Towards new chemistry of metal-TEMPO complexes as activators of CO_2 and H_2 molecules.

The organic TEMPO radical and metal-TEMPO systems (TEMPO – 2,2,6,6-tetramethylpiperidine-N-oxyl) have been widely used in a variety of industrial applications for chemical transformations. A number of recent studies demonstrate that metal-TEMPO complexes attract considerable attention due to their unique properties and unexpected reactivity, showing there is plenty of room in this field. The chemistry of metal-TEMPO complexes is developing quietly in the shadow of the progressing area of fertile landscape of stable organic nitroxyl radicals, which is mainly focused around the radical chemistry of catalytic and stoichiometric reactions in organic syntheses. Strikingly, the synthetic methodology of metal-TEMPO complexes is a highly undeveloped area and essentially limited only to synthetic pathways concerning direct redox reaction of radical TEMPO• with organometallic or inorganic compounds. One of the most emerging fields involving TEMPO molecules is converting the energy of sun-light directly into electricity and its storage. Solar cells and lithium-based rechargeable batteries lead the way in current development in this field. TEMPO molecules are successfully utilized in solar cells (DSSC) and supercapacitors, which are alternative storage devices for electricity. Moreover, the CuI/TEMPO based aerobic catalyst system enables chemoselective oxidation of benzylic, allylic and aliphatic primary alcohols to the corresponding aldehydes, with rates at least an order of magnitude higher than those earlier used. Hence, the development of the metal-TEMPO systems and understanding the factors affecting them is very important.

The proposed project is directed to further advancing the fundamental knowledge of the synthesis and structure of metal-TEMPO complexes. The main project objectives include: *i*) studies on the synthesis and structure of metal-TEMPO complexes with selected metals, supported by organic ligands, *ii*) interpretation of the factors governing the stability and structure of obtained complexes, *iii*) investigation on the controlled transformations of well-defined metal-TEMPO complexes triggered photo-, thermo- and mechanochemically and *iv*) investigation on the activation of small molecules such as CO_2 and H_2 in controlled conditions with well-defined metal-TEMPO complexes.

The project investigations should provide both a more in-depth mechanical understanding of the formation of metal-TEMPO complexes and their initial and subsequent steps of transformations and pave the way for new structurally well-defined clusters and oxo-metal complexes. The proposed novel synthetic methodology pathway is simple, high yield and selective. Moreover, this project is relevant to expanding knowledge about the reactivity of metal-TEMPO complexes toward activations of molecular CO_2 and H_2. It may pave the way for novel, well-defined stoichiometric and catalytic systems for industrial processes and the development of modern energy generation and storage technologies.