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Field-effects on single molecular circuitry

Electronic transport from synthetic to biological models

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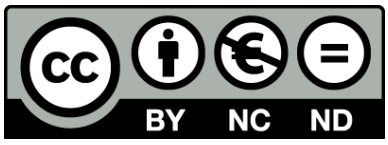

Part III

SUMMARY AND OUTLOOK

Chapter 6

Conclusions of the Thesis

From the study conducted on this thesis about the field-effects on molecular circuitry, can be extracted the following conclusions:

- Both studied force fields affect at the single-molecule level. Magnetic fields act intramolecularly, affecting to the electronic structure and spin-carrier molecular preferences. On the other hand, the electric field, affect intermolecularly orienting reactant molecules and stabilizing the formed adducts transition states.
- Derived from the different manners to affect the molecules, the studied force fields present different ways to be applied.
    1. The magnetoresistive effects can be employed according the main propose of molecular electronics, which is the miniaturization of the conventional electronic components, thanks to the easy control and tunability of the single-molecule conductance that this field offers.
    2. The electric field effect which served to tune the interactions between two reactant molecules, can be used as a derived technique for the STM-BJ approach employed as nanoreactor.

The conclusions regarding the effects of ***external magnetic fields*** *on electron transport, can be summarized as follows:*

- A controlled spin-filtering is achieved on single-molecule circuits at room temperature, the associated magnetoresistive effects offer similar results to the reported by SMMs at low temperature, therefore it represents a more plausible application in a real device since the evident inconvenience of working at low temperature regimes.

- The achieved spin-filtering effect is observed in three different kinds of molecules, metal complexes, metalloporphyrins and chiral peptides. Since the different characteristics between such systems, additional capabilities analogous to microelectronics functions, emerged together with the magnetoresistance effect, as the diode behavior observed on chapter 2 and the variable resistor behavior of chapters 3 and 4.

- All the obtained effects by the three studied systems are due a molecular origin. As a consequence, the observed effects occurred on the limit of zero voltage. It offers the capability to operate under effective very small currents ranges, a valuable feature to build low-power systems.

- The Spintronics experiments for this thesis have focused on the *manipulation stage* of the three stages which may present every Spintronic device. On chapters 2 and 3 the *manipulation stage* is a direct consequence of the external magnetic field since the target molecules are paramagnetic and thus susceptible to be magnetically aligned. Contrary, for the employed peptides on chapter 4, the *manipulation stage* is independent to the magnetic field since is defined by the helicity, and it depends on the current sense and chirality.

- The presence of independent electron-pathways in the same molecule, like in the metalloporphyrins, represent a new understanding of the electron transport through a molecule. Such non-correlated electron-pathways present substantial differences between them, such as significant different conductances (ca. 1 order of magnitude) and different dependences to the polarized current.

- The preferences for the spin-polarized electrons presented by the different molecules employed on this thesis, are explained due the different energy and interaction of (i) alpha and beta spin-polarized molecular orbitals respect the fermi level of the electrodes or (ii) differentiated polarized-electron scattering processes due the helicity. But the perpendicular polarization is not included on such models, despite causes a significant increment of the magnetoresistance effects. Further research is needed.

- In chapter 2 and 3 the Spinterface had a relevant role on the observed spin-filtering effect, attributed to the high SOC due the paramagnetism of the molecules. Contrary, on chapter 3 its contribution was reduced significantly due the peptides' diamagnetism. In that case, peptides present spin-filtering capabilities due the chirality and the associated CISS effect, despite of it, the presented magnetoresistance efficiency is equivalent to the observed by some of the studied paramagnetic molecules of other chapters. It can be understood as alternative way to obtain magnetoresistive devices without involving metal and/or paramagnetism.

- Regarding the previous point, since the Spinterface is not a requirement to achieve magnetoresistive response employing chiral systems, a derived research can be based on using different substrates than Au.

- The Spinterface, in all Chapters, reveals preferences for the minority carriers regardless of the employment of paramagnetic or diamagnetic molecules. The possible origin of such parallelism between the spin-carriers' preferences of the three different studied systems could be the single common point between them: the interface formed by the S/Se-Au highly polarizing bond. This point should be ascertained in future research employing other anchoring groups.
- Peptides as spin-filters present a more complex behavior due the helicity, compared to the analogous metal complexes and metalloporphyrins, because the CISS effect depends not only on the polarized current, but also on the direction of the current. Such effect can limit slightly the applicability in real devices depending their operating mode, despite the multiples advantages which offer commented in other points of this chapter.
- Despite metal complexes offer a very high magnetoresistance efficiency, from the point of view of the applicability, it is easier to design devices based on metalloporphyrins and peptides structures since the exhaustive synthesis research behind them, which allows to access to a wide variety of molecules.

