

1 Introduction

1.1 The Rare Earth Elements

Lanthanides are the first period of f-block elements ranging from Cerium to lutetium (La-Lu, $Z = 57-71$) in the periodic table. Together with scandium and yttrium, they are called rare earth elements (REEs). Lanthanides have traditionally been divided into two groups: the light rare earth elements (LREEs), lanthanum to europium ($Z = 57-63$), and the heavy rare earth elements (HREEs), gadolinium to lutetium ($Z = 64-71$). When they were first discovered and isolated, they were called "rare earth" elements due to the assumption that they are less abundant compared to other elements. Indeed, all lanthanides (except radioactive promethium) including the least common element, thulium, are more abundant in earth's crust than bismuth, arsenic, cadmium, mercury and other precious metals.^[1]

Table 1.1 Some properties of lanthanide atoms and ions.

| Atomic number | Name | Symbol | Electronic configuration | | $E^0(\text{V})^{[2]}$ |
|---------------|--------------|--------|------------------------------|---------------|-----------------------|
| | | | Atom | M^{3+} | |
| 57 | Lanthanum | La | $[\text{Xe}]5d^16s^2$ | $[\text{Xe}]$ | -2.38 |
| 58 | Cerium | Ce | $[\text{Xe}]4f^15d^16s^2$ | $4f^1$ | -2.34 |
| 59 | Praseodymium | Pr | $[\text{Xe}]4f^36s^2$ | $4f^2$ | -2.35 |
| 60 | Neodymium | Nd | $[\text{Xe}]4f^46s^2$ | $4f^3$ | -2.32 |
| 61 | Promethium | Pm | $[\text{Xe}]4f^56s^2$ | $4f^4$ | -2.29 |
| 62 | Samarium | Sm | $[\text{Xe}]4f^66s^2$ | $4f^5$ | -2.30 |
| 63 | Europium | Eu | $[\text{Xe}]4f^76s^2$ | $4f^6$ | -1.99 |
| 64 | Gadolinium | Gd | $[\text{Xe}]4f^75d^16s^2$ | $4f^7$ | -2.28 |
| 65 | Terbium | Tb | $[\text{Xe}]4f^96s^2$ | $4f^8$ | -2.31 |
| 66 | Dysprosium | Dy | $[\text{Xe}]4f^{10}6s^2$ | $4f^9$ | -2.29 |
| 67 | Holmium | Ho | $[\text{Xe}]4f^{11}6s^2$ | $4f^{10}$ | -2.33 |
| 68 | Erbium | Er | $[\text{Xe}]4f^{12}6s^2$ | $4f^{11}$ | -2.32 |
| 69 | Thulium | Tm | $[\text{Xe}]4f^{13}6s^2$ | $4f^{12}$ | -2.32 |
| 70 | Ytterbium | Yb | $[\text{Xe}]4f^{14}6s^2$ | $4f^{13}$ | -2.22 |
| 71 | Lutetium | Lu | $[\text{Xe}]4f^{14}5d^16s^2$ | $4f^{14}$ | -2.30 |

^[2] $\text{Ln}^{3+} + 3e^- = \text{Ln}$

The rare earth elements along with some of their principal characteristics are listed in Table 1.1. Going from lanthanum to lutetium, fourteen 4f-electrons are added, causing the electronic configuration to change from $[\text{Xe}]5d^16s^2$ to $[\text{Xe}]4f^{14}5d^16s^2$, with slight irregularities in the case of some elements (Table 1.1). Also, the highly electropositive character of lanthanide elements is comparable to that of alkali and alkaline earth metals. The formation of predominantly ionic compounds is expected, and the +3 oxidation state is the most stable. In fact, the energy of the 4f orbitals is lower than that of the 6s and 5d orbitals; therefore, two 6s electrons and one 5d electron are easier to remove than the 4f electrons leading to a +3 oxidation state. The +2 and +4 oxidation states also exist, but they can revert to +3 *e.g.* Sm(II), Eu(II) and Yb(II) lose one electron to become +3. Thus, these divalent lanthanides are good reducing agents. Eu(II) and Yb(II) are the most stable divalent species^[3] because they are somewhat stabilized by the $4f^7$ and $4f^{14}$ configuration (from exchange energy) and enjoy the stability of half-filled and filled subshells.^[4] In contrast, the tetravalent lanthanide ions can be reduced to adopt the +3 oxidation state, making them good oxidizing agents. Generally, an oxidation state +4 is exhibited by cerium, praseodymium, and terbium but in aqueous solution only cerium(IV) is stable (kinetically). Some of its salts are cerium(IV) ammonium nitrate, cerium(IV) sulfate, etc.

