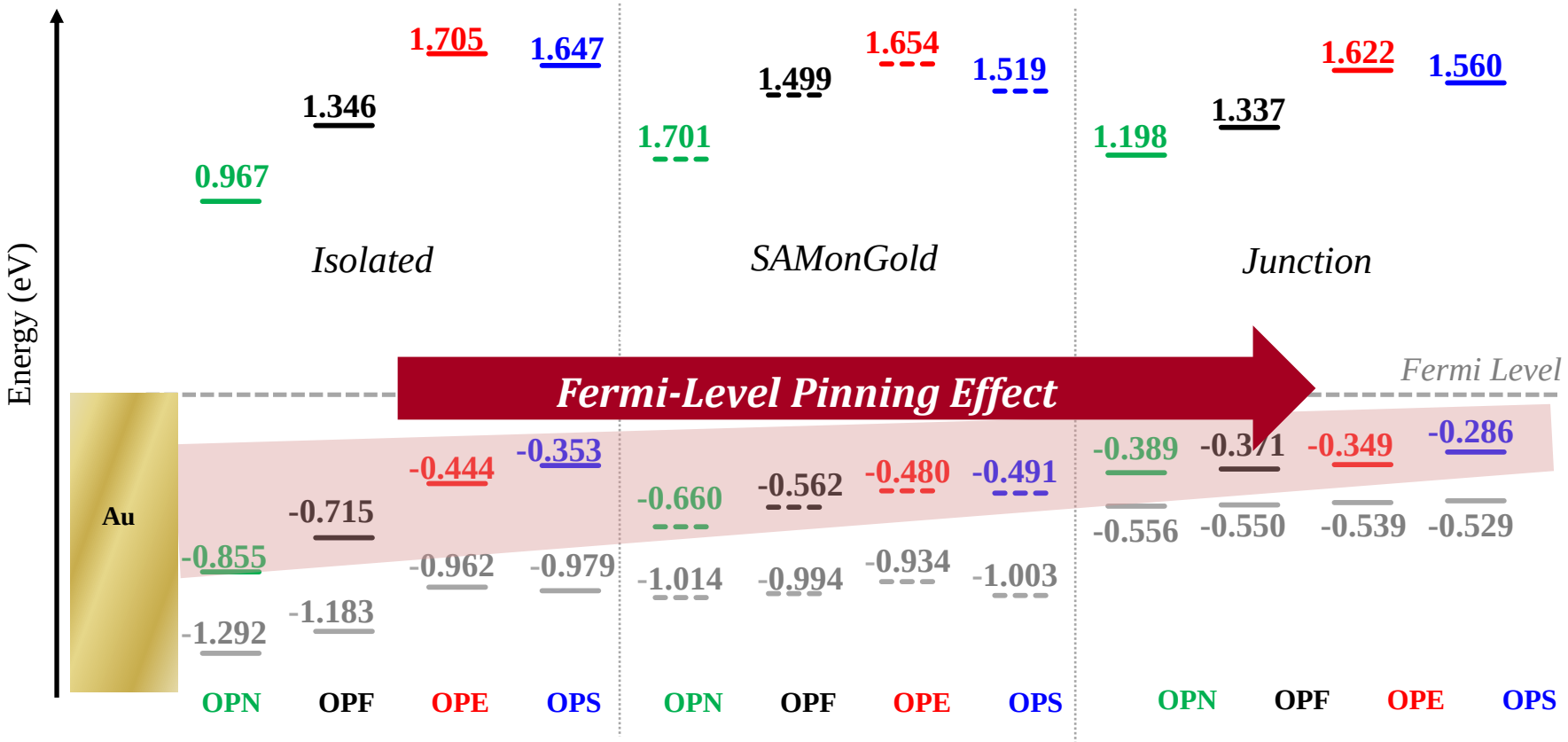
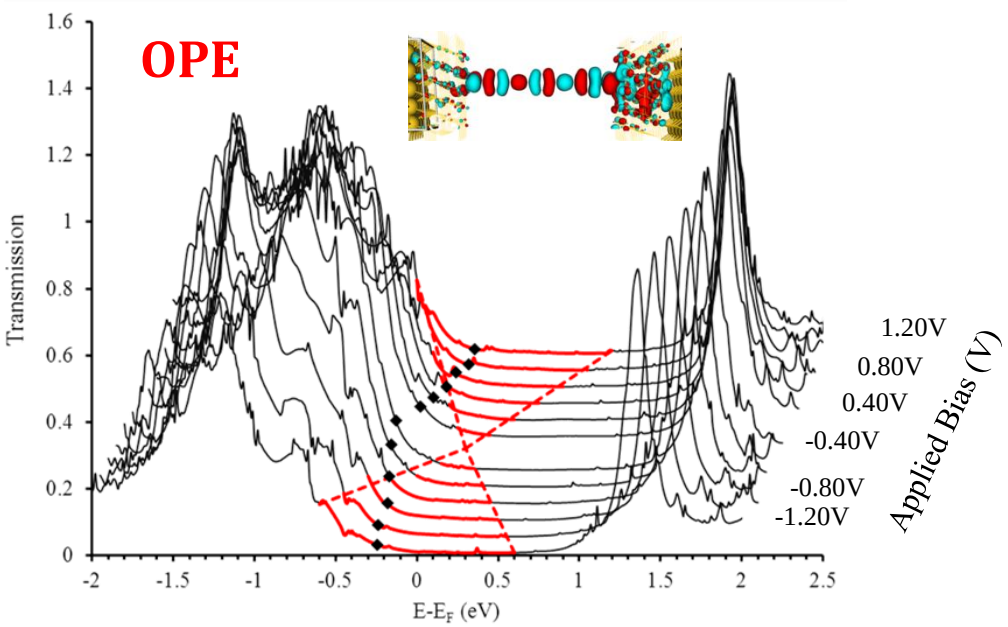
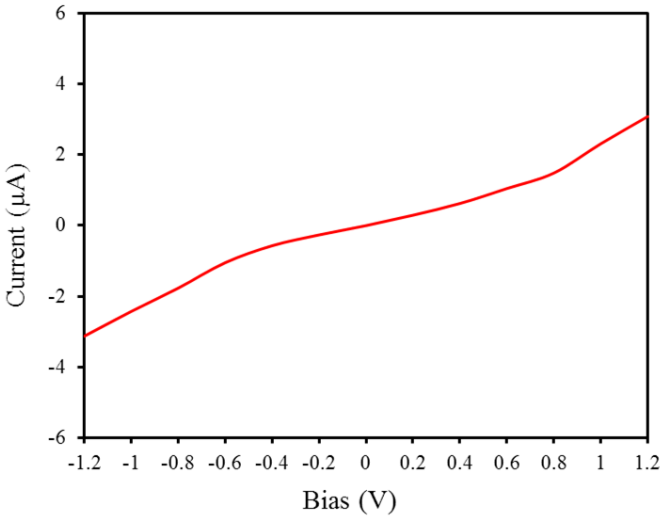


