Chapter I

Introduction

Metal-organic frameworks (MOFs) are a recently identified class of porous polymeric materials, consisting of metal ions linked together by organic bridging ligands, and are a new development on the interface between molecular coordination chemistry and materials science. Over the past fifty years, research into porous materials has resulted in a number of applications, which have had a direct impact on domestic life and large scale industrial processes.\(^1\) The establishment of porosity in these polymeric metal-organic structures has been a challenging field since, by analogy with zeolites it opens up possibilities for new chemical separations, ion exchange, sensing and storage behavior. The porosity of these materials allows guest molecules to diffuse into the bulk structure, and the shape and size of the pores leads to shape- and size-selectivity over the guests which may be incorporated or diffused through. Since the early 1990s, research into materials with polymeric, sometimes porous, structures based on metal ions and organic bridging ligands like polycarboxylates has increased greatly.\(^2\)\(^-\)\(^10\) Compared with conventional porous materials such as zeolites or activated carbons, the MOFs have a higher potential because of designable framework, high micro-porosity, and flexible framework based on a variety of coordination geometries of metal centers and multi-functionality of bridging organic parts.\(^11\)
Porous coordination materials can be divided into three categories: First generation porous materials contain cavities and channels but these structures lose their crystalline nature after removal of the guest molecules and are not useful for the required applications. Second-generation MOFs remain crystalline and stable, as they are totally desolvated. Third generation MOFs are dynamic and flexible ones which respond to external stimuli in changing their structures. The transformations during the removal of the guest molecules is regarded as a “crystal to amorphous transformation” in first generation metal organic frame works, where as the transformations in the two other cases are named “crystal-to-crystal” ones. In Fig. 1.1 is given the crystal structures of two typical MOFs.\textsuperscript{12,13}

![Fig. 1.1](image)

\textbf{Fig. 1.1} (a) Crystal structure of $\left[\text{Zn}_3(\text{OH})_2(\text{bpdc})_2\right]2\text{H}_2\text{O}$ (bpdc: 4,4-biphenyldicarboxylate) consisting of a 3D network with large channels and (b) a MOF consisting of copper(II) terephthalate-pyridine.

The MOFs have to be highly crystalline and porous, but it is well known that free space is against nature in crystals. When cavities appear
in these frameworks, they are filled either by interpenetration or by counter ions, solvents molecules or additional co-crystallizing organic molecules (Fig. 1.2). These latter molecules can be regarded as templates determining the pore shapes and sizes. Particular emphasis has been placed on the use of organic structure-directing agents (SDAs), the original purpose of which was to act as a ‘template’ around which a new framework may form in well directed pattern, with subsequent thermal or chemical removal of the template producing a genuinely ‘micro-porous’ material, for future guest incorporation. However, in a much wider sense the use of an SDA for purpose other than templating is a field which has not been explored greatly. The presence of the SDA will most often lead to framework topologies which would otherwise be inaccessible without the SDA, or with an SDA of a different size, shape or chemical nature. It is clear that judicious use of the SDA may eventually lead to the rational design of new framework topologies which may have tailored connectivities between appropriate ‘active’ framework sites to give specific physical or chemical properties. The guest ion is often associated with organic molecules or other ions, such as water, unidentate aliphatic amines, ambidentate $\alpha,\omega$-diaminoalkanes, aromatic amines, pyrazine or piperazine. These compounds are necessary to fill up the void space for stabilizing the crystal structure.
1.1 Metal organic coordination networks (MOCNs)