The lanthanides exhibit a feature, called lanthanide contraction,^[5] which refers to the penetration of the 4f subshell by the 5s and 5p, such that the 4f orbital is not shielded from the increasing nuclear charge. An atomic radius decreases throughout the lanthanide series with increase in atomic number; hence, the ionic radii of lanthanide ions decrease from lanthanum to lutetium. To illustrate this concept, ionic radii of the nine coordinate trivalent lanthanides and yttrium are shown in Table 1.2.

The 4f orbitals of the lanthanides have less radial extension than the filled $5s^2$ and $5p^6$ orbitals and are thus shielded from external perturbations. The 4f electrons have little involvement in covalent interactions upon the formation of chemical bonds, therefore, Ln(III) ions display large and variable coordination numbers (CN = 8–12).^[6]

Table 1.2. Ionic radii of trivalent nine-coordinate rare earth metal ions.

| Ln ³⁺ | Ionic radius [Å] | Ln ³⁺ | Ionic radius [Å] |
|------------------|------------------|------------------|------------------|
| La | 1.216 | Tb | 1.095 |
| Ce | 1.196 | Dy | 1.083 |
| Pr | 1.179 | Y | 1.075 |
| Nd | 1.163 | Ho | 1.072 |
| Pm | 1.144 | Er | 1.062 |
| Sm | 1.132 | Tm | 1.052 |
| Eu | 1.120 | Yb | 1.042 |
| Gd | 1.107 | Lu | 1.032 |

The variable and versatile coordinating behavior of lanthanide ion, Ln³⁺, limits its selective introduction into organized molecular or supramolecular architectures.^[7] Several types of lanthanide-based complexes have been successfully developed into functional molecular devices, such as luminescence sensors and light converters, nuclear magnetic resonance (NMR),^{[7],[8],[9]} magnetic resonance imaging (MRI),^{[10],[11]} catalysts in organic synthesis and biological reactions,^{[12],[13]} gas adsorption^[14] and magnetism^[15] in the fields of chemistry, biology, medicine and materials science, respectively. Recent interest in coordination chemistry to synthesize lanthanide-based metal organic frameworks (MOFs) has been sparked because of their unique properties, offering a wide range potential applications including nonlinear optics, gas storage and catalysis.

1.2 Metal Organic Frameworks (MOFs)

1.2.1 History and Scope

One of the very first MOFs was isolated in 1943, formulated as [Ag₂(C₂O₄)]_n, although similar studies from the early 1930s are also known.^[16] In 1965, Tomic *et al.* synthesized a series of metal complexes from an aromatic carboxylic acid, which would nowadays be called MOFs.^[17] In the late 1980s and early 1990s, this field was further developed by Robson after he initiated his famous "node-and-spacer" concept.^[18] Then, in the late 1990s, the concept of

reticular design was initiated by Yaghi *et al.*^{[19],[20]} The development of these two concepts has caused this field to become a hot topic in chemistry, and now a plethora of MOFs are known.

MOFs are a type of coordination polymer constructed from metal ions or metal ion clusters and organic bridging ligands.^{[21],[22],[23],[24],[25]} The organic ligands act as linkers and are considered "struts" that bridge metal centers. The combination of a metal center and a linker are regarded as inorganic secondary building units (SBUs), which act as joints in the resulting MOF architecture.^{[23],[26],[27]} The metal centers and ligands are connected to each other by coordination bonds, which, together with other intermolecular interactions, form a network with a definite topology. In most cases, the organic linkers are multidentate ligands - usually carboxylates, azoles, nitriles, etc. The metal centers used for this purpose are mainly 3d metal ions such as zinc, nickel, iron, copper, manganese and cobalt ions.^[26] For example, **MOF-5**, reported by Yaghi *et al.* is formulated as $[\text{Zn}_4\text{O}(\text{BDC})_3 \cdot (\text{DMF})_8 \cdot (\text{C}_6\text{H}_5\text{Cl})]$ (H_2BDC = 1,4-benzenedicarboxylate).^[28]

Due to the size of the ligands, inorganic connecting points and network connectivity, the porosity of MOFs can be readily tuned to afford open channels and pores with dimensions from several angstroms to several nanometers. Because of their stability, MOFs can be used for gas storage,^{[29],[30]} separation,^{[31],[32]} magnetic materials,^[33] luminescence,^[34] drug storage and drug delivery.^{[35],[36]}

Usually, MOFs are synthesized by a common method known as the solvent evaporation process,^[37] in which a saturated solution is slowly evaporated or cooled, resulting in crystalline or amorphous materials. A wide variety of other methods such as diffusion, microwave reaction and ultrasonication have also been established.^{[38],[39],[40]} Another very useful method for the synthesis of MOFs is the hydro(solvo)thermal process. Usually, the temperature that is used in this approach ranges from 80-260°C (*i.e.* higher than the boiling point of the solvent molecule). Frameworks, regardless of their synthetic method, are heavily influenced by factors such as structural characteristics of the ligands, the coordination nature of the metal ions, the solvent systems, the template, the pH value of the solution, steric requirement of the counterion, reaction temperature and the metal to ligand ratio.

