Abstract

The Habilitation thesis entitled *Cyanido-based molecular materials* covers the main research and academic achievements following the PhD thesis defended in 2009, Order of the Ministry of Education, Research and Innovation No. 6026 /27.11.2009.

The habilitation thesis is divided in two Parts:

Part I: RESEARCH AND ACADEMIC ACTIVITY
Part II: MAIN SCIENTIFIC RESULTS

Part I presents, chronologically, the most relevant academic and scientific achievements. Since I started as a teaching assistant at the University Politehnica of Bucharest, in 2009, my academic accomplishments were related to:
- supervising students in their scientific work (diploma or master thesis)
- teaching courses (among the most relevant, the Inorganic Chemistry and Transition Metals Chemistry courses)
- the scientific events organized by the Faculty of Chemical Engineering and Biotechnologies, such as "Communication Session for Students", "Costin D. Neniţescu" national contest for high school students, and "Petru Spacu" contest for 1st and 2nd year students.

Regarding the scientific achievements which I referred to in **Part II**, the first relevant results were obtained during the two Postdoctoral stages (between 2010 - 2013 and 2013 - 2015) that I had the opportunity to carry out at the University of Bucharest under the supervision of Acad. Marius Andruh. Also, since 2012, I have been on several research stages at the University of Valencia and Sorbonne University, where I had the chance to work with Prof. Miguel Julve and Prof. Rodrigue Lescouëzec, most of the obtained data being published and included in this habilitation thesis. Some of the results were milestones for our research in the field of molecular magnetism. In the following, I will point out a series of accomplishments which were, at the time of their publication, rare examples of types of compounds with structures having interesting magnetic properties.

Part II describes significant results for molecular magnetism (**Chapter 1**) and fluorescence/luminescence (**Chapter 2**) domains which are covered by this Habilitation thesis. **Part II** also contains the Perspectives (**Chapter 3**) of the research activity I will pursue.

Chapter 1, entitled *Cyanido-based molecular magnetic materials*, is the most consistent of all three, and belongs to the molecular magnetism field. This chapter is structured in two parts: *Cyanido-based molecular nanomagnets* (1.1), and *Spin crossover cyanido molecules* (1.2). In (1.1), a series of five new $Co^{II/III}$ building-blocks: $\{Co^{III}(AA)(CN)_4\}$, $\{Co^{III}_2(\mu\text{-}2,5\text{-dpp})(CN)_8\}$, and $\{Co^{II}(dmphen)(CN)_3\}$ are presented, where AA = ethylenediamine, 2-(aminomethyl)pyridine, 4,4'-dmbipy = 4,4'-dimethyl-2,2'-bipyridine, and phen = 1,10-phenanthroline; 2,5-dpp = 2,5-*bis*(2-pyridyl)pyrazine, and dmphen = 2,9-dimethyl-1,10-phenanthroline. Based on these tectons, six coordination polymers assembled from diamagnetic spacers connecting Single-ion magnets (SIM) were obtained:

- three coordination polymers (CP) of Mn^{III} SIMs:
  - 1-D **$\{Co^{III}(dmbipy)Mn^{III}\}$**, $\{[Mn^{III}(salen)(\mu NC)_2Co^{III}(4,4'\text{-dmbipy})(CN)_2]\cdot H_2O\}_n$
  - 1-D **$\{Co^{III}(dmphen)Mn^{III}\}$**, $\{[Mn^{III}(salen)(\mu NC)_2Co^{III}(dmphen)(CN)_2]\}_n$
  - 2-D **$\{Co_2^{III}Mn^{III}salen\}$**, $[\{Mn^{III}(salen)\}_2\{(\mu\text{-}NC)_4Co_2^{III}(\mu\text{-}2,5\text{-dpp})(CN)_4\}]_n$.

- three monodimensional coordination polymers of Co^{II} SIMs:
  - **$\{Co^{III}(dmphen)Co^{II}\}$**, $\{[Co^{II}(CH_3OH)_2][(\mu\text{-}NC)_2Co^{III}(dmphen)(CN)_2]_2\}_n\cdot 2nH_2O$
  - **$\{Co^{III}_2dppCo^{II}\}$**, $[Co^{II}(CH_3OH)_2(DMSO)_2(\mu\text{-}NC)_2Co_2^{III}(\mu\text{-}2,5\text{-dpp})(CN)_6]_n\cdot 4nCH_3OH$
  - **$\{Co^{III}_2dppCo^{II}bik\}$**, $[Co^{II}(bik)(H_2O)(DMSO)(\mu\text{-}NC)_2Co_2^{III}(\mu\text{-}2,5\text{-dpp})(CN)_6]_n\cdot 1.4nH_2O$.

[H_2salen = N,N'-ethylenebis(salicylimine; DMSO = dimethylsulfoxide; bik = *bis*(1-methylimidazol-2-yl)ketone].

The SIM fragments consists of complex cations of Co^{II} and Mn^{III} ions, their anisotropy being the origin of the slow relaxation of the magnetization.

I have also included in Part (1.1) one ferrimagnetic chain: **$\{Co^{II}Mn^{III}\}$**, $\{[Mn^{III}(salen)(\mu\text{-}NC)_2Co^{II}(dmphen)(CN)]\cdot 2H_2O\}_n$, comprising high-spin $[Mn^{III}(salen)(H_2O)]^+$ nodes and low-spin $[Co^{II}(dmphen)(CN)_3]^-$ spacers. This was *the first* published example of magnetic coupling between the Mn^{III} and low-spin Co^{II} ions through a cyanido bridge.

