Summary of PhD's Thesis

In the 1960s, Gordon Moore predicted that the number of transistors on a microprocessor chip would double every two years. Since then, the size of the transistors has fallen from 90 nm in 2004 to 10 nm in 2017 (more recently 7nm by Apple Inc.). The question 'What is next beyond Moore' has been posed by many scientists. Since 1974, it has been proposed that Solid-state molecular electronic devices (MJ) could be an alternative solution where the molecules are sandwiched between two electrodes (a cross-bar structure, see Figure 1).

Molecular electronics generally refers to studies using molecular building blocks as electronic components, the length of the molecular blocks is usually less than 20nm. The field emerged explosively in the late 1990s, accelerated by developments in scanning probe microscopy and nanofabrication techniques. Recently, molecular electronics has been proven as molecular rectifier, memristor, photo-switcher. However, it is still a **challenge to have reliable molecular electronic solid-state devices associated with functionalities** and equally important it still **lacks systematic studies**.

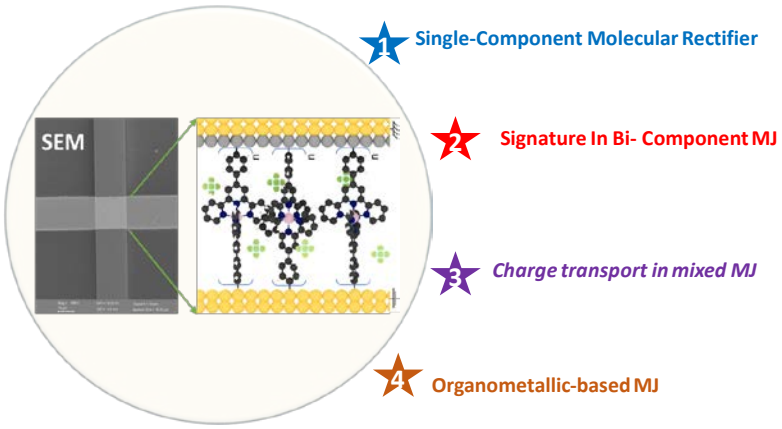

Figure 1 Scheme of a Cross-Bar Metal/Molecular/Metal Junction and Overview of Phd's Objectives

My interdisciplinary PhD is aimed at **studying the transport through large area Metal/Molecules/Metal junctions (20×20µm^2) using ultrathin layers 2-20nm** thick and **exploring new functionalities** that could occur in such ultrathin MJs. To fabricate such MJs, I have combined Complementary Metal-Oxide-Semiconductor (CMOS) processes and surface modification by electroreduction of diazonium salt. Organic layers were deposited by electro-generated radical grafting processes, then E-beam evaporator was used to deposit metals directly onto the grafted organic layer. The transport understanding has been inferred by analyzing the dependence of current-voltage (IV) curves on the thickness of the molecular layer (β plot) and the temperature (Arrhenius plot). The main objective is to **systematically study the role of molecules on charge transport through the molecular layers** and **look for electronic function** in cross-bar molecular junctions without changing electrode contacts.

The thesis is based on the expertise of the Nanoelectrochemistry group (NEC) in surface science and nanoelectrochemistry. Metal/Molecules/Metal junctions are fabricated in a clean room at the Paris Diderot University. Transport measurements are performed in both the NEC and the TELEM groups (Paris Diderot University). Some work in the thesis was done in an international

collaboration with Professor Richard McCreery at the University of Alberta, Canada. The thesis focuses on several objectives as pictured in Figure 1.

First, I have studied the rectification behavior of single component asymmetric MJs by using several molecules including donor, acceptor, donor-acceptor molecules. I have shown that the **rectification ratio can be varied by 5 orders of magnitudes by changing the used molecule**, **the polarity of the rectification can be reversed**. I have also reported **the first examples of solid state monolayer molecular rectifier**. Moreover, a **new system showing nearly on-resonant transport** was developed.

Second, I have studied the transport in bilayer molecular junctions in which bilayer containing two different molecules, is deposited layer-by-layer by either an overgrafting approach or a diazonium approach. We found that the overgrafting approach generates a new layer in which a first layer is strongly electronically coupled with a second layer whereas the diazonium approach generate a bilayer in which a first layer is weakly coupled with the second layer. Using the **first approach we developed another system in which transport is dominated by on resonant tunneling** whereas the **second approach always leads to a decrease of the conductivity but with interesting rectification properties**.

Third, I have also investigated the electrical properties of mixed component molecular junction in which a first molecular layer is deposited using a host/guest complex which allows removal of the host to create free holes. A second deposition step generates the mixed layer. We demonstrate that **below a layer thickness of 5 nm, the transport in mixed molecular junction occurs by direct tunneling but that the current depends on the number of active channels in the layers, which has never been experimentally reported in the literature**.

Finally, I have studied the electrodeposition of organometallic compounds and charge transport through organometallic molecular junction. Above direct tunneling, I found that the conductivity of organometallic MJs is always higher than that obtained for most molecular junction based on pi-conjugated organic molecules. I **also observed a highly efficient long-range transport in Cobalt(II) terpyridyl MJs** suggesting again the transport is probably operated by resonant tunneling. We evidenced **light emission in Ru(II) bipyridyl MJs which is one of the first direct proof of ultrafast redox events in solid state MJs** and finally we partially explored **the role of counter ion in organometallic MJs**.

To summary, during my PhD, I have fabricated reliable large-area solid-state molecular electronic devices in which the molecular layer is in between 2 and 20 nm thick. I have systematically explored the role of the molecules in the transport and found a lot of functionalities in MJs such as rectification, molecular wire, photoemission. Equally important, I have found that the redox event can occur in ultrathin devices (4nm). So far, my PhD data led to **5 peer-reviewed papers** such as high rectification ratio (published in ***JACS 2017***) and good rectification for monolayer MJs (***Chem Com 2017, inside cover art***), light emission (***JACS 2017, editor's choice in Science***), *Highly efficient long-range transport (****JACS 2018****),* **6 submitted** manuscripts and **9 others** are in preparation. Some of my achievements and concepts can be obviously extended toward rectifying molecular devices, nanobattery, Iontronic molecular devices as well as solar cell device.