Although many MOFs have been synthesized so far, it is still a challenge to explore successful synthetic strategies that lead to MOFs with promising applications and intriguing structures. In this thesis, attempts were made to design new MOFs using the self-assembly of metal ions (mainly manganese, iron, nickel and copper with lanthanides) and salen ligands.

1.2.2 Salen Frameworks

Salen ligands are common ligands in coordination chemistry. The name "salen" is abbreviated from the contraction of "salicylaldehyde" and "ethylenediamine" (*i.e.* salen = 2sal + en). This type of ligand is synthesized by a simple condensation reaction of a salicylaldehyde and ethylenediamine. In contrast to salen ligand, the schiff base ligand which contain the azomethine group (-CH=N-) and it is synthesized by the condensation reaction of a primary amine with carbonyl compound. Salen ligands form complexes with metal ions *via* nitrogen and oxygen donor atoms.^[41] Steric and electronic effects around the metal core can be finely turned through the appropriate selection of electron-withdrawing or electron-donating substituents of different size in the salen ligands (Figure 1.1). The nitrogen and oxygen atoms induce two opposite electronic effects: the phenolate oxygen atoms are regarded as a hard donor, which stabilizes higher oxidation states of the metal ion, while the imine nitrogen atoms are softer donors and will stabilize lower oxidation states.^[42] As a result, these ligands can stabilize many different metals in various oxidation states; therefore, metallosalens have the potentials to be used in different areas such as catalysis, zeolite matrices, luminescence, magnetism.^{[43],[44],[45],[46]}

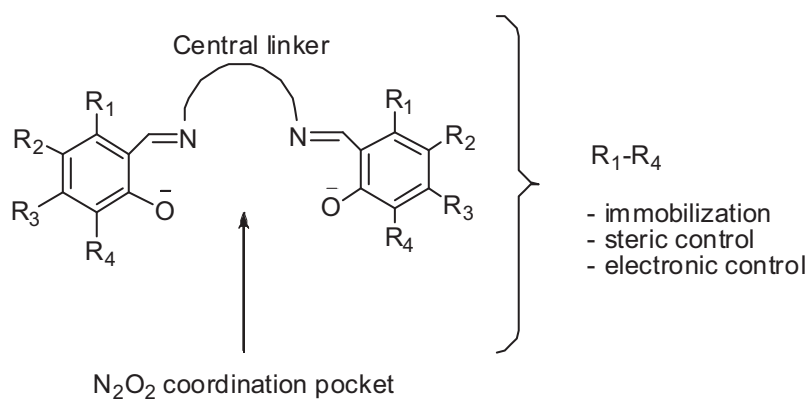
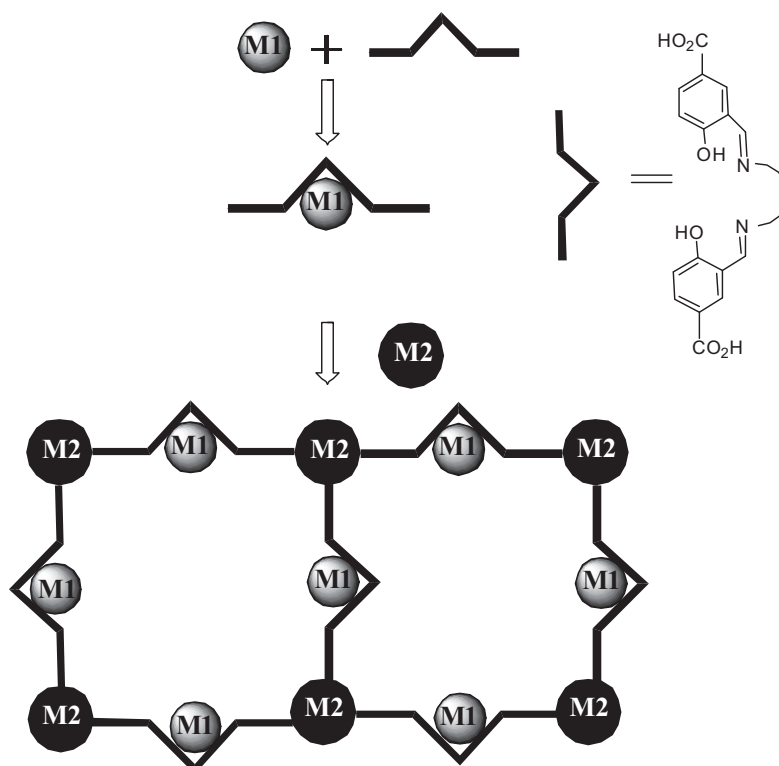