While MOFs are generally porous materials there are innumerable number of coordination polymers which do not have functional porosity. Such coordination polymers are generally known as metal organic coordination networks (MOCNs). The term MOCN is used widely to describe any extended structure based on metals and organic bridging ligands. The process of building a coordination polymer is principally directed by the coordination bond. Energy of such interactions is usually evaluated to be at around 50kJ mol$^{-1}$. Weaker interactions such as hydrogen bonds and $\pi-\pi$ interactions also strongly influence the formation of coordination polymers. The H…A distance should be in the range 1.5-2.2 Å for strong O-H…O/N hydrogen bonds (with D-H…A angles in the range of 140-180°) and 2-3 Å for weak C-H…O/N contacts. Energy of such interactions varies from 15 to 40kJ mol$^{-1}$ for moderate hydrogen bonds. Sometimes $\pi-\pi$ interactions can also be of prominent importance during the coordination polymer formation. Janiak reviews this kind of interactions in metal complexes with aromatic nitrogen containing...
Aromatic-aromatic interactions involve face-to-face alignment. These interactions are based on the sum of several contributions (electrostatic, vander Waals interactions, repulsive and charge transfer), and the aromatic rings preferentially stack in an optimal way to minimize all the repulsive interaction components and maximize attraction. For face-to-face interactions, the centroid-centroid distance is found between 3.4 and 3.8 Å. The energy of π-π interactions is estimated at 5-10kJ mol⁻¹.

With the rapid development of supra-molecular chemistry of metal complexes, a large number of supra-molecular coordination compounds have been constructed by coordination molecules which consist of metal ions functioning as nodes and organic ligands as bridges, through coordination bonding, hydrogen bonding, π-π stacking interactions as well as vander Waals forces and exhibit a wide range of infinite 0D, 1D, 2D or 3D frameworks with different interesting structural features (see Scheme 1.1). On the other hand, many coordination supra-molecular structures based on metal-organic ligands, in fact, have been designed for purely symmetry and aesthetic grounds. The intense interest in this field, given impetus by synthetic and theoretical chemists, crystallographers and materials scientists has resulted not only in beautiful and diversified structures, but also in potential applications as electronic, magnetic, optical, absorbent and catalytic materials. For the chemist, polymeric coordination networks synthesis could be considered as “construction games”: the final architecture depends on the building modules (metal centres, the counter ions, solvent molecules and organic ligands) and their compatibilities.
1.1.1 Building Modules of MOCNs

The main building units of MOCNs are metals, solvent molecules, counter ions and organic ligands. The use of metal ions in coordination polymers offers several possible advantages over purely organic chains, grids or frameworks which are organized by non-covalent interactions. Metal-ligand bonds have more directionality than other weak interactions. An attractive feature of metal atoms is the availability of orthogonal (90°) angles for the construction of polymeric architectures. Appropriate stopper ligands can restrict the number of metal coordination sites less than the usual four or six. Together with a difference in size, hardness/softness, ligand-field stabilization energy and various coordination geometries metal ions can opt (octahedral, tetrahedral, square planar, linear, trigonal-planar, T-shaped, square pyramidal, trigonal prismatic, trigonal-bipyramidal etc.) they provide a wide range of construction possibilities. Transition metals are most widely used: choosing one or another metal means choosing the coordination geometry, i.e. the node shape, as well as choosing the potentially required
properties of the future materials. Counter ions are present in the structure when neutral ligands are used. They can not only influence the metal ion environment but also the overall structure, even by involving in weak interactions.

*Solvent molecules* may co-crystallise, increasing the number of possible weak interactions in the final solid state packing, and can also act as guest molecules in the vacant space between the polymers construct. They may play a crucial role when it comes to the construction of highly porous materials. As nature usually avoids large empty spaces, solvent molecules may come in the first synthetic step itself as space fillers which can be removed once the final network is formed and stabilized in the solid state.

The *organic ligands* used in the construction of coordination polymers have to bridge between metal ions. This requires usually multi-dentate ligands which are called di-, tri-, tetra topic depending on the number of donor atoms. Another structure determining factor is the “body” of the organic ligands, their shapes (rigid or not), their lengths and their functionalities. Generally N, O and S donor ligands feature prominently in the construction of coordination polymers. Finally, the ligand molecules can be symmetric, chiral or not, i.e.; combining different functionalities on the same molecule. It is the bridging organic ligand, which allows further large diversity in topologies and possible properties of metal organic co-ordination net works. Some of the commonly used N-and O-donor ligands are given below.
Aliphatic mono and diamines:

- methylamine
- ethylamine
- n-butylamine
- 1,2-diaminoethane
- 1,3-diaminopropane
- 1,4-diaminobutane
- 1,6-diaminohexane

Pyridine type ligands:

