

The main objective of the project is verification of practical **exploitation possibilities** of the **remarkable differences** in electrochemical potentials between transition metal ions to develop single molecular machine with functionality of macroscopic devices. The characteristic feature of such system is existence in hetero-polymetallic core difference (internal gradient) of electric potential with respect to its ends, resulting in polarization of interactions between metallic centers. Besides the **working principle** should be established on reversible change of this polarization (scaling and/or switching to opposite direction) caused by external factors (like electric field, bias of nanoelectrodes, or optical excitations), through mechanism involving intramolecular (preferably excluding direct participation of ligands) reversible redox processes or excitations to different spin states. The research goal is also testing if it is possible to obtain system with significantly enough variable polarity of metallic core that different bistable states of dipole moment could be distinguished. Another objective is **assessment** if these properties have switching (transistor) or rectifying (diode) applications therefore are useful in molecular electronics and to recognize interrelations and mutual effects between different features exhibited by these systems (polarity of metal core, magnetic and spin states, excited states, redox states, ligand properties, behavior in electric field, etc.).

The mentioned compounds will be modeled using quantum chemical methods, particularly DFT functionals (meta-GGA and hybrid). Methodology will be verified against available experimental data for known bimetallic complexes. **Critical properties** regarding polarity and nature of interactions between metal centers will be determined using various population analyses and electronic structure study. The abilities and tendencies of these systems to regroup and achieve different redox and spin (magnetic ordering) states will be deduced based on relative energies and broken symmetry calculations. The potentials of electron transfer processes, particularly for  $(M'M)^{+3,+4,+5}$  and  $(M''M'M)^{+5,+6,+7}$  of metallic core also will be found. Moreover intramolecular redox processes on metallic centers will be studied with conceptual DFT tools, such as electronegativity equalization method. Stability (metastability) of states and reversibility of redox processes will be shown also under external electric field perturbation or in spin excited states. The possibility of rectification, switching or negative differential resistance effects will be tested by calculations of I-V characteristics. The 4<sup>th</sup> period transition metals are in the main scope of this proposal considered within 4 types of ligands coordinating metal ions in trigonal bipyramidal or octahedral fashion. Additionally the effects of ligand properties on electronic structure of metallic core will be researched, such as substitution with functional groups, basicity of coordinating sites, ligand field energy, ligand dipole moment.

The primary goal of **emerging branch of science** called molecular electronics is development of systems in molecular scale resembling and functioning as macroscopic devices in order to satisfy for further miniaturization, increase efficiency and energy savings. The heteropolymetallic compounds have growing applications in different fields due to differences in bonding character and reactivity comparing to homometallic complexes and as precursors for new materials. The metalorganic compounds offer richness of effects (spin and redox states, cooperative and quantum effects) and possibilities to control these properties. The **fundamental beneficial aspect** of this project comes from systematic study of several experimentally known bimetallic complexes exhibiting substantial intramolecular electrochemical gradients with the use of theoretical methods in the context of applications unimolecular devices in molecular electronics with the role of transistors, diodes or sensors. Another prospective of this proposal is later analysis for the first time of the unknown trimetallic counterparts. The major result of research will be explanation of interdependences between characteristic features of these systems and the possibilities of exploiting them as different channels for controlling and manipulation and as mechanisms of functioning of these devices. At least 3 systems will be proposed characterized by heterometallic core and intramolecular electrochemical potential gradient that could be used as switches, diodes or resistors with negative differential resistance. Systematical qualitative and quantitative studies are necessary for understanding of mechanisms, which will allow for transition from macro to unimolecular analogues of electronic devices.