Figure 1.1 General structure of a symmetrical salen. The substitution at the phenyl rings may be used for immobilization and/or easy control over the ligand properties.

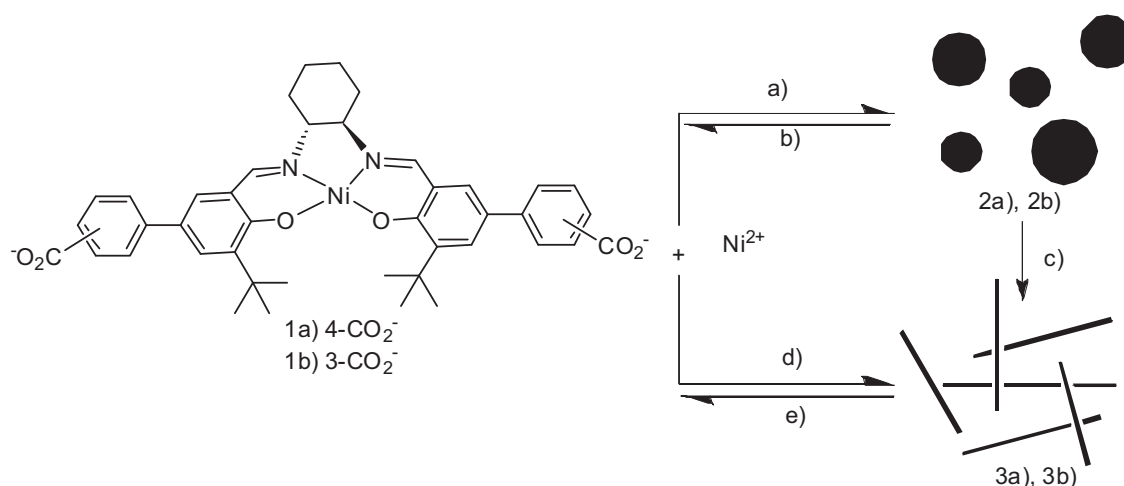
Some previously reported work demonstrate the various features of the chemistry of salen ligands. These examples are compared to the results obtained during this thesis work. Kitagawa and coworkers reported microporous coordination polymers (MCPs) with unsaturated metal centers (UMCs) using metalloligand (ML) systems. The assembly of the MCPs is a two step process: (1) synthesis of ML by the reaction of well-defined salen ligands and metal ions (mainly 3d metal ions) that together act as a linker (M1), and (2) reaction of

ML with another metal ion (M2), which acts as a nodal unit in a framework.^{[47],[48]} Thus, two types of metal centers are present in MCPs which shown in Scheme 1.1.



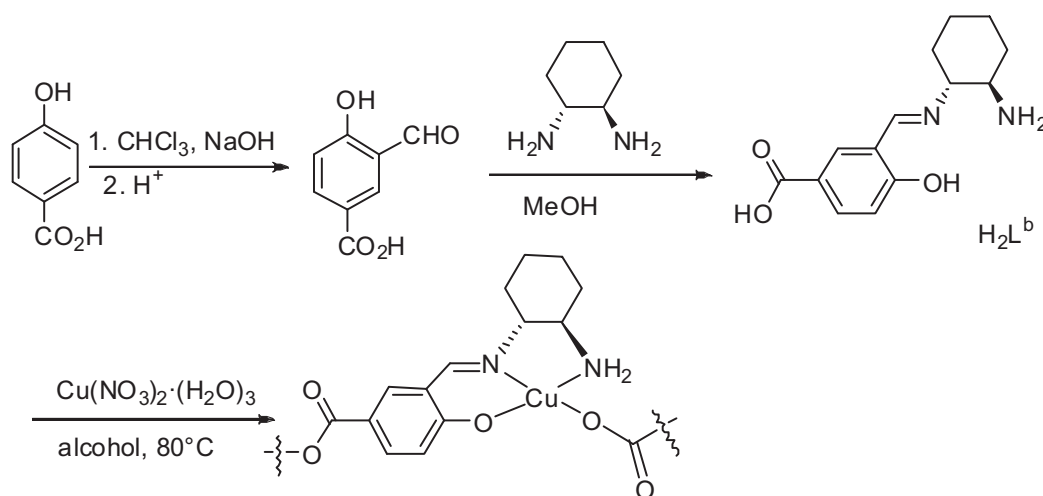
Scheme 1.1 MCPs formed upon addition of M2 from metalloligand system.