In part (1.2), *Spin crossover cyanido molecules*, a series of six compounds constructed from diamagnetic cyanido metalloligands and $[Fe(tptz)]^{2+}$ moieties is described. Four of them (two double chains and two complex cation-complex anion compounds) are assembled using the $[M^{II}(CN)_4]^{2-}$ metalloligands and the $[Fe(tptz)]^{2+}$ complex cations, where M = Pd and Pt; tptz = 2,4,6-tri(2-pyridyl)-1,3,5-triazine)):

- 1-D **$\{Fe^{II}Pd^{II}\}_n$** and **$\{Fe^{II}Pt^{II}\}_n$**, $\{[Fe^{II}(tptz)(\mu\text{-}CN)_3M^{II}(CN)]\cdot 2H_2O\cdot CH_3CN\}_n$
- 0-D **$[Fe^{II}Pd^{II}]$** and **$[Fe^{II}Pt^{II}]$**, $[Fe^{II}(tptz)_2][M^{II}(CN)_4]\cdot 4.25H_2O$

The double chains are constructed from the $[M^{II}(CN)_4]^{2-}$ spacers connecting the $[Fe(tptz)]^{2+}$ nodes, while the ionic salts are formed from the $[M^{II}(CN)_4]^{2-}$ and $[Fe(tptz)]^{2+}$ complex ions.

The other two compounds, one being a trinuclear complex and the other, a complex cation-complex anion compound, are built from the $[Au(CN)_2]^-$ building-blocks and $[Fe(tptz)]^{2+}$ units:

- 0-D **$\{Fe^{II}tptzAu_2^{I}\}$**, $\{Fe^{II}(tptz)(H_2O)[(\mu\text{-}CN)Au^{I}(CN)]_2\}$
- 0-D **$[Fe^{II}tptz][2Au^{I}]$**, $[Fe^{II}(tptz)_2][Au^{I}(CN)_2]_2\cdot 5H_2O$

The double chains, **$\{Fe^{II}Pd^{II}\}_n$** and **$\{Fe^{II}Pt^{II}\}_n$**, undergo an incomplete SCO transition, while the ionic salts analogues, **$[Fe^{II}Pd^{II}]$** and **$[Fe^{II}Pt^{II}]$**, are diamagnetic in the 2-400 K temperature range. The trinuclear complex, **$\{Fe^{II}tptzAu_2^{I}\}$**, is high-spin in the temperature range, while the corresponding ionic salt is of low-spin between 2-300 K.

Chapter 2 outlines the results on *cyanido-based emissive molecular materials*. In the first subchapter, three complexes of Ag(I) and one heteronuclear Ag(I)Zn(II) which exhibit ligand-centered fluorescence are discussed:

- two 3-D coordination polymers of Ag(I) with TPymT ligand, **$[Ag_4(TPymT)(CN)_4]_n$**, and **$[Ag_5(TPymT)(CN)_5]_n$**; TPymT = 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine
- a trinuclear heterobimetallic $\{Ag^{I}Zn^{II}\}$ discrete molecule with tptz ligand, **$[Zn(tptz)(H_2O)][(\mu\text{-}CN)Ag(CN)]_2$**; tptz =2,4,6-tri(2-pyridyl)-1,3,5-triazine
- a 3-D network of Ag(I), **$[Ag_6(CN)_6(TPymT)_2]_n$**.

The second subchapter (2.2) is devoted to the use of organic ligands and cyanido metalloligands as *antenna* for stimulating the luminescence of the Ln^{III} ions. The examples of complexes with organic ligands as *antenna* which were discussed are:

- the discrete mononuclear complex: **$Tb(tptz)(NO_3)_3(H_2O)$**
- a series of Ln(III) complexes with dppn ligands with three different structures: **$[Ln(dppn)(NO_3)_3(H_2O)_2]\cdot CH_3CN$**, Ln^{III} = Nd, Sm, Eu and Gd; **$[Ln(dppn)_2(NO_3)_3]\cdot H_2O$**, Ln^{III} = Tb, Dy; and **$[Ln(dppn)_2(NO_3)_3]\cdot CH_3CN$**, Ln^{III} = Ho, Er; dppn = 3,6-di(2-pyridyl)pyridazine.

Having cyanido metalloligands as *antenna*, the heterometallic trinuclear, **$[Ln(DMSO)_6(H_2O)(\mu\text{-}NC)Co_2^{III}(\mu\text{-}2,5\text{-}dpp)(CN)_7]\cdot 2MeCN\cdot 3H_2O$** complexes are described (Ln^{III} = Gd, Tb, and Dy; DMSO = dimethylsulfoxide; 2,5-dpp = 2,5-*bis*(2-pyridyl)pyrazine].

In **Chapter 3**, the professional development plans are summarized. These perspectives are based on convincing preliminary results. The following research subjects will be explored:

- *Luminescent Single-ion and Single-molecule magnets*. Having in mind the new Co^{III} cyanido complexes itemized in **Chapter 1**, which are suitable as metalloligands towards Ln^{III} ions, a series of emissive nanomagnets can be synthesized. Also, other diamagnetic metalloligands, such as tetracyanopalladate/platinate(II) are envisaged to be employed
- *Spin crossover cyanido-based complexes*. The diamagnetic metalloligands mentioned previously, and other low-spin cyanido complexes of Fe^{II}, Co^{III} or Ag^{I} will be used against Fe^{II} complexes to form coordination polymers of spin crossover Fe^{II} units
- *Nanostructured materials obtained from cyanido complexes* through soft chemistry approaches, such as hydrothermal synthesis, by using cyanide complexes as precursors, which usually afford oxide-based products.