ε_h (eV)	Iso	SAM on Gold	Junction		Exp
OPN	0.855	0.660	0.389		*
OPF	0.751	0.562	0.371	ε_h	0.61
OPE	0.444	0.480	0.349		0.59
OPS	0.353	0.491	0.286		0.51

* CP-AFM measurements (Not for OPN, yet)

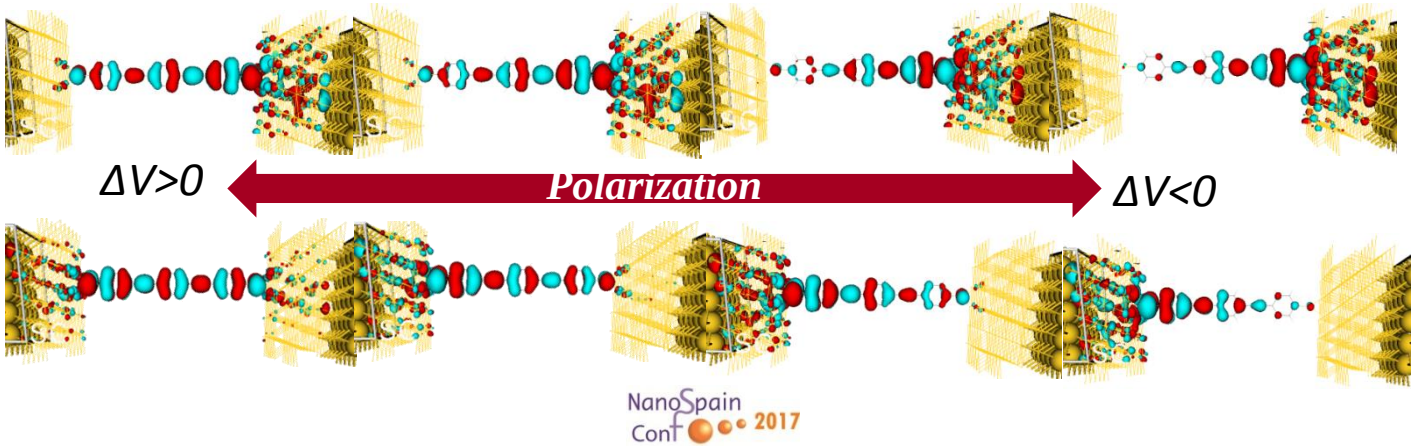
Application of Bias





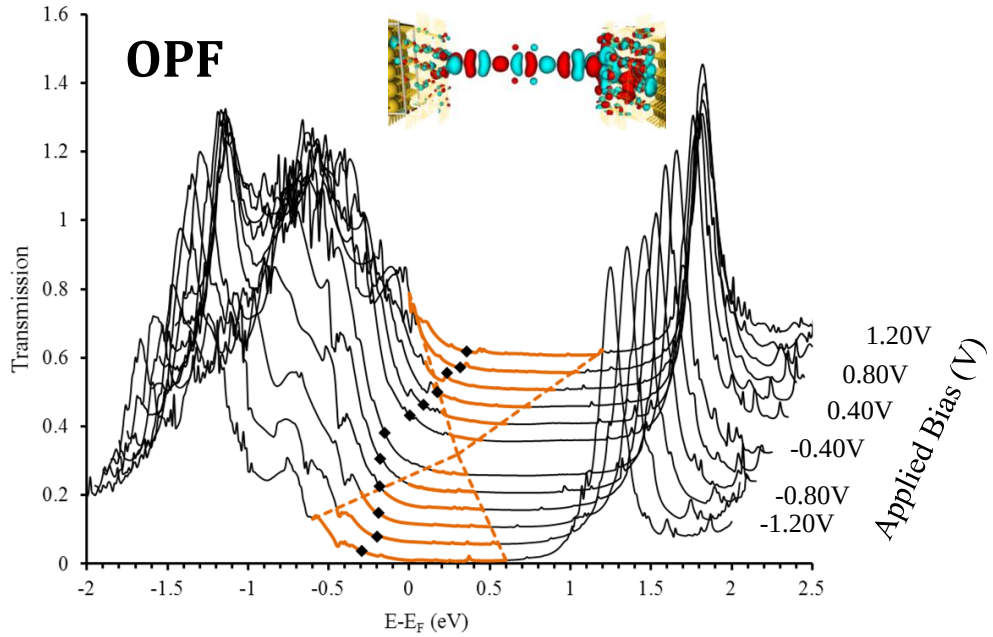
CONTINUOUS INCREASE OF CURRENT

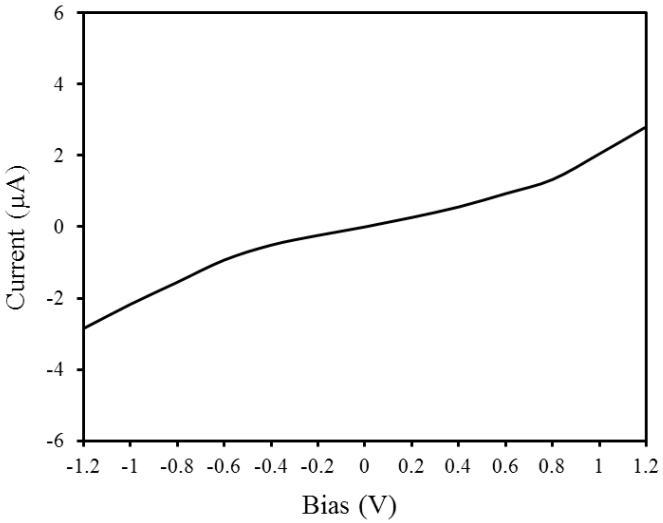
HOMO follows the destabilized electrode! → ***Intramolecular >Interfacial Coupling***