- pyridine
- 3-picoline
- 4-picoline
- 4,4’-bipyridine
- 2,2’-bipyridine
- 1,10-phenanthroline
- imidazole
- 1,4-diaza-cyclo(2.2.2)octane
- pyrazine

Aliphatic saturated α,ω-dicarboxylic acids:

- oxalic acid
- malonic acid
- succinic acid
- glutaric acid
Introduction

Adipic acid

Pimelic acid

Suberic acid

Azelic acid

Sebacic acid

**Aliphatic unsaturated α,ω-dicarboxylic acids:**

Maleic acid

Fumaric acid

Muconic acid

Tamaric acid

Tecic acid
Benzene di-, tri and polycarboxylic acids:

- phthalic acid
- isophthalic acid
- terephthalic acid
- trimesic acid
- pyromellitic Acid
- mellitic acid

1.1.2 Carboxylates as linkers in MOCN

Ligands of the carboxylate family are among the most widely used O-donor bridging ligands for designing poly-nuclear complexes having interesting properties. Over the past decades, enormous efforts have been dedicated to the rational design of supra-molecular polymeric architectures, and exploitation of carboxylate anions as linkers is of growing interest in construction of supra-molecular systems. The versatility of carboxylates as ligands is illustrated by the variety of coordination modes they display while acting as bridges. There are many bridging modes available to carboxylic acid complexes and some of these are illustrated below (see Fig. 1.3).
Monocarboxylate

\[
\begin{align*}
\text{unidentate} & \quad \text{chelate} & \quad \text{syn-syn} & \quad \text{anti-anti} & \quad \text{anti-syn}
\end{align*}
\]

Dicarboxylate

\[
\begin{align*}
\mu_2\eta^3\text{-chelation} & \quad \eta^1\text{-bridging} & \quad \mu_3\eta^1\text{-bridging} & \quad \text{two (}\mu_2\eta^1\text{-bridging)}
\end{align*}
\]

\[
\begin{align*}
\text{monodentate + }\eta^4\text{-chelation} & \quad \mu_2\eta^4\text{-chelation} & \quad \text{non bridging}
\end{align*}
\]

Fig. 1.3 Various coordination modes of carboxylate ligand.

The simplest dicarboxylic acid is oxalic acid. It acts as a rigid bidentate ligand and facilitates the formation of extended structures by bridging metal centers. The aromatic dicarboxylate phthalate and its isomers isophthalate and terephthalate ligands can also form multi dimensional compounds owing to its multi binding ability with regard to metal ions. Metal organic frameworks constructed from multifunctional cyclic aliphatic and aromatic carboxylates have also been reported.
Some typical MOCNs containing aromatic carboxylates\textsuperscript{21-24} are given in Fig. 1.4 and 1.5.

![Fig. 1.4 Crystal structure of (a) copper isophthalate MOCN and (b) $[\text{Mn(phth)}(\text{bpy})(\text{H}_2\text{O})_2]_n$](image1)

![Fig. 1.5 (a) Building unit present in crystals of $\text{Zn}_4\text{O}(\text{BDC})_3(\text{DMF})_8^{-}(\text{C}_6\text{H}_5\text{Cl})$ (b) a primitive cubic lattice (c) the porous crystal and (d) a La isophthalate complex.](image2)

These structures clearly demonstrate the ability of rigid cyclic carboxylates to provide complex architectures from simple inorganic secondary building units (SBU’s) formed by metal–oxygen polyhedra. Poly
nuclear complexes are of considerable interest in relation to the nature of magnetic exchange interaction between metal ions through bridging ligands and as models for the active sites of metalloenzymes. Many of these compounds are prepared in attempts to mimic the behaviour of various di-copper proteins such as haemocyanin, tyrosinase etc.

