CHAPTER V
SUMMARY

This final chapter is divided in two parts. In the first part the main conclusions drawn from the work described in chapters 2, 3 and 4 are summarized. The aim of present work, as described in section 1.7, is discussed. In the second part some considerations dealing with the perspectives and possible applications of the obtained results are given.

5.1 Summary of the Research Described

This thesis describes research in the field of porous coordination polymers. Two series of coordination polymers with 4,4'-bipyridine and monocarboxylato ligands have been studied. The first series of coordination polymers deals with zinc(II)-**4,4'-bpy**-carboxylato polymers and their applications, whereas the second series of coordination polymers deals with copper(II)-**4,4'-bpy**-carboxylato polymers and their applications.

The aim of this research was to gain more insight into design and synthesis of metal organic frameworks assembled from the combination of **4,4'-bpy** and monocarboxylate-regulator as a bridge, and transition metal ions and to investigate the influence of the monocarboxylato ligands on the overall solid-state structure of coordination polymers. Their properties and functions have been investigated in detail.

A general introduction is given in Chapter 1. The first part of the introduction describes the general coordination polymers with stable pores which were first classified in the three categories, 1st, 2nd and 3rd generation. The 1st generation compounds have microporous frameworks, which are sustained only with guest molecules and show irreversible framework collapse upon removal of the guest molecules. The 2nd generation compounds have stable and robust porous frameworks, which show permanent porosity without any guest molecules in the pores. The 3rd generation compounds have flexible and dynamic frameworks, which may respond to external stimuli, such as light, electric field, guest molecules, and may change their channels or pores reversibly (Figure 1.15). The principles in synthesis and the type of porous structures are described. The functions and properties of coordination polymers have attracted the attention of chemists, physicists, and material scientists, because of their potential applications in industry, such as separation, heterogeneous catalysis, ion-exchange and gas storage.

Synthetic procedures and characterizations of two series of metal organic frameworks are given in Chapter 2. Eleven zinc(II)-**4,4’-bpy**-carboxylato coordination polymers, namely {[Zn$_3$(**4,4’-bpy**)$_{3.5}$(μ-OOCH)$_4$(H$_2$O)$_2$](X)$_2$}$_n$ when X = ClO$_4^-$•H$_2$O (**1**), PF$_6^-$ (**2**), BF$_4^-$•H$_2$O (**3**), {[Zn(**4,4’-bpy**)(*μ*-OOCH)(H$_2$O)$_2$] (CF$_3$SO$_3$)(H$_2$O)}$_n$ (**4**), {[Zn$_4$(**4,4’-bpy**)$_4$(*μ*-OOCH)$_5$(H$_2$O)$_5$](NO$_3$)$_3$(**4,4’-bpy**)$_2$(H$_2$O)$_3$}$_n$ (**5**), {[Zn$_3$(**4,4’-bpy**)$_3$(μ-OOCCH$_3$)$_4$(H$_2$O)$_2$](PF$_6$)$_2$(H$_2$O)$_2$}$_n$ (**6**), {[Zn$_3$(**4,4’-bpy**)$_4$(μ-OOCCH$_2$CH$_3$)$_4$](ClO$_4$)$_2$(**4,4’-bpy**)$_2$(H$_2$O)$_4$}$_n$ (**7**), {[Zn$_3$(**4,4’-bpy**)$_4$(*μ*-OOCC$_2$H$_5$)$_4$ (H$_2$O)$_2$](PF$_6$)$_2$(H$_2$O)$_2$}$_n$ (**8**), {[Zn$_2$(**4,4’-bpy**)$_2$(*μ*-OOCC$_2$H$_5$)$_2$(OH)(H$_2$O)](BF$_4$) (H$_2$O)$_2$}$_n$ (**9**), {[Zn$_2$(**4,4’-bpy**)$_2$(μ-OOCC$_2$H$_5$)$_2$(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$}$_n$ (**10**) {[Zn$_3$(**4,4’-bpy**)$_4$(μ-OOCC$_2$H$_5$)$_4$(H$_2$O))$_2$](NO$_3$)$_2$(H$_2$O)$_3$}$_n$ (**11**) and nine cooper(II)-**4,4’-bpy**-carboxylato coordination polymers {[Cu$_3$(**4,4’-bpy**)$_2$(*μ*-OOCH)$_4$(H$_2$O)$_2$](X)$_2$ (H$_2$O)$_6$}$_n$ when X = ClO$_4^-$ (**12**), PF$_6^-$ (**13**), BF$_4^-$ (**14**), CF$_3$SO$_3^-$ (**15**), {[Cu(**4,4’-bpy**)(*μ*-OOCH) (NO$_3$)]}$_n$ (**16**), {[Cu$_2$(**4,4’-bpy**)$_2$(*μ*-OOCCH$_3$)$_3$](X)(H$_2$O)}$_n$ when X = ClO$_4^-$ (**17**), PF$_6^-$ (**18**), BF$_4^-$ (**19**), CF$_3$SO$_3^-$ (**20**) are obtained and have been crystallographically characterized.

