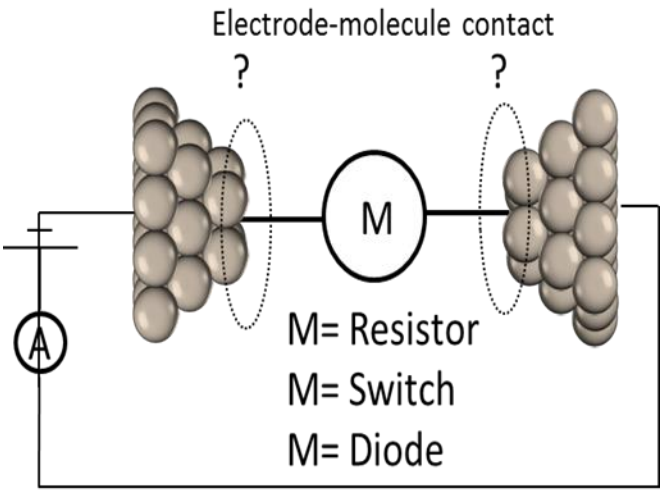
Title: Single-molecule switches

Overview of results:



The use of single molecules in electronics represents the next level of miniaturization of electronic components which would enable us to meet the expanding demands of modern technologies and to continue the downscaling trend in electronic devices.[1-4] This project introduced novel methods of wiring single molecules between electrodes and created, for the first time, single-molecule switches triggered by light and chemical responses and have translated the concepts of single-molecule junctions from metal electrodes to silicon electrodes which is a major step to commercialize this technology in everyday nano-devices. The project had three specific aims which have been all achieved:

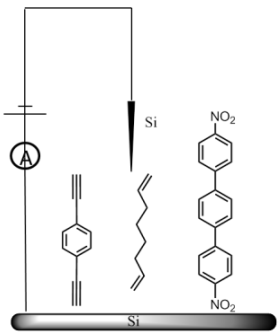
Results:

1-Exploring different anchoring chemistries to metal electrodes

One of the critical parameters for the design of future nanoscale devices is the choice of the chemical group contacting a single molecule to the electrode surface which governs the stability and the electrical properties of single-molecule devices. As part of this Marie Curie Fellowship and specifically to Aim 1, we have reported the formation of stable molecular junctions with contact groups that are used for the first time (1-alkynes).[5] Self-assembled monolayers that forms spontaneously from diluted solutions of 1,4-diethynylbenzene (DEB) were used to build single-molecule contacts and assessed using a scanning tunneling microscopy-break junction approach (STM-BJ. It is demonstrated that single-molecule junctions form spontaneously with terminal alkynes and requires no electrochemical control or chemical deprotonation. The alkyne anchoring group was compared against typical contact groups exploited in single-molecule studies, i.e. amine (benzenediamine, BDA) and thiol (benzendithiol, BDT) contact groups. The alkyne contacts showed conductance magnitude comparable to that observed with amine and thiol groups. The lifetime of the junctions formed from alkynes were only slightly less than that of thiols and greater than that observed for amines. These findings are important as a) they extend the repertoire of chemical contacts used in single-molecule measurements to 1-alkynes, which are synthetically accessible and stable and b) alkynes have a remarkable affinity toward silicon surfaces, hence opening the door for the study of single-molecule transport on a semiconducting electronic platform.

Further and under aim 1 of the project, we have implemented novel anchoring chemistries which changes the way we think of how to form single-molecule wires. We developed a technique whose working principle is simply instead of pre-synthesizing a complete molecular wire and then using it in conductance measurements; we showed that we can perform this process sequentially.[6] Hence, we showed that we can functionalize both the two metal electrodes with chemical ligands and then close the electrical circuit by ¨fishing¨ a single porphyrin[6] or phthalocyanine[7] molecule via coordination chemistry with its metal center.[6] Therefore, instead of using complicated, costly and time-consuming chemistries to modify synthetically a porphyrin molecule for instance, we simple use pyridine ligands on the two electrodes that can catch the porphyrin molecule from its metal center.[6,7] In this study, it was the first time single electron transport across porphyrin molecules were investigated while the porphyrin molecules are positioned in a flat configuration.[6] The new flat configuration resulted in single-molecule junctions of exceedingly high lifetime and of conductance three orders of magnitude larger than that obtained previously for similar porphyrin molecules but wired from either end of the porphyrin ring. Such new configuration mimics the electron transport process across porphyrins in naturally occurring phenomena such as photosynthetic and transmembrane electron transport. This study again opens the door for new studies that we are planning to perform which extends beyond the current project. For example we used the same configuration to gain insights on the electron transport across phthalocyanine molecules which are exceedingly important for the electrocatalysis of oxygen reduction. This work presented a new concept of building highly efficient single-molecule electrical contacts by exploiting metal coordination chemistry.[6,7]

2- Exploring alternatives to the common gold electrodes to form single-molecule junctions and exploring specific anchoring chemical routes to these electrodes.



