Abstract: This thesis aimed to study surfaces modified by photoactive molecular layers in two different configurations: a “horizontal configuration” and a “vertical configuration”.

The first configuration is shedding a light on the use of methods and techniques for assembling and organizing photoactive molecules on surfaces. I studied with the scanning tunneling microscope (STM) the self-assembly and the photoswitch of two photochromic derivatives: An azobenzene derivative (AZO) and a diarylethene derivative (DAE). Both were functionalized with terminal bipyridine units (bpy) to give the systems (bpy-AZO-bpy) and (bpy-DAE-bpy). They were deposited by droplet deposition at the solid/liquid interface (s/l) and at a room temperature. A major observation, that has been noted, shows that 2D supramolecular structures can be generated and the constructed structures can be controlled using several external stimuli (solvent/pH and light irradiation). These stimuli provide us with high-level control between multiple stable molecular orders and reversible switching (at the single molecule level), by controlling the adsorption process of each isomer, which is rarely observed under ambient conditions.

Following this, I continued to use photoactive molecules on surfaces but this time by positioning them in a “vertical configuration” in order to generate new switches that can be used in metal/molecule/metal devices with molecular layers of d = 3nm to 20nm thick. The thickness of the layer has an important influence on the transport according to the simplified theoretical equation of Simmons ($J = Jo$ e $(-\beta d)$, where d is the thickness of the layer, J the current density and β is the attenuation factor). In addition, the control of the thicknesses will lead to the control of the transport regime, which will permit us to study the physical properties of the molecular junctions (MJs). We performed the metal/molecules/metal MJs by using gold surfaces, reducing diazonium salts to graft molecules with controlled thicknesses, and a tip of a conducting- Atomic Force Microscopy C-AFM to complete the MJs. First, we studied the behavior of MJs incorporating DAE oligomers with two different thicknesses. The junction formed by DAE_{3nm} gave an ON/OFF current ratio of 2-3, while the junction formed by DAE_{9nm} gave an ON/OFF ratio of 200-400. Secondly, we studied transport in bilayer molecular junctions made up of two different molecules $(DAE/BTB)_{9nm}$. ON/OFF ratios greater than 10 000 have been obtained reproducibly. The ratios were therefore further improved. This bilayer structure provides a novel way to fabricate switching systems and achieve high ON/OFF ratios rarely seen in photochromic based devices.