In 2007, Mirkin *et al.* studied the interconversion between amorphous and crystalline microparticles that are built from Ni-salen-dicarboxylic acid and an excess amount of $\text{Ni}(\text{OAc})_2 \cdot (\text{H}_2\text{O})_4$ (Scheme 1.2).^[49] The same authors synthesized the chiral building block (*S*)- H_4L^a by using an imine coupling reaction of the enantiopure (*S*)-binaphthyl diamine and 4-formyl-3-hydroxybenzoic acid. This (*S*)- H_4L^a ligand was further reacted with $\text{Cu}(\text{OAc})_2 \cdot (\text{H}_2\text{O})_6$ to form homochiral triangular macrocycles and helical coordination polymers.^[50]



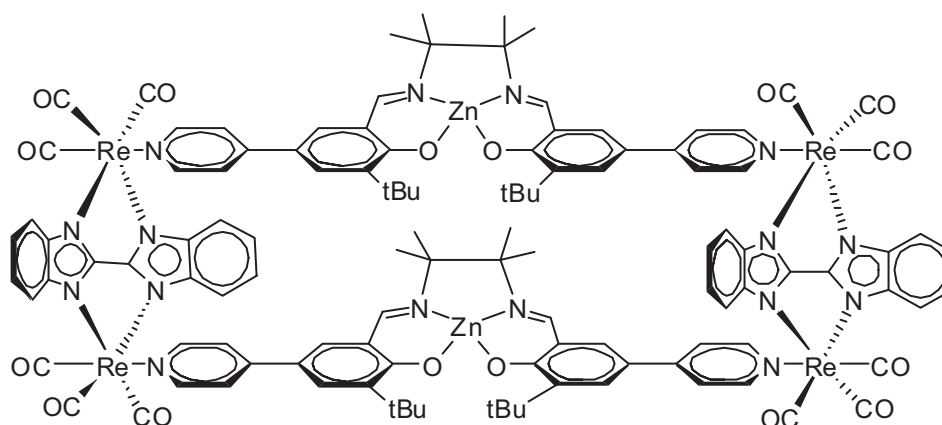
Scheme 1.2 Synthesis of salen based microparticles and their dynamic solvent-triggered crystallization process: (a) pyridine / ether, (b) pyridine, (c) methanol, (d) pyridine / methanol, (e) pyridine. Amorphous microparticle: 2a, 2b; crystalline rod: 3a, 3b

Cui *et al.* carried out chiral recognition and separation using a 2D coordination polymer built from unsymmetrical chiral Schiff base metal complexes (Scheme 1.3).^[51]



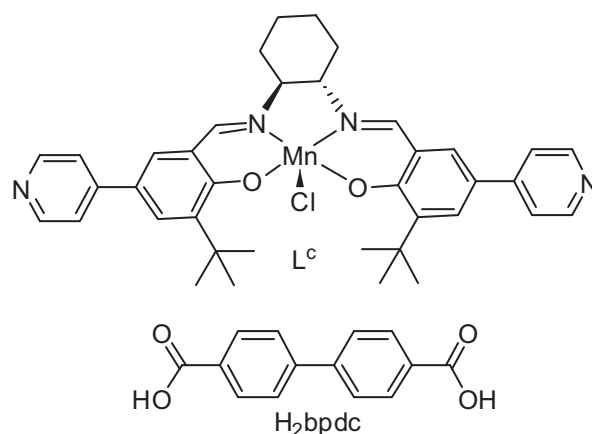
Scheme 1.3 Synthesis of the H₂L^b ligand and copper polymer.

Nguyen and Hupp established a salen-containing loop-type structure synthesized from a platinum precursor.^[52] A subsequent ligand rigidification, either by post-metalation or direct use of the respective Zn-salen precursors, favors the formation of box-like structures. Moreover, Hupp *et al.* reported a box-assembled coordination polymer, in which Zn-salen coordinates to a rhenium center (Scheme 1.4). This compound exhibits photophysical properties.^[53]



Scheme 1.4 Scheme of the box like assemble for zinc-rhenium complex.