Comparing to aromatic polycarboxylates, aliphatic dicarboxylates have good conformational freedom due to their flexible spacer moieties (Fig. 1.6a). Extensive researches on self-assemblies of transition metals with pyridyl ligands and saturated α,ω-dicarboxylate anions indicated that the saturated α,ω-dicarboxylate anions are excellent versatile flexible ligands interlinking metal atoms into coordination polymers and because of the significant molecular recognition in the form of π-π stacking interactions (Fig. 1.6b) the incorporated pyridyl ligands play crucial roles in construction of supra-molecular architectures with specific topologies.25-26

![Fig. 1.6](image)

\[a\] A Co(II-succcinate polymer and \(b\) supramolecular assembly of the 1D \([\text{Mn(phen)}(\text{C}_4\text{H}_2\text{O}_4)]\) chains into 2D layers via π-π stacking interactions.28

In comparison to the flexible aliphatic dicarboxylates, the unsaturated α,ω-dicarboxylates display less conformational freedom
owing to incorporation of the C=C bond. However lesser work has been done on mixed ligand complexes of transition metals involving unsaturated α,ω-dicarboxylate ligands. Fumaric acid and maleic acid are the simplest unsaturated aliphatic dicarboxylic acids. Compared to succinate anions, fumarate and maleate anions exhibit less conformational freedom because of the C=C double bond. As one of the lowest members in the unsaturated α,ω-dicarboxylate families, the maleate anions may exhibit interesting co-ordination features. Hitherto, however, a fewer coordination polymers have been synthesized using the fumarato and maleato ligands. 29–45

1.1.3 Dimensionality and motifs

The organization of the building blocks can lead to MOCNs of different dimensionalities: one- two- or three-dimensional architectures. Given in Fig. 1.7 is a drawing of the three types of dimensionalities. 17

Fig. 1.7 Dimensionality of MOCNs (M, metal ions; D- donor groups of the ligand; S- spacer inside the ligand).

In one-dimensional motifs the metal ion is coordinated with two ligand molecules and metal ions and organic ligands alternate “infinitely”
leading to a chain. One dimensional chain organization is simple; there are many possible permutations in the packing - linear chains, zig–zag chains, double chains, ladder-like, helix, etc (see Fig.1.8).\textsuperscript{17}

![Fig. 1.8](image)

Fig. 1.8 (a) Linear chain of \([\text{Co(H}_2\text{O)}_4\text{(pyrazine})](\text{NO}_3)\text{]}_2\text{2H}_2\text{O} \) (b) zig-zag chain (c) double chain (d) helical and (e) ladder-like chains.

Two-dimensional compounds are obtained with three or four ligand molecules coordinating around the metal ion and motif expands in two directions. Square grid networks are the simplest example of the two
dimensional motifs. In these coordination polymers the metal to ligand composition is usually 1:2. The metal centres are coordinated with four different ligand molecules and the repetition of this unit allows the propagation of the structure in two dimensions. Fig. 1.9 represents a two dimensional MOCN.\(^46\)

![Fig. 1.9 2D network](image)

A three dimensional network is based on the extension of the framework in the three directions from octahedral nodes. It is sterically very difficult to co-ordinate six ligand molecules around one metal center and generally the apical positions of the octahedral metal ions are occupied by water molecules, other solvent molecules or counter ions. Fig. 1.10 illustrates a 3D network.\(^47,17\)
Introduction

Fig. 1.10 (a) 3-D arrangement in Zn$_2$(fum)(ina)$_2$ (ina – isonicotinate, fum - fumarate$^{52}$ and (b) another 3D network.

1.1.4 Applications of MOCNs

MOCNs have wide applications, such as gas storage, anion exchange, catalysis, conductivity, luminescence, chirality, magnetism, spin transition behavior, deposition of thin films etc.

Gas Sorption

Sorption of gases has been used to probe the possibility of future applications in gas storage. For example Yaghi reported nitrogen absorption by zinc terphthalates.$^{48}$ Kitagawa reported that copper-4,4’-bipyridine compounds was able to sorb very large quantities of methane.$^{49}$ In fact, relative to framework weight, more methane was absorbed by this material than by zeolite 5A, which was taken as the optimum conventional zeolite for methane sorption. A great impetus for studying this kind of sorption is the need for low-pressure storage media for gases such as methane and hydrogen, due to the potential applications of the latter as ‘clean’ fuels. Yaghi et al. reported still greater weight-for-weight methane sorption of 240cm$^3$ g$^{-1}$ in Zn-carboxylate frameworks.$^{50}$ When
compared to a conventional gas cylinder, at a pressure of 205 atm, the results suggested that this material could store 70% as much methane in the same volume, but at a lower pressure of 36 atm.