The X-ray structures of a series of zinc(II)-**4,4’-bpy**-carboxylato compounds are described in Chapter 3. Three representative porous coordination polymers, *i.e.* the three-dimensional framework, {[Zn$_3$(**4,4’-bpy**)$_{3.5}$(μ-OOCH)$_4$(H$_2$O)$_2$](ClO$_4$)$_2$(H$_2$O)$_2$}$_n$ (**1**), the one-dimensional three-leg ladder {[Zn$_3$(**4,4’-bpy**)$_3$(μ-OOCCH$_3$)$_4$(H$_2$O)$_2$] (PF$_6$)$_2$(H$_2$O)$_2$}$_n$ (**6**), and the two-dimensional layered network {[Zn$_3$(**4,4’-bpy**)$_4$ (μ-OOCCH$_2$CH$_3$)$_4$](ClO$_4$)$_2$(**4,4’-bpy**)$_2$(H$_2$O)$_4$}$_n$ (**7**) are structurally described in full detail and compared with those of the remaining compounds (**2-5**, **8-11**) and other relevant coordination polymers. The influence of small secondary ligands, namely anionic formato (**1-5**), acetate (**6**) and propionato ligands (**7-11**), on the overall solid-state structure of zinc(II)–**4,4-bpy**–carboxylato coordination polymers has been investigated. The combination of Zn(II), **4,4’-bpy** and formate generates an intricate 3D framework for **1**. The sole replacement of formate by acetate results in the formation of a 1D network for **6**. This simple framework is built from trinuclear acetato-bridged units that are linked to two adjacent ones, to form a three-leg ladder. The use of propionate as co-ligand, however, yields a 2D network for **7** which presents similarities with the structure of **6**. These three-leg ladders are connected to each other via **4,4'-bpy** ligands, thereby generating 2D layers.

This study shows that the change from a formato ligand to an acetato and a propionato ligand gives rise to the formation of drastically distinct metal-organic frameworks, apparently as the result of the different steric bulk of the used carboxylato unit. Such studies are of great interest for the crystal engineering chemist and this field is likely to contribute to a further increase of knowledge about crystallization processes and framework design and structure prediction.

The thermal and optical properties, potential cation-exchange properties with structure retention by doping zinc(II) compounds with copper(II) and manganese(II), anion-exchange and catalytic reactivity, as well as dynamic structural transformation by removal and reintroduction of guest molecules for eleven novel coordination polymers, belonging to the second generation of porous coordination compounds have been investigated. The removal/reintroduction of water guest molecules is accompanied by a crystalline-to-crystalline structural transformation for compounds **6-11**, which exhibits rigid vacant host channels. Furthermore, compound **1** shows quite interesting anion-sensing properties in an aqueous solution exhibiting reversible processes. Interestingly, these zinc(II) compounds are effective heterogeneous catalysts for the high-yield cyanosilylation of acetaldehyde in dichloromethane. Moreover, the MOF catalysts show size-selective behavior, since acetaldehyde is efficiently converted, whereas the conversion of benzaldehyde is significantly slower.

