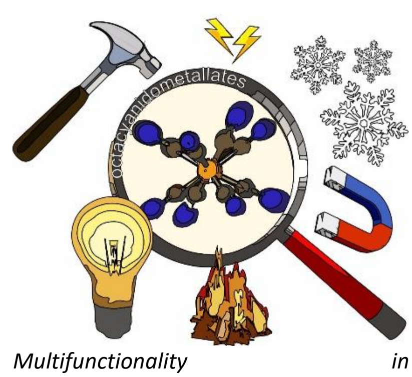
Spin transitions in multifunctional polycyanidometallate molecular materials

Abstract for the general public

Spin transitions are intrinsically related to the spin state change of each individual magnetic center in an extended molecular material. The spin state controls the color of the compounds as well as its magnetic and electric properties. The centers showing the ability to change their spin state can be directly incorporated in the coordination framework of the target material as its key components or play the role of a molecular guest that could be removed from the host framework either by ion exchange or directly by using relevant solvent. Nevertheless, the most important feature of 'spin transition materials' is the possibility to control the spin state of the constituent metal centers using external stimuli as well as the possibility to read these states through the observation of their color and physic-chemical properties.

The proposed research "*Spin transitions in multifunctional polycyanidometalalte molecular materials*" focuses on the design and preparation of heterometallic molecular materials based on policyanidometallates, that would show the desired spin transitions and the intrinsically related multifunctionality. Multifunctionality is a unique property that allows the material two react in a very specific way in response to a sophisticated combination of external stimuli. It will be achieved by pursuing three main research pathways: (i) combination of building blocks with the ability to undergo spin crossover (SCO) transitions with organic ligands showing luminescence, (ii) combination of SCO-capable centers with building blocks that will introduce order-disorder transitions and possibly ferroelectric properties (these building blocks are the are specific tertiary ammonium cations), (iii) the third approach will rely on spin transition systems that would also show light-induced excited spin state trapping effect (LIESST effect) enabling photoswitching of the spin state of individual centers. Finally, an attempt towards truly multifunctional systems combining all types of functionalities (i-iii) will be made in order to achieve multifunctional magneto-optical molecular material with tunable luminescence. The construction of the target compounds will be based on policyanidometallates and other complementary building blocks which will be introduced via coordination and supramolecular chemistry as well as crystal engineering methods. The basic characterization of the target materials will revolve around magneto-structural correlations using X-ray diffraction structural analysis and SQUID magnetometry. The most promising ones will be tested for luminescence, ferroelectricity and LIESST effect and for the switching behavior enforced by external stimuli: temperature, pressure, light, guest molecules, magnetic and electric field. Selected candidates that combine all desired functions will undergo advanced characterization such as magnetization-induced second harmonic generation or circularly polarized luminescence.

The implementation of the project will have a huge scientific and sociological impact: (i) it will accelerate the development of switchable molecular materials responsive to external/environmental stimuli, (ii) it will lead to key discoveries in the field of molecular sensors and switches and enable the construction of their prototypes in the near future, (iii) it will bring new insights related to advanced cross-effects such as magnetization-induced second harmonic generation and their introduction into multifunctional molecular materials.



Multifunctionality in polycyanometallate-based materials. Reproduced from Chem. Soc. Rev. ***2020****, 49, 5945-6001.*