Hupp and coworkers also reported a homochiral MOF constructed from chiral Mn-salen, biphenyl-4,4'-dicarboxylic acid (H_2bpdC) and Zn^{2+} ions (Scheme 1.5). The framework, $[Zn_2(bpdC)_2(L^c) \cdot (DMF)_{10} \cdot (H_2O)_8]_n$ (abbreviated $[Zn_2L^c(bpdC)]_n$), was obtained under solvothermal conditions and shows a two-fold interpenetrating 3D network with 57% solvent accessible volume (Figure 1.2).^[54] The channels in the a and c directions possess dimensions of $6.2 \times 6.2 \text{ \AA}$ and $6.2 \times 15.7 \text{ \AA}$, respectively. Due to the diagonal displacement of the network, all Mn(III) ion sites are accessible through the channels. This homochiral MOF was examined for asymmetric olefin epoxidation reactions, and it was shown to effectively catalyze the epoxidation in 82% ee (Scheme 1.6).



Scheme 1.5 Chiral bridging Mn-salen complex and the achiral ligand H_2bpdC .

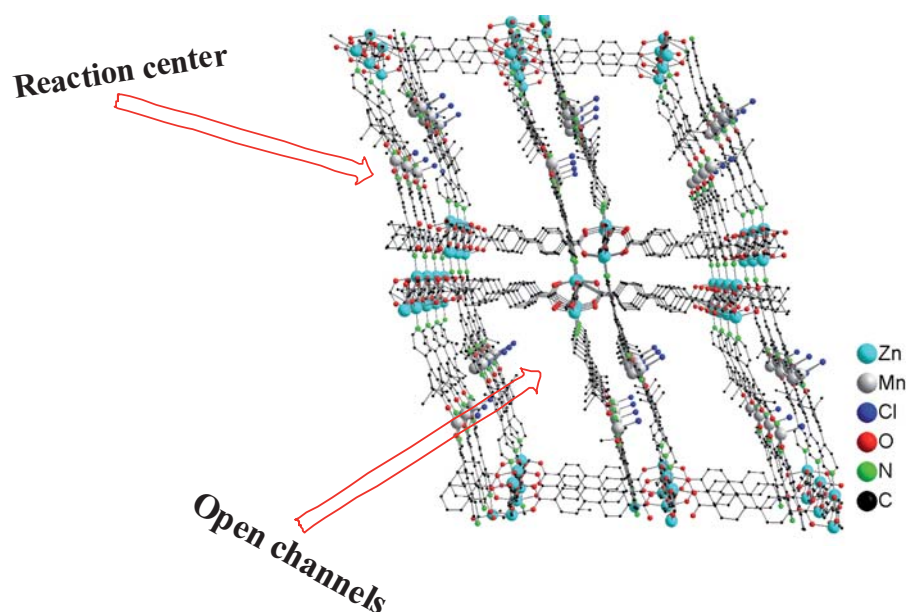
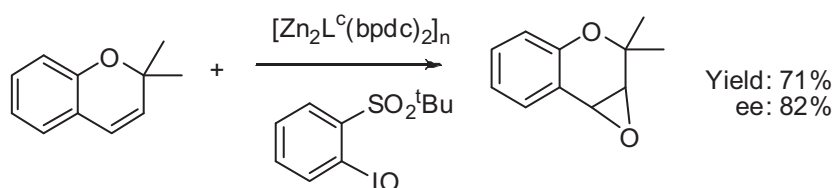
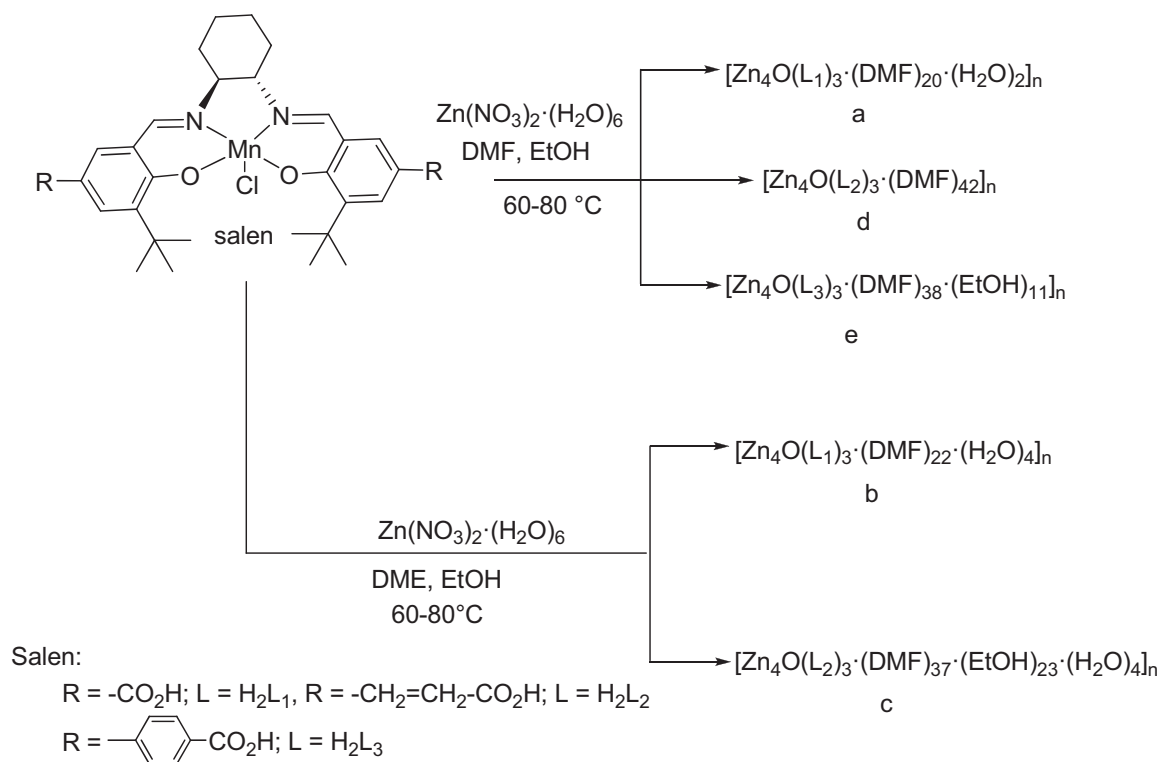