The conclusions related with the application of ***external electric fields*** *on electron transport, can be summarized as follows.*

- The presented adaptation of the STM-BJ approach represents a novel system suitable for reactivity studies at the single-molecule level, since it allows the appropriately settlement of reactant molecules as well as the control of applied electrical fields in strength and orientation. It takes full advantage of the STM set-up via the attained precise nanometric separation between tip and substrate electrodes and also by sharpness of the tip, together they favor the electron flow between reactants through a strong electric field. The precisely controlled field orientation is defined via biased electrodes, used to provide the required electrical charge (polarity) for the attached molecules to stabilize them.
- This proposed new platform along with the obtained results can be used as the basis to study and control at the single-molecule level chemical bimolecular reactions. Therefore, both Molecular Electronics and the adapted STM-BJ approach, can be used as a fundamental platform to study electrical controlled nano-catalysis, employing the former as the technique and the latter as the platform.
- External electric fields can accelerate chemical reactions despite lacking electroactive species. It can represent an early stage to replace traditional bulk chemical reactants by electric fields, representing a cheaper and more efficient way to control reactions precisely and externally. Therefore, is opened the gate for the development of chemical reactor controlled electrically.

Chapter 7

Future Perspectives

In addition to the conclusions, since the novelty of this research, the obtained results open the door to the advance in different topics and fields, summarized below:

- In the studied metalloporphyrins, the employed way to discern between electron-pathways by promoting different binding sites via modifying the electrodes separation and the associated conformations. Despite the effect was controlled, it requires an extended research to elucidate the relationship between electron-pathways inside the same molecule as well as the factors that cause them and define their significant differences.

- Metalloporphyrins present medium magnetoresistance efficiency under a spin alignment parallel to the electrical field, but employing the orthogonal polarization, such efficiency presents an increment of 2 orders of magnitude. Despite the observed effects attest the potential of the anisotropic magnetoresistance, it represents a very preliminary result, therefore is needed continue with the research using such polarization direction.

- Through the experiments performed under magnetic fields, have been demonstrated the two-different molecular origins of the spin-filter capabilities predicted by the theory, the paramagnetism and the chirality; for this reason, the immediately continuation of the research should be a combination of both concepts employing chiral structures with metals inside. It can provide new information about the mechanisms and the possibility to increase the magnetoresistance efficiency.

- The low-dependent spin-filtering behavior respect to the Spinterface effect in the chiral peptides, converts them into the best candidates to develop real spintronic devices based in other materials cheaper and more accessible than gold. Therefore, similar experiments to the performed, should be done as immediately continuation of the presented research, but employing alternative materials for the metal leads. Likewise, it opens the door to combine the observed capabilities with the Si's inherent ones if it is used as platform.

- Since the DFT methods cannot predict accurately the SOC contribution on the surface for the studied systems, to determine such superficial effect, ARPES characterization represents a very accurate tool to quantify it.

- The -S/Se terminated anchoring groups, according to the performed experiments (and by literature), affect significantly to the spin-filtering since their superficial polarization effects and the consequences over the Spinterface. For this reason, in future works should be used other anchoring groups already tested in Molecular Electronics experiments, to analyze their effect on the Spinterface and the magnetoresistance.

- Despite the confirmed coherent tunneling mechanisms through the α-helical structures, the obtained *spin-polarization power* values for the studied α-22AA-peptides are comparable to those obtained for larger chiral structures, e.g. measuring DNA in photoemission experiments. This opens the door to further research with the aim to find the possibility to include a partial incoherent hopping mechanism to transport phenomena conducted at energies above and below the work function.

- The studied chiral peptide structures represent a starting point for future research, because the use of larger molecules and different radius of the helix or pitch can affect to the polarization power.[566,567]

- With the aim to elucidate enzymatic reaction mechanisms, via the study of the local electric fields behind, it can be done employing the presented adaptation of STM-BJ, and making use of surface science mimicking enzyme's active sites cages on the substrate electrodes, jointly attaching to the tip electrodes the active parts or equivalent molecules of charged residues.

- If the observed effects of the applied external electric field can be scaled up thanks to developing a new bulk technique, the industry sector will be largely benefited as a consequence of the huge economic impact since the low-cost implementation of controllable electrical fields in industrial processes, compared to the offered by the present-day employed catalysts like synthetic molecules and noble metal substrates or nanoparticles. Besides, the replacement of chemical catalytic species by external electrical fields means a reduction of the inherent contamination and unwanted side-reactions, thus indirectly is generated another economical positive impact.

- Due the different advantages involved by both magnetic and electric fields, the ideal third part for this thesis, it should have been employing both force fields together at the single molecule level using the presented adaptation of STM-BJ approach. A possible scenario to study, can be the role of the magnetism/spin states in electrostatic catalysis or enzymatic. Such concept was introduced at the beginning of this thesis, with the established relation of some heterogeneous catalytic processes with the spin alignment of the reactants.