During the course of Aim 1, we have discovered that terminal alkynes have a remarkable affinity towards both metal and silicon semiconducting surfaces, hence opening the door for the study of single-molecule transport on a semiconducting electronic platform. This enables the investigation of metal-molecule-semiconductor systems at the single molecule level. This aspect simplify the transition of the charge-transport knowledge generated to date in the Molecular Electronic field into semiconducting platforms, a required step towards the design of nanoscale molecular circuitry.

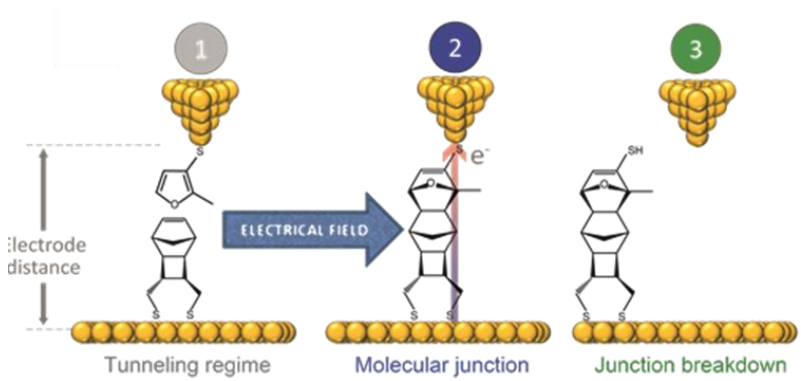
For this Aim, we have successfully formed single-molecule junctions, for the first time, on a silicon platform. The resulting junctions were significantly more stable than what was previously achieved with metal electrodes. In addition, using different type and doping of the semiconducting electrode we were able to control the charge transport across the junctions. This study not only covers Aim 2 of the project but extends beyond the project to future projects which we are aiming to continue in the near future. An article reporting the results obtained from Aim 2 is under preparation and is anticipated to be published in a high-quality journal by the end of 2015.[8]

3- External gating of single-molecule junctions

After successfully implementing the technical addition to the instruments and after obtaining thoughtful synthetic targets, we have performed measurements on photochromic molecules both in the bulk solution using spectrophotometry techniques and at the single-molecule level using the STM-break junction technique. Here we focused, on **spiropyran,** photochromic molecules that switch between completely conjugated form in the open form and a broken conjugated form in the closed state. Several outstanding observations and novel information has been obtained. Namely, we managed to synthesize unique type of photo-switches, bifunctional spiropyran with complete control on their time-scale of switching and switching schemes upon irradiation with light. We also managed to access and understand how such molecules can switch in conditions of multiple stimuli i.e. in addition to light, such molecules were found to switch by chemical stimuli. The design, observations and analysis allowed us to perform single-molecule electrical switches where this unique chemistry switching is changed to electrical switching in a nano-device. This study constitutes the first example of a multi-responsive single-molecule electronic device.[9] Relevant to this aim as well, we have showed that the resistance of carotenoids molecular wires can be fine-tuned using chemical substituents of controlled orientations. [10]

Socio-economic impact of the project:

The results obtained from this project contribute to the next generation of electronic components where molecules and atoms will replace today´s conventional micro-sized electronics. These tiny molecular circuits can reduce the costs and the sizes of electronic devices and therefore have economic and environmental impacts and can enhance our quality of life by improving existing technologies such as computers, mobile phones and memory devices. They can also lead to revolutionary analytical devices for the early detection of harmful chemicals and biological markers reflecting the beginning of diseases and therefore has implication in health and diagnostic methods. In addition, this research line will enable us to use atoms and molecules just like Lego, snapping them together to create tiny structures and machines that open up a realm of possibilities that may allow us to lead better and more efficient lives. In this vein, we have recently shown that 2 single-molecule reactants can be joined to form a product, an aim which extends beyond the current project and open the door for electrostatic catalysis of non-redox reactions.[11]



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