Figure 1.2 Pictorial representation of the open channels and catalytic active sites of compound $[\text{Zn}_2\text{L}^a(\text{bpdc})]_n$



Scheme 1.6 Asymmetric epoxidation catalysed by the homochiral MOF $[\text{Zn}_2\text{L}^c(\text{bpdc})]_n$.

Chen *et al.* reported a mixed metal organic framework (M'MOF), formulated as $[\text{Zn}_3(\text{BDC})_3\{\text{Cu}(\text{Pyen})\} \cdot (\text{DMF})_5 \cdot (\text{H}_2\text{O})_5]_n$ (H_2BDC = 1,4 benzenedicarboxylic acid and H_2Pyen = 5-methyl-4-oxo-1,4-dihydro-pyridine-3-carbaldehyde), containing 36 tessellated $\text{Zn}_3(\text{BDC})_3$ 2D sheets that are pillared by $\text{Cu}(\text{Pyen})$ to form a 3D network.^[55] This compound has slightly greater D_2 -surface than H_2 -surface interactions, while D_2 - D_2 interactions are lower than H_2 - H_2 interactions. Interestingly, Lin *et al.* reported isoreticular chiral metal organic frameworks (CMOFs) which are constructed from $[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CR})_6]$ (R = organic linker) SBUs and systematically elongated dicarboxylate struts that are derived from chiral Mn-salen catalytic subunits (Scheme 1.7).^[56]



Scheme 1.7 Synthetic scheme of compounds **a-e**.

Compounds **a-e** are highly effective catalysts for the asymmetric epoxidation of a variety of unfunctionalized olefins up to 92% ee. The rate of the epoxidation reaction depends on the dimensions of the open channel of the CMOFs. These compounds can be reused after catalytic transformations.

1.3 Single Molecule Magnets (SMMs)

In the early 1990s, the discovery of single molecule magnets (SMMs) created a new research field in physics and chemistry.^{[57],[58]} The final goal of this research activity is to modulate the quantum properties of these nanosized magnets in order to store and address a large amount of information in specialized devices and to provide basic components for future quantum computers.^{[59],[60]}