Chapter 4 describes the structures of two representative porous coordination polymers in a series of copper(II)-**4,4'-bpy**-carboxylato compounds, namely, the two-dimensional layered networks $\{[Cu_3(\mathbf{4,4'\text{-}bpy})_3(\mu\text{-}OOCH)_4(H_2O)_2](ClO_4)_2(H_2O)_6\}_n$ **(12)** and $\{[Cu_2(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCCH_3)_3](PF_6)(H_2O)\}_n$ **(18)**. They are structurally compared with those of the remaining compounds (**14** and **16**) and other relevant coordination polymers from the literature. The crystals of $\{[Cu_3(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCH)_4(H_2O)_2](X)_2\ (H_2O)_6\}_n$ when X = PF_6^- **(13)**, $CF_3SO_3^-$ **(15)**, and $\{[Cu_2(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCCH_3)_3]\ (X)(H_2O)\}_n$ when X = ClO_4^- **(17)**, BF_4^- **(19)**, $CF_3SO_3^-$ **(20)**

appeared unsuitable for X-ray structure analysis, thus the structures of these compounds have been proposed by elemental microanalyses, spectroscopic properties and XRPD pattern. They have been found to be isostructural to compounds **12** and **14** (for **13** and **15**) and compound **18** (for **17**, **19** and **20**). The steric effect on the architecture has been investigated by using a slightly different monocarboxylato anions, namely formato and acetato moieties as secondary co-ligands of [Cu(II)/**4,4'-bpy**] coordination units, applying the same reaction conditions.

The structures lead to the formation of distinct structural motifs. The combination of Cu(II), **4,4'-bpy** and formate generates a triple-stranded 2D frameworks for **12-15**. Replacing formate with acetate, the structure packing and environment were found to be transformed to the formation of 2D networks for **17-20**, containing tetranuclear acetato-bridged units that are linked to two adjacent ones, to form quadruple-stranded layers. This study clearly indicates that the carboxylate-regulator can play an important role in construction of coordination frameworks. The thermal stability of the corresponding open frameworks and the dynamic structural transformation have been investigated. Unfortunately, the dynamic structural transformation behavior for all Cu(II)–**4,4-bpy**–carboxylato compounds cannot be achieved after re-immersing in water. In addition, compounds **12** and **18** are explosive when elevating at high temperature and this similar behavior is expected for other corresponding compounds.

This chapter also describes the anion-exchange studies for eight copper(II) coordination polymers (**12-15** and **17-20**). Interestingly, the anion-exchange behavior is highly selective, the anions in the original compounds can be completely replaced with different counteranions. However, the exchange of all products appears not reversible. This finding may provide a basic concept for an anion-exchange based on spectroscopic properties, and implies that the combination of **4,4'-bpy**-bridge and the monocarboxylate-regulator is suitable for the construction of new metal organic frameworks.

Furthermore, the catalytic reactivity of all copper(II)-**4,4'-bpy**-carboxylato compounds (**12-20**) have been investigated and found that some of copper(II) compounds are effective heterogeneous catalysts. It is noted that the catalytic reactivities of compounds **17-20** in THF are higher than other compounds, probably as a result of the higher Lewis acidicity of the metal center in these cases. The copper(II) centers of **17-20**, which have no donating H_2O ligands, are more cationic than other compounds, so their Lewis acidity increases leading to the more effective binding of the substrate and give a high conversion for THF. The cationic nature and Lewis acidity of the Cu^{2+} center may play a key role and lead to significantly different in the conversion. However, as compared with a series of zinc(II) catalysts, the copper(II) center is less cationic and less Lewis acidic than the zinc(II) center, explaining the reduced conversion for all reaction conditions.

Chapter 5 summarizes the research described in this thesis and presents an outlook to the future. Parts of this thesis have been published or submitted for publication.[70,71]

5.2 Perspectives

5.2.1 Introduction

To develop the chemistry and physics of confined molecules and atoms in the low-dimensional nanospace, the precise controlling and tuning of the pore size, shape, and periodicity of a unit are of great importance. For such a study, possible candidates are mesoporous silicas (for mesopores) and coordination polymers (for micropores). For di- and tri-atomic molecules, microporous compounds are the most relevant, because their frames are well suited for trapping and arranging such molecules in a channel. In particular coordination polymers can play an important role in the "gas molecule-accumulation science" of gases, such as H_2, O_2, CO, NO, CO_2, and CH_4, which are associated with important environmental and energy issues.