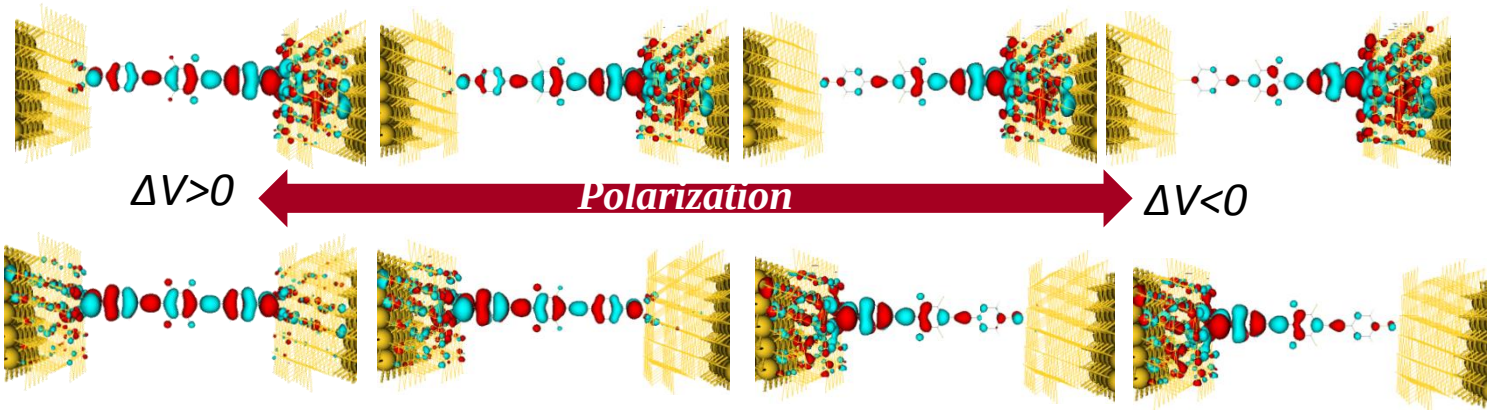
Application of Bias

UMONS

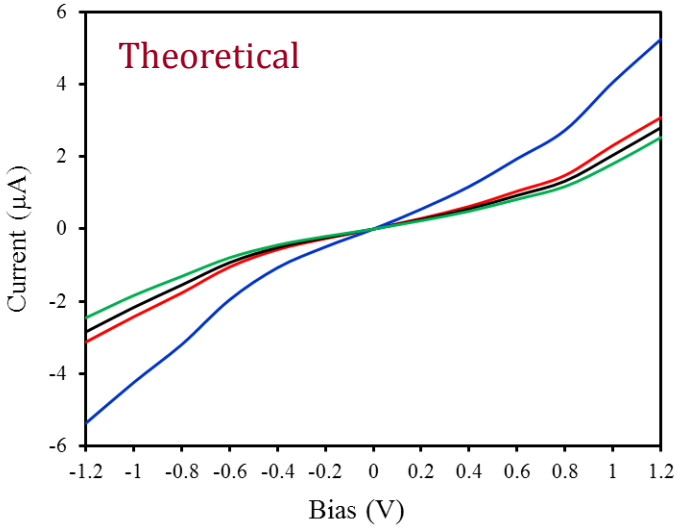


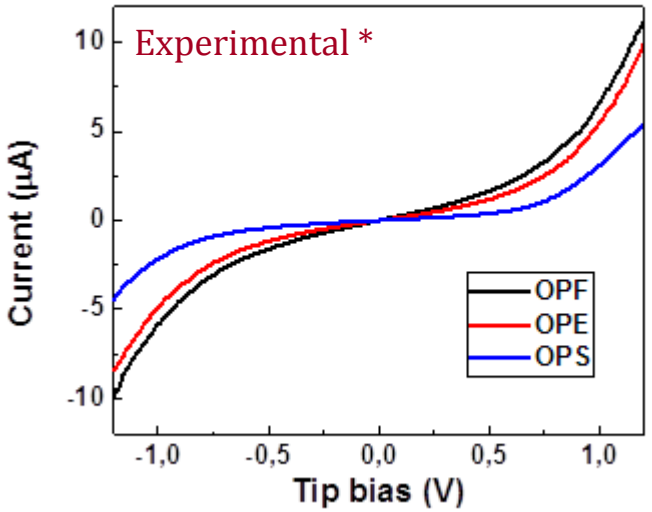


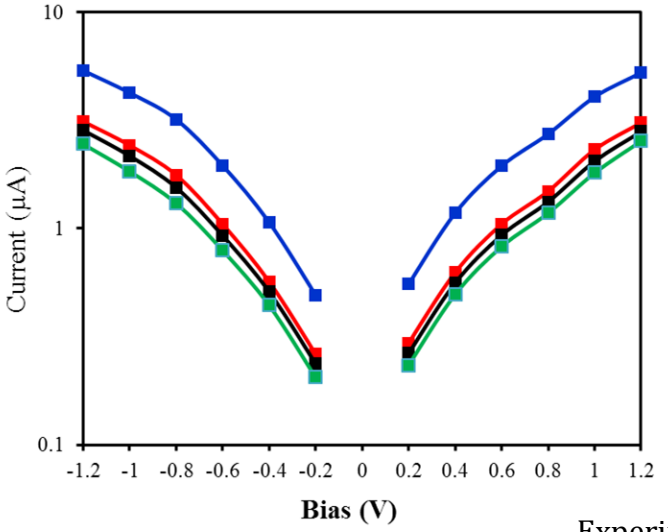
HOMO follows the destabilized electrode! → ***Intramolecular >Interfacial Coupling***



I-V Curves







No impact of the substituents in lineal molecules on the I-V curves

Experimental curves obtained by means CP-AFM Junction, geometry is unknown

Conclusions

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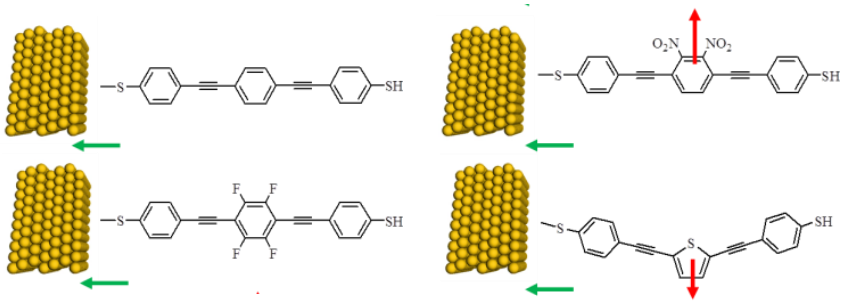
1.- Φ modulation is dominated by changes in the net moment dipole along the perpendicular direction to metal surface.



2.- The appearance of interface dipoles, makes the energy of the dominant molecular transmission channel, insensitive to functional group substitutions, pointing a **Fermi Level Pinning Effect** .