SMMs are nanoscale magnetic molecules that exhibit slow relaxation of magnetization at low temperatures, *i.e.* below their blocking temperature, T_B .^{[61],[62]} The main requirements for observing such behavior in molecules are a high spin ground state (S) and a significant negative zero-field splitting (D) of that ground state. The negative axial anisotropy ($D < 0$)

removes the degeneracy in the M_s levels of the ground spin state, placing higher magnitude levels at lower energies. The selection rule, $\Delta M_s = \pm 1$, for allowed transitions results in an energy barrier (U), separating the two lowest energy levels, $M_s = \pm S$. The spin reversal energy barrier will be $U = S^2 |D|$ and $U = (S^2 - 1/4) |D|$ for integer and half-integer S values, respectively. A positive D value causes $M_s = 0$ levels to be lowest in energy, such that there is no energy cost for losing direction of the spin (*i.e.* in going from $M_s = +S$ to $M_s = 0$). This means that for a molecule to behave as a SMM, it should have a negative D value. Experimentally, a SMM shows superparamagnet-like properties, exhibiting both a frequency-dependent out-of-phase alternating current (ac) magnetic susceptibility signal and a hysteresis plot of magnetization versus applied direct current (dc) magnetic field.

The field of SMMs, or molecular nanomagnets, started with the mixed-valence complex, $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4] \cdot (\text{HOAc})_2 \cdot (\text{H}_2\text{O})_4$ (abbreviated Mn_{12}Ac).^{[63],[64],[65],[66],[67]} Mn_{12}Ac contains twelve manganese ions, in which there are four Mn(IV) ions and eight Mn(III) ions. All of these Mn(IV) and Mn(III) ions are independently ferromagnetically coupled with $S = 3/2$ and $S = 2$, respectively. Since four Mn(IV) ions are coupled antiferromagnetically with eight Mn(III) ions in the cluster, the total spin is $S = 8 \times 2 - 4 \times 3/2 = 10$ and it therefore possesses $M_s = +10$ to -10 , which is divided by a potential energy barrier of around 50 cm^{-1} (as $U = S^2|D|$) (Figure 1.3).

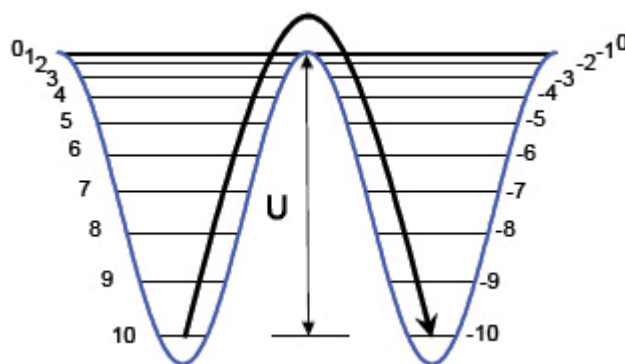


Figure 1.3 Energy of a classical $S = 10$ magnetic moment as a function of the angle between the moment and the main anisotropy axis (green). The horizontal lines are the energies of the spin microstates belonging to the $S = 10$ multiplet.^[57]

The ac magnetic susceptibility measurements enable the measurement of the relaxation rate. In this process, the susceptibility of a sample is measured using a small ac magnetic field that switches direction at a fixed frequency. As the switching frequency starts to approach the

relaxation rate for the magnetization of the molecules, the in-phase, or real component, of the ac susceptibility (χ') starts to decrease, while the out-of-phase, or imaginary component, of the ac susceptibility (χ'') increases. Since the energy levels are thermally activated, the energy barrier (U_{eff}) and the relaxation rate (τ) of the molecule can be estimated by using an Arrhenius plot according to the Arrhenius expression,

$$\tau = \tau_0 e^{(U_{eff}/K_B T)}$$

where τ_0 is a pre-exponential factor and U_{eff} is the energy barrier to reverse the direction of magnetization in the molecule. A plot of $\ln(\tau)$ versus $1/T$ (T = temperature) of this molecule is linear, and the slope and intercept obtained correspond to U_{eff} and τ_0 , respectively.

Although most SMMs are based on polynuclear transition metal complexes, trivalent lanthanides also play a special role because of their unique magnetic properties.^[68] Some lanthanide ions have a significant spin and/or a large intrinsic single-ion anisotropy arising from the large, unquenched orbital angular momentum; therefore, lanthanide ions have become attractive candidates for constructing new SMMs.^[69] Murugesu *et al.* have recently reported a Dy₄ butterfly compound that displays the largest anisotropy barrier (~170 K) reported for a polynuclear species.^[70] Interestingly, even mononuclear complexes can show strong, slow relaxation behaviour at relatively high temperatures, as reported by the Ishikawa group.^[71] In this regard, clusters of mixed 3d-4f metals are of considerable interest because a combination of properties may allow the observation of high spin clusters with a large anisotropy resulting from magnetic interactions between the ions. For this reason, a number of polynuclear heterometallic 3d-4f clusters have recently been reported,^{[72],[73]} some of which display SMM behavior.^{[73],[74]}