**Catalysis**

An important application of the coordination polymer network is catalysis. The coordination polymers may be helpful as, they can be porous, can contain catalytically active transition metal centres and can be designed in order to offer metal centres and specific organic groups to the reagents. The 2D square network material Cd(NO$_3$)$_2$(4,4'-bipy)$_2$ catalyses the cyanosilylation of aldehydes.$^{19}$ No reaction took place with either Cd(NO$_3$)$_2$ or 4,4'-bipy alone. Shape specificity towards the aldehyde was manifested in the product yield and ascribed to the cavity size of the network. The non-porous polymer In$_2$(OH)$_3$(1,4-bdc)$_{1.5}$ was found active for the hydrogenation of nitro aromatics and the oxidation of alkyl phenyl sulfides.$^{19}$

**Magnetism**

Coordination polymer based strategy is furthermore employed for the design of molecular based magnet. Indeed antiferromagnetism, ferrimagnetism and ferromagnetism are cooperative phenomena of the magnetic spins within a solid. They require an interaction or coupling between the spins of the paramagnetic centres. An efficient coupling in magnetic material can occur through open shell organic ligands. The dicarboxylic acids, as a super-exchange pathway between the metal ions [Cu(II), Mn(II), Ni(II), etc.], have received considerable attention in the field of molecular magnetism.$^{37}$ In order to allow efficient magnetic coupling metal ions should be bridged by small ligands allowing short metal-metal contacts.
Introduction

Conductivity

Electrical conductivity of polymers continues to be one of the most important research areas in materials science. Conductivity may be an interesting research topic providing that short inorganic or conjugated organic bridges exist in the metal organic coordination network. The conductivity is due to the interaction between the metal $d$-orbital and the $\pi^*$ level of the bridging ligand. In some cases coordination polymers can have semiconductor behavior. Coordination polymers with Ag...Ag interactions may possess electrical semiconductive properties. The 3D polymer $[\text{Ag(H}_2\text{btc})_2][\text{Ag}_2\text{Hbtc}]$ with Ag...Ag interactions (2.963-3.278 Å) shows a weak semiconductivity of $1.06 \times 10^{-6}$ S cm$^{-1}$.

Luminescence

Luminescent supra-molecular architectures have recently attracted much interest because of their potential applications in optoelectronic devices or as fluorescent sensors and probes. Indeed inorganic–organic coordination polymers often afford more stability than the pure organic ligands and may affect the emission wavelength of these organic molecules. Examples include $[\text{Cd}(1,4\text{-bdc})(\text{py})]$ where complex formation significantly (about 100 times) enhances the fluorescent intensity of the free 1,4-bdc ligand. The combination of organic spacers and transition metal-centers in coordination polymers is seen as an efficient method for obtaining new types of electroluminescent materials for potential applications in light-emitting diodes (LEDs). Frame works based on Zn(II) or Cd(II) and mixed pyridine carboxylate ligands give second order NLO response of three times that of potassium dideuterophoshate (KDP).
Chirality

With chirality being an element of life there is also a great interest in the formation of chiral coordination polymers. Chiral metal-organic frameworks are interesting because they could be applied to enantioselective separations. Particularly intriguing is, of course, the formation of homochiral (helical) coordination polymer from achiral components through spontaneous enantiomer resolution.\(^{19}\)

Spin-transition behavior

Spin-transition or spin-crossover is the thermal, light or pressure induced (cooperative) transition between a low-spin (LS) and high-spin (HS) states. Spin-crossover materials could have potential applications, as temperature sensors, as active elements of various types of displays, as optical switches in new electronic devices, and in information storage and retrieval. Spin-transition studies are, so far, mostly carried out on mononuclear and occasionally dinuclear molecular complexes. Some carboxylato manganese complexes have been used as model compounds for photosynthetic oxygen-evolving complexes (OEC).\(^{34}\)

