

Magnetic materials (magnets) are now essential for continued advance in almost any of modern technologies. Organic chemistry provides with means and solutions to handle molecules with almost unlimited freedom of modification hence enabling a precise tailoring and tunability of properties in designed systems. Molecular magnets based on organic radical scaffolds are currently very underrepresented in research, interest in such systems is however increasingly growing, mainly due to basic economical factor: no metals are required. Modern inorganic magnetic materials often consist of rare earth metals, control over its deposits is therefore of strategic importance and governs the ability to produce advanced electronics on large industrial scale. Organic magnetic materials removes necessity for expensive metals or at least minimize their use. The aim of research proposal presented herein is synthesis and physicochemical characterization of organic molecules based on 1,1-dioxo-1,2,5-thiadiazole unit. Compounds containing this motif in their structure exhibit very rich and complex electrochemistry and are often able to be isolated as stable organic radicals which can be employed, for example, in construction of molecular magnetic materials. In frame of proposed research a library of new polycyclic systems with several 1,1-dioxo-1,2,5-thiadiazole units in one molecule is about to be established. Those will in particular be based on hexaketocyclohexane, triphenylene, coronene (or triazacoronene) and triptycene scaffolds, attempts will be taken on preparation of porphyrazine analogues. Said compounds will be prepared both with conventional synthetic methods and with use of mechanochemistry, in planetary mill, as it was previously shown possible in our laboratory, it is also a "green", eco-friendly approach with minimal to zero solvent use and unique selectivity allowing, in some cases, for better control over product composition. Multiple advanced techniques will be employed to properly characterize physicochemical properties of obtained materials, including SQUID magnetometry, cyclic voltammetry (CV), differential pulse voltammetry (DPV), EPR for radical species, NMR, IR, UV-Vis, fluorescence spectroscopy, and others.

All compounds proposed within this research are currently unknown and new therefore any information acquired will be an important step towards understanding of chemistry of that type of organic radicals. Preliminary investigations indicate that molecules in question indeed can be synthesized and display complex electrochemical properties, with many accessible oxidation states, with several different radical states, all within one molecular structure. This may enable preparation of systems where change in formal oxidation state of organic ligand may switch the magnetic response on and off depending on the spin multiplicity of the system. Furthermore, change of oxidation state is followed by different reactivity: neutral species of hexaketocyclohexane derivatives participate in extraordinarily strong anion- π interactions, with distances being one of the shortest ever reported, the same or stronger interactions are expected for other examples presented within this proposal. Monoanions and trianions are radicals, therefore they are magnetically active and on their own, they are an interesting example of purely organic systems with chance for non-trivial magnetic behavior. These radicals can also be used as ligands for d- and f-block metals to yield either SMMs (Single-Molecule Magnet) or extended coordination polymers. S-block salts (Na, Li etc.) conduct electricity and may be of interest in terms of energy storage.