3.- The final I/V response is due to a compromise between the degree of orbital polarization/ hybridization with the electrodes, governing the screening or amplify the electric field across the molecular backbone.

4.- Theory allows rationalize the I/V characteristics in well-defined molecular architectures, in contrast to many experimental results using different techniques and lacking details about the exact contact geometry or the number of molecules in the junction.

Acknowledgements

Collaborators:

C. Daniel Frisbie

Zuoti Xie

Stéphane Rigaut

Karine Costuas

Silvio Osella

Colin Van Dyck

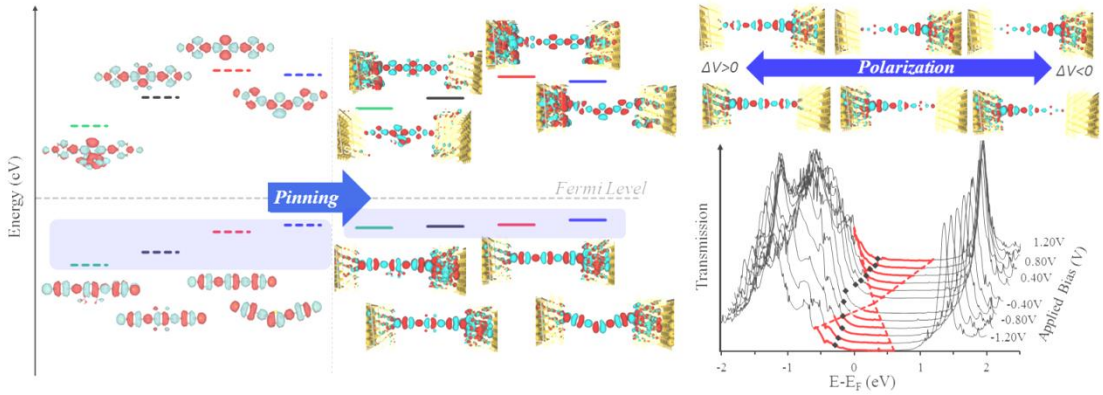
Jéôme Cornil

Membres de la bureau B154

Organizing committe:

fnrs FREEDOM TO RESEARCH

Financial Support



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