# FROM THE CHEMISTRY OF MULTIVARIATE COORDINATION SYSTEMS TO THE NANOCHEMISTRY OF ZINC OXIDE

## Abastract

This thesis is the fruit of the efforts to take the Romanian School of Chemistry to ever higher heights, presenting succinctly the most important scientific contributions from the branches of coordination chemistry and nanochemistry, but also with the special contribution of organic chemistry, which were attained in the last 10 years after the defense of the doctoral thesis. Much of the research undertaken is related to the continuation of the work carried out during the doctoral studies in the branch of coordination chemistry, being focused on the development of new coordination systems with polydentate azole ligands for various applications. In parallel with these, on the occasion of accessing a postdoctoral scholarship, I approached a new branch of Chemistry, namely nanochemistry, in which I focused the attention on obtaining new series of nanoparticles based on zinc oxide modified with various organic agents, with dimensions that are of quantum dot level, for optoelectronic and biological applications.

In order to make the reading of this thesis as accessible as possible, the research presented has been grouped into four major themes, namely: Obtaining and characterizing organic compounds with the role of ligands (section B.1.1), Coordination polymers and metal-organic frameworks (section B.1.2), Metal complexes (section B.1.3) and Surface modification of zinc oxide nanoparticles with organic agents (section B.1.4).

Section B.1.1 is dedicated to the presentation of the results regarding the synthesis, by classical methods and non-conventional methods belonging to green chemistry, of some organic compounds with the role of ligands for the construction of new coordination systems with diversified crystalline structures and functional properties. Among the ligands thus obtained are mentioned rigid and flexible polydentate azole ligands, azolyl-carboxylate type ligands, poly(pyrazolyl)borate or scorpionate ligands, as well as N-heterocyclic diquaternary salts.

Section B1.2 is dedicated to presenting the results regarding the synthesis of new classes of coordination polymers and metal-organic frameworks based on polydentate azole ligands and azolyl-carboxylated ligands with various transition metal ions, highlighting the variation of the structural typologies of these compounds depending on the nature of the ligands, the stereochemical preferences of the metal ions and the synthesis parameters used. For certain

categories of coordinated polymers and metal-organic frameworks, studies of the thermal behavior by thermogravimetric and thermodiffractometric analysis are also presented, as well as interesting studies on the microporous, solid-state photoluminescence, catalytic, and antibacterial properties in the case of silver coordination polymers.

Section B.1.3 presents privileged results on the synthesis, characterization and studies of the functional properties of various classes of metal complexes, such as scorpionate complexes with antioxidant activity, copper(I) thiocyanate complexes with nitrogen- and phosphorus-donor aromatic ligands with photoluminescent properties, polymeric copper(II) complex with pyridine ligand explored as voltammetric sensor for electrochemical detection of catechol, but also a series of dinuclear and polymeric lanthanide complexes with dipyridinium ylide type ligand for antitumor activity.

Section B.1.4 is dedicated to studies on the modification of the surface of zinc oxide nanoparticles with agents of the organosilane class, whose use in increasing concentrations leads to obtaining nanoparticles with very small sizes, even at the level of quantum dots (below 5 nm), simultaneously with the increase of photoemission intensities in the visible range and an inverse variation of the bandgap energy values. In certain samples of zinc oxide nanoparticles modified with organosilanes, remarkable antibacterial and antitumor activities, dependent on their size, are highlighted. The catalytic effect of zinc oxide nanoparticles on the transformation of non-fluorescent diquaternary pyridinium salts into new fluorescent organic species was also highlighted.

The second part of this thesis (section B.2) presents the professional career development plan from both a scientific and didactic perspective, as well as the modes of action for the successful fulfillment of the proposed objectives. On a scientific level, three major research directions are presented and described, namely *the Exploration of organic compounds with multiple coordination abilities*, *Multivariate coordination systems* and *Modification of ZnO nanoparticles*, with the indication and description of the objectives related to each research direction.

Section C includes a number of 241 bibliographic references, which include 20 of the personal works cited in support of the presentation of the results of scientific research within this thesis, references that were used for the purpose of documentation, as well as to comment on my research in those reported by other authors working in the same branches of coordination chemistry and nanochemistry.