1.1. Abstract

This chapter describes the chiral porous metal-organic frameworks (MOF's) and their applications towards enantioselective separations, asymmetric catalysis and nonlinear optics. Chiral porous metal-organic frameworks constructed from reduced Schiff base ligands and the scope of present investigation are also discussed.
1.2. Introduction

The significance and impact of self-assembly are demonstrated by the porous zeolites that combine the acidic properties of the aluminosilicate with the channels and pores of the supramolecular structure to generate catalytically important materials. The presence of cations inside the channels and cavities of zeolites also make them ideal choices for ion exchange process. They have varied practical applications in the production of many consumer products such as gasoline, detergents etc. In light of importance of chirality in biological and catalytic process, there have been tremendous research efforts devoted to the development of chiral zeolites. Several attempts to synthesize chiral zeolites found to be unsuccessful. Special design strategies are needed to prepare chiral zeolitic type porous materials that may find application in chirotechnology.

On the other hand, a major research effort has focused on using the molecular building block approach to generate analogous materials with 3D organic, metal-organic and inorganic frameworks. Strategies for the