1.1.5 Synthetic methods of MOCNs

There are mainly four main synthetic strategies for obtaining coordination polymers. Saturation methods allow the crystal formation from a mixture of the different reagents. This technique needs convenient conditions. Crystals grow in saturated solutions. Ideal concentrations can be achieved by slow evaporation of the mother liquor. Solubility increases with temperature and crystals can appear during the cooling step, which has to be well-controlled as far as speed of cooling and final temperature is concerned. Diffusion methods are preferred to get single crystals suitable
for X-ray diffraction analysis of non- or poly-crystalline-products, especially if the products are poorly soluble. The principle of this method is to slowly bring into contact the different species. *Hydro (solv) thermal methods* are originally used for the synthesis of zeolites, but have been adapted to the formation of coordination polymers. They exploit the self-assembly of products from soluble precursors. The running temperature range is usually 120-160°C inside a closed space (bomb calorimeter) under autogenous pressure. Under these conditions the reduced viscosity of water enhances the diffusion process and thus extraction of solids and crystal growth from solution is favoured. As the difference of solubility between organic and inorganic components in the same solvent is often a barrier in the formation of single crystals, hydrothermal experiments can be a good alternative as solubility of starting materials can be increased. The crystallization technique is a non-equilibrium synthesis and may lead to meta-stable products. *Microwave and ultrasonic methods* are so far less used methods for the co-ordination polymer formation. These methods are also based on the improvement of solubility in order to better react or crystallize the involved species and products.

Metal carboxylates have also been used as precursors in modern low temperature preparation routes of a number of oxides and other advanced inorganic materials with technologically important properties. These methods often called “*soft solution processing,*” provide low-energy pathways to more homogeneous, nano-structured materials, compared to those obtained by the more generally used “*ceramic techniques.*” An additional advantage of the soft solution methods is the use of simple, inexpensive reagents combined with environmentally benign synthesis
conditions. The most detailed structural information will be gained from single crystal X-ray crystallography. Indeed, without knowing the crystal structure, it is going to be very hard to interpret any subsequently observed properties. Therefore, synthesis in this area is strongly directed toward obtaining X-ray quality single crystals.

1.2 Metal maleates and fumarates

Metal derivatives of unsaturated dicarboxylic acids constitute an abundant group of compounds that are interested not only in the view point of coordination and macromolecular chemistry but due to the practical significance of maleates and fumarates as coatings with specific properties, efficient catalysts and medicinal. By virtue of the multiple bonds, salts of unsaturated dicarboxylic acids are also potential metal containing monomers whose polymerization transformations can open new routes for the preparation of valuable products. Metal-fumarates such as copper(II)-fumarate show gas adsorption. Metal maleates and fumarates containing paramagnetic metal centers show unusual magnetic properties. The fungi toxic activity of Mn-fum-bip/phen derivative has been reported. Fumarate and maleate anions have been used in design of polynuclear metal carboxylates. The different coordination modes adopted by this anion, in combination with nitrogen donor ligands lead to different architectures. Considerable interest has been shown in using complementary H-bond interactions as part of the design strategy for the development of new solid state materials. Varying both the number and arrangement of H-bond donors and acceptors, and steric factors can influence the solid state structure significantly. Complexes containing fumarate and maleate as counter ions are interesting in this regard.
Only very recently have attempts been made to combine both coordination bonds and weaker non-covalent forces such as H-bonding and π-π contacts to crystal engineer organic-inorganic materials. In this regard, maleic and fumaric acids are good candidates as bridging ligands for designing new organic-inorganic hybrid materials as it may participate in both types of interaction as well as their diverse coordination modes.37 There are a few scattered reports on some of the metal maleates52,67 and metal fumarates.68-70,45 However, data on the synthesis, structure and reactivity of these compounds are rather scarce compared to metal-monocarboxylates or even other MOCNs of saturated aliphatic dicarboxylates and benzene polycarboxylates.

1.3 Scope and objective of the present work

Among all polycarboxylic acids benzene di-, tri and polycarboxylic acids are seen to be given considerable focus in rational design of MOFs and MOCNs. By contrast, aliphatic α,ω-dicarboxylates are less studied because of their flexible nature both in terms of their conformational and coordination behaviour. Growing attention is seen to be given to the rational design and synthesis of coordination polymers using saturated aliphatic dicarboxylate ligands also but, comparatively, only a few cases have been reported. Compared to saturated aliphatic dicarboxylates, the unsaturated aliphatic dicarboxylate anions exhibit less conformational freedom because of the intervening -HC=CH- double bond. Being the lowest members of unsaturated aliphatic dicarboxylic acids, maleic acid and fumaric acid are of interest on their own merits. In addition to the conjugative interaction possible between the two carboxylate ends through –HC=CH-, the spacer unit in both fumaric acid and maleic acid is
made up of the lighter elements (C and H only) making them attractive candidates for developing light weight, highly porous and functional MOFs or MOCNs.