A great number of coordination polymers have been reported (see Figure 1.1). The data on these compounds should be categorized into 1) structure and 2) function. In addition to these functions, form (shape, and size of crystals) needs to be considered. The following subchapters describe categories for future porous coordination polymers:

5.2.2. Cooperative properties with functional framework and guest molecules

Actually, porous coordination polymers, whatever their structural demonsionality, possess two inherent characteristics; a porous framework and a guest molecule. Not only the properties of functional guests, but also those of porous frameworks (nonlinear optical properties, conductivity, magnetism, spincrossover, chromism, and fluorescent properties) have been hitherto, independently, studied. Several examples of properties that framework functionalities change by inclusion and removal of guest molecules, which induce the change of the environment of metal centers, are also known. In these systems, guest molecules have no function in themselves. The next step is to study their cooperative properties[116] i.e. with functional frameworks and guest molecules. In a restricted micropore, unprecedented cooperative properties are to be expected. They are so-called third generation compounds.[1]

5.2.3. Low-dimensional form-thin layer compounds

Researchers control the size, shape, and distribution of pores and will establish this engineering in the near future. However, even when they have nanosized channels or cavities, compounds are at least μm-sized microcrystals, insoluble in any solvents, and therefore are hard to prepare in a thin layer form. Because of this, new methods to prepare a 2D sample are to be developed.

5.2.4. Mesoscale compounds

The next challenge in this field is the use at the mesoscale, with the aim of closing the gap between so-called top-down and bottom up approaches to materials assembly. The ultimate goal is the ability to control the arrangement of channels, which means the formation of porous modules for various nanodevices. In order to do so, small nanocrystals are required, which can act as wells, wires, rods, and dots.[117]

5.2.5. Introduction of anisotropy

The resolution of chiral frameworks for enantioselective sorption and asymmetric heterogeneous catalysis remains challenging and is a mainly unexplored area. The use of chiral template molecules or the employment of enantiomerically pure organic linkers is one of the options for the preparation of the functional chiral frameworks.[46]

5.2.6. Redox frameworks

Another exciting and so far undeveloped area is the systematic design and synthesis of redox-active porous frameworks, i.e. oxidation and reduction of the overall framework to be performed by the guest molecules, but without overall decomposition of the network. If a neutral open framework could be oxidized, it would include free counter anions in the channels or pores, and then it might be applied for anion-exchange materials and also will affect the other properties, such as magnetism, etc.[118]

The interesting point of future based on this work is to explore the catalytic properties of metal-organic frameworks. From the structural and esthetical point of view, MOFs are engineered by linking cluster building blocks at their coordination sites via multifunctional linkers into perfect and esthetic architectures, the topology being pre-defined by the arrangement of the coordination sites and the orientation and number of the binding groups in the linker. However, an aspect often overlooked is that connecting the coordination sites to the linker may also blocks such sites for catalytic transformations. A change in coordination geometry is often required for dissociation-association mechanisms that are responsible for the high catalytic activity of molecular transition metal complexes in organometallic chemistry.

Another suggestion for future research aims as the porous coordination polymers have the potential to be applied in heterogeneous catalysis, ion exchange and molecule adsorption etc. This development arises from the advent of thermally stable and robust open frameworks in the absence of guest molecules. In practice, robust porous frameworks can be formed from the three-dimensional linkages of coordination bonds or interdigitation of two-dimensional networks of coordination bonds. They are further evolving applying a kind of zeolite mimicry to the creation of new functions characteristic of molecularly inorganic-organic hybrid compounds.

Based on these achievements, there are two approaches to creating new porous functions in coordination polymers. One is to prepare functional pores with a chemical affinity, this is related to a new class of open-framework solids with the goal of being able to carry out shape- and size-selective chemical reactions within the pores of a microporous solid. In the other approach the pores are dynamic ones that respond to chemical and/or physical stimuli. These properties could come from the capability of the structure to regenerate and recover following collapse by the removal of the guest molecules. This sort of compound has the potential for specific selective guest binding by the cooperative effect of physical size, shape, and chemical functionality. Dynamic structural transformation based on flexible porous frameworks form one of the most interesting phenomena in coordination polymers, like new generation compounds, coupled to novel porous functions.