

## **The impact of structural factors on ferromagnetic spin interactions in aminocarbazole oligomers; design, DFT calculations, synthesis and evaluation of physicochemical properties**

The last decades of XX century brought a spectacular progress in the field of materials chemistry which was manifested in an elaboration of a completely new area of research called organic electronics. It combined very specifically synthetic organic chemistry with electrical properties of the synthesized molecules, which resulted in a spectacular change of our way of thinking about conductors and semiconductors. Organic electronics has drawn so much scientific attention that it led to awarding Alan J. Heeger, Alan G. MacDiarmid and H. Shirikawa a Nobel Prize in chemistry in 2000. Their initial discovery founded a basic playground for utilization of organic semiconductors in such sophisticated technologies as field effect transistors, OFETs, light emitting diodes, OLEDs and various photovoltaics devices (OPV). The utility of organic materials in comparison to their inorganic counterparts was attributed to a series of benefits *i.e.* low density, possibility of fine-tuning of electrical and optoelectrical properties and upon adequate functionalization - solution processability. On the other hand, the magnetic properties of organic semiconductors remained somehow abandoned for a long time, leaving an open space for a new area of research to come - organic spintronics. In general, spintronics deals with interactions between intrinsic magnetic moments of electron (spins) and their capability of exhibiting collective behavior. This particularly interesting property can contribute to a significant progress in an information transfer technology and therefore eventually to energy conservation. Unfortunately, as primarily in the case of organic electronics, the spintronics still remains fundamental and a mostly inorganic domain. Thus, in the light of the abovementioned facts it becomes clear that further development in the field of organic magnets will certainly constitute a historical breakthrough. First however, a comprehensive, step-by-step explanation of rules staying behind collective magnetic behavior must be formulated.

The main aim of this project is an efficient synthesis of organic semiconductors, which upon chemical doping and generation of radical cations will furthermore attract them to interact ferromagnetically. This constitutes an ambitious proposal since ferromagnetic coupling is in general rare and not favored by nature. According to Pauli principle each two electrons occupying the same space must form a Lewis doublet. Thus to overcome this problem it is necessary to effectively localize the spins of the unpaired electrons at short enough distance and force them to interact ferromagnetically through a specifically designed molecular structure. This brings us to the so-called topological model approach, in which ferromagnetic coupling is reached by adjusting the molecular backbone so that it consisted of alternating two units, one capable of spin generation and the other of spin-coupling. This model constitutes a starting point of this research proposal and so far is the most explored tool in the field of organic high-spin compounds. It does not however answer all questions that raised during exploration of ferromagnetic spin-interaction in purely organic materials. **Therefore, an important scientific novelty of this project is a unique combination of three distinct domains of chemistry and physics in order to elucidate a correlation model linking chemical structure of the molecule with its ferromagnetic properties.** This approach covers mutual utilization of Broken-Symmetry DFT calculations, organic synthesis with retrosynthetic analysis and advanced spectroscopy (EPR) for the design and the preparation of organic high-spin compounds. According to recent trends in modern chemistry the most beneficial is the incorporation of initial DFT calculations prior to performing synthesis of target compounds since it allows to predict the desired magnetic properties and initially evaluate their usefulness. Taking into account multi-step character of most of the organic transformations it highly contributes to time and resources saving and thus indirectly to green chemistry.

Within the framework of this project we intend to obtain two carbazole-based derivatives, one linear and the other as a cyclophane (cyclic oligomer), which will exhibit enhanced ferromagnetic coupling. Since they both possess a similar structure also their corresponding medial materials will be the same. Therefore, in our first approach we plan to properly functionalize 6-nitro-9*H*-carbazol-3-amine, which has a unique three-site architecture, capable of gradual functionalization *via* substitution. Then in a series of palladium-catalyzed Buchwald-type aminations the target compounds will be formed and thoroughly characterized spectroscopically (NMR, HRMS, IR, X-ray, elemental analysis). Subsequently, the target compounds will undergo electrochemical study, which will provide oxidation potentials determination. Then radical cation formation and tracking of its localization will be performed during a series of chemical doping experiments combined with mutual recording of UV-vis-NIR spectra. In the last step, the title ferromagnetic properties will be examined by means of pulsed EPR spectroscopy and magnetization measurements. This final studies will allow to determine the magnitude of spin-ordering capabilities in organic systems. To summarize, taking into account the above presented outline of the project we expect to greatly contribute to the total progress in three domains of chemistry: organic synthesis, computational chemistry and spectroscopy, but most of all to organic spintronics.