Even though on steric grounds the trans-isomer fumaric acid is considered more stable compared to the cis-isomer maleic acid, the stability of the latter with its two cis-disposed –COOH groups is well accounted for by the strong intra-molecular H-bonding existing in it. One of the special attributes of maleic acids is this internal H-bond which makes it to deprotonate only successively (pKa’s 1.5 and 6.5). Associated with this phenomenon can be several interesting molecular properties for maleic acid. Further, there is also a brief reference about the possibility of a cis- to trans- isomerization by which maleic acid can be converted into fumaric acid.\textsuperscript{71-72} But this aspect has not been well investigated. Most of the studies reported on the interaction of fumaric and maleic acids with metal ions have been in making simple coordination polymers but comparatively the number of such coordination polymers is also rather limited. The work envisaged in the present study is, therefore, mainly aimed at making use of the unique characteristics of maleic acid to bring about some unprecedented transformations and probing the possibility of using them for developing novel and interesting MOCNs and a few functional materials. Some interest also has been on developing structurally tuned metal maleates and fumarates through auxiliary ligands and investigating on their structural and electronic properties. Specifically the main focuses made in the present study are on the following aspects:

1. Since metal maleates and fumarates are the starting materials in our work, we have made an attempt to synthesise various metal(II)-
maleates (both the molecular M(II)-*bis*-hydrogenmaleate and the polymeric M(II)-*mono*-maleates) and fumarates in different experimental conditions and made a systematic study on the structure and electronic properties on them using all possible analytical techniques such as elemental analysis, FTIR, electronic and EPR spectra, magnetic susceptibility measurements, PXRD and single crystal X-ray diffraction studies.

2. We were able to observe that unlike fumaric acid which forms only polymeric metal(II)-fumarates, maleic acid tends to form two categories of metal(II)-maleates: one with the expected polymeric form and the other an unprecedented molecular type species which we could confirm as metal(II)-*bis*-hydrogenmaleates, M(Hmal)$_2$(H$_2$O)$_4$. During the course of our attempts to generate ternary type coordination polymers using these M(Hmal)$_2$(H$_2$O)$_4$ we could notice some unprecedented transformation happening when these metal *bis*-hydrogenmaleates are reacted with pyridine. Our initial focus has been on deciphering the nature of such a reaction and identifying/characterising some of the novel products which get formed during the reaction. We were able to observe an unprecedented and facile *cis* to *trans* (from maleate to fumarate) transformation that happen with M(Hmal)$_2$(H$_2$O)$_4$ along with the formation of a novel chiral zwitterion through pyridine insertion in almost quantitative yield. We have made attempts to monitor this reaction in detail with a wide variety of M(Hmal)$_2$(H$_2$O)$_4$ and characterize the products in each case by structural and single crystal XRD studies.
3. As an extension of this study we have also made attempts to look at the above reaction using various substituted pyridines of the type picolines, 4,4’-bipyridine, 2,2’-bipyridine and 1,10-phenanthroline with a view to generate several substituted chiral zwitterions and also to monitor the feasibility of cis-trans isomerization in each case.

