

Executive Summary

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Project "Functional organic and organometallic materials for molecular electronic applications"

The goal of this fundamental-research project was to assess the potential of organic and organometallic molecular compounds for future molecular electronic applications. Mononuclear complexes bearing Fe, Ru and Mo as metal centers and dinuclear organometallic compounds bearing Fe as metal centers in their backbone, as well as purely organic azulenebased compounds with variable acetylene-substitutions were synthesized by the University of Zurich. All compounds are intrinsically redox-active and designed in such a way, that the redox state should have maximum influence on electron transport. All compounds were electrically characterized in a break-junction mechanisms at IBM Research – Zurich enabling single-molecule measurements under well-defined conditions and variable temperatures. The experiments target the electrical addressing of the molecular-intrinsic redox states via the electric field present in a two-terminal molecular junction without the need of a gate electrode enabling ultimate miniaturization.

In a first step, the anchoring groups to organometallic dinuclear Fe complexes were systematically varied from coordinative to covalent aiming at achieving a high conductance required for electronic building blocks due to power issues. It could be evidenced that molecular wires can be achieved by combining an excellent molecular level alignment due to metal center incorporation and ligand schemes to establish a delocalized electron system between the metal centers. As a result of this strategy, conductance values were measured that are among the highest reported in literature so far for a given molecular length, on contrast, however, the intrinsic redox functionality was prevented by the high hybridisation of molecular and metal states.

In a second step, these findings were taken into account to achieve a slightly weaker coupling but maintain the redox activity in mononuclear Fe, Ru and Mo complexes. Here, hysteretic switching behaviour was found with highest on/off ratios exceeding 1000 for Mo. By DFT calculations, performed by the University of Vienna, a microscopic molecular orbital picture was developed that attributes the abrupt switching in the Mo complex to the presence of a localized molecular orbital, which is close to the Fermi energy of the electrodes due to its spin-polarized ground state. This finding could pave the road for highly functional redox-based molecular switches in memory applications.

As the transport properties of these functional single-molecule junctions were promising, the solid-state implementation of molecular assemblies into real device architectures was approached in the last year of the project. The goal was to develop a wafer-scale platform compatible with standard micro- and nanofabrication technologies. Here, ensembles of molecules should be implemented into nanopores and sandwiched by bottom and top electrodes in cross-bar geometries. In the remaining, short timeframe of the project, we could achieve the required atomically-flat bottom electrodes by template stripping and pore etching techniques by atomic-layer deposition in combination with dry and wet selective etching. The proof-of-principle of the novel platform was started by implementing well-known alkane molecules of different lengths. Here, high yields of 90 % of working nanopore devices without filament formations and a conductance-length dependence in excellent agreement with literature could be demonstrated.