The main goal of the proposed research grant is the elaboration of a new generation of hybrid materials consisting of nanocrystalline-size semiconducting inorganic core stabilized with organic ligands also of semiconductor nature. Inorganic semiconductors nanocrystals are interesting materials whose physical properties and in particular their luminescence spectra can be tuned through the so called “quantum confinement effect”. In other words the color of their light emission is dependent on their size. Nanocrystals are objects of few nanometer size and for this reason are thermodynamically unstable and must be sterically stabilized by appropriate surfacial ligands. Nanocrystals are principally used in the fabrication of energy converting devices such as light emitting diodes, photovoltaic cells and others. A different domain of applications involves biosciences and in particular bioimaging.

Initially developed nanocrystals (CdSe, PbS) were of binary nature and contained toxic elements. In these perspective the research directed towards ternary and quaternary nanocrystals is very desirable. First, it allows to get rid of toxic elements, second it makes possible more precise tuning of the luminescent properties not only by quantum confinement effect (i.e. by changing the size) but also for nanocrystals of the same size through alloying. Apart from toxic elements, the main disadvantage of this first generation nanocrystals is the fact that their stabilizing ligands are of insulating nature which impedes energy or charge transfer between particular components of the active layer in a given energy converting device. For this reason the performance of nanocrystals-based devices is far from being optimal. Methods of initial ligands removal were proposed, for example via their replacement by “labile” ligands which could be removed in the next step of the nanocrystals processing. However, such “naked” nanocrystals represent several disadvantages, strong tendency to agglomerate, among others. In the project we propose the design and elaboration of new generation toxic metals-free nanocrystals which are stabilized by organic ligands of semiconducting nature, preferably donor-acceptor ones. An important feature of these ligands is their ambipolarity i.e. capability of conducting holes and electrons. In these hybrids both energy and charge transfer as well as charge transport in the active layer will not be impeded by the insulating ligands.

These functionalized ligands, in addition to their semiconducting unit, must contain solubilizing substituents and an anchoring group, i.e. a group capable of binding to the nanocrystal surface. In the synthesis of these new ligands concepts and reactions of heterocyclic chemistry will be applied. Precise adjustment of the inorganic core and semiconducting ligand energy levels is vital in the design of such hybrids. In the case of ligands this can be done by selecting appropriate donor and acceptor segments. In the case of nanocrystals – by alloying. Alloyed nanocrystals of the following type Cu-In-Zn-S, Ag-In-Zn-S are especially interesting since they show very strong luminescence which can be tuned by changing their composition as demonstrated by our preliminary studies. Ternary Cu-Fe-S and quaternary Cu-Zn-Sn-S are in turn promising thermoelectric materials whose thermoelectricity can be enhanced through the presence of conducting ligands. These new hybrids are also interesting electrochromic materials i.e. materials whose color can be changed by application of electrical potential.

The elaborated hybrids must be deeply characterized by several methods. Their structure must be determined by X-ray diffraction studies. The composition of surfacial ligands by X-ray photoelectron spectroscopy – special technique devoted to investigation of surfaces. Electroluminescence of these hybrids i.e. their capability of shining light induced by applied voltage must be determined as well as other electrical and optoelectronic parameters. Chemical properties of the hybrids must also be studied such as their resistance against oxidative degradation and photodegradation. The most promising materials will be tested as components of such energy converting devices as light emitting diodes (LEDs) i.e. devices converting electricity into light, photovoltaic cells – devices converting light into electricity (inversed with respect to LEDs) and thermoelectric devices – converting thermal energy into electrical energy. All these devices can be prepared using solution processing – a simple and cheap technique, impossible to apply in the case of classical inorganic semiconducting materials. The project authors treat these application attempts as a proof of concept rather than a technological application. The proposed research remains basic in all its aspects.

To summarize, the project authors propose elaboration of a new generation of electroactive hybrid materials exhibiting a set of interesting optical, electrical and electrochemical properties difficult to match or even, in some cases, unmatched by conventional materials.