4. Realizing the fact that molecular M(II)-bis-hydrogenmaleate molecular M(Hmal)$_2$(H$_2$O)$_4$ contains two free and reactive –COOH groups we have explored the possibility of using them as ‘metallogligands’ and attempted developing some novel coordination polymers by reacting with various alkyl amines. We were able to generate a few new coordination polymers with unprecedented structural and topological features containing [M(mal)$_2$]$^{2-}$ as structural motifs using M(Hmal)$_2$(H$_2$O)$_4$ as metallo-ligands. Structural characterization using single crystal XRD and spectral studies showed that the polymeric products formed have unusual structural features having cyclically interconnected units and one-dimensionally extended chain-like framework with alkyl ammonium moieties acting as cationic templates. We have also tried to develop similar type of MOCNs using alkyl diamines so that they can act as cationic templates through both their –NH$_3^+$ ends and can interconnect coulombically the one-dimensionally extended chains made up of [M(mal)$_2$]$^{2-}$ units to generate 2-dimensionally stacked MOCNs. We intend to discuss in detail in the thesis the structural (through single crystal XRD) and spectral features of these novel coordination polymers and exploring some of their properties including photoluminescence behaviour.
5. Considering M(Hmal)$_2$(H$_2$O)$_4$ as metallo-ligands analogous to organic dicarboxylic acids we have probed the possibility of reacting M(Hmal)$_2$(H$_2$O)$_4$ with various metal salts of the type M’X$_2$ to generate -M-mal-M’-mal- type polymeric ‘bimetallic’ maleates which can be expected to have unusual materials properties including anomalous magnetic behaviour because of their periodically arranged M and M’ ions that are linked through maleate functions. We could develop several such heterobimetallic maleates in almost phase pure form which have almost similar structure and bonding features as in simple polymeric metal maleates. During our preparative stage we could, however, observe that some of these heterobimetallic maleates get formed as bundles of regularly stacked fibers. Even though we were not able to get their crystal structure analysis done so far we could infer based on electronic, FTIR and PXRD data that there is only marginal difference in the overall bonding of maleate functions to the metal ions in these nanosized fibers compared to that in polymeric metal maleates. The details will be presented in detail along with their morphological characterization through PXRD, EDAX, SEM and TEM.

6. By employing metal maleates (1:1) which are polymeric in nature we have also made some attempts to generate their structurally and electronically modified ternary type MOCNs by interacting with a series of Lewis bases. Such a modular synthetic approach has enabled us to develop a series of new and interesting N-base modified metal maleates with unprecedented structures. Many of these MOCNs could be structurally (through single crystal XRD) and spectrally characterized. We have employed a series of Lewis
bases for this purpose which include monoamines (methylamine, ethylamine), diamines (1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane and 1,6-diaminohexane) and the pyridine type ligands (pyridine, picolines, 2,2′-bipyridine, 4,4′-bipyridine, 1,10-phenanthroline and imidazole).

7. In the course of our study using metal maleates and alkyl diamines as reagents we were able to generate an unprecedented Ni(II) derivative (50) which contained a novel chiral amino acid, (HOOC-CH(NH-CH₂-Ch₂-NH₂)-CH₂COOH) containing two COOH functions and an –NH₂ unit and a –NH moiety) that acts as a compact tetradeutate ligand to form 50. We could structurally characterize this novel compound through single crystal structure. The details will be presented in the thesis.

8. We were also able to generate a series of auxiliary ligand modified metal fumarates which could be structurally and spectrally characterized. Some of the interesting compounds include M(en)₃-fumarate that has comparable structure as that of M(en)₃-oxalate. The special features of various MOCNs/compounds developed along with the conformational aspects of Ni(en)₃ moieties in the above two compounds would be discussed in detail in the thesis.

9. During the course of our synthetic attempts involving M(Hmal)₂(H₂O)₄, M(mal)(H₂O)ₙ and metal fumarates we could see the formation of some metal-free products which include chiral zwitterions 16 and 23 formed through the insertion of N-bases like pyridine and picolines in the maleic acid constituent. We have also made some studies to see whether alkyl amines can be inserted in
the maleic acid moieties the results of which would also be discussed in detail.

10. We were successful in developing a novel coordination polymer that has a paddle-wheel type structure and which contains a chiral zwitterion and also fumarate moiety linearly linked. The structural features of this unprecedented Cu(II) MOCN would be discussed in detail in the thesis. We have also made attempts to characterize a Ca salt of the zwitterions 23 using FTIR, NMR, PXRD and single crystal XRD analysis.

11. All the products discussed in the thesis have been fully characterized using various analytical techniques such as elemental analysis, thermal analysis, FTIR, electronic, $^1$H NMR, $^{13}$C NMR, Mass and fluorescence spectroscopy, magnetic susceptibility measurements, SEM, TEM, PXRD and single crystal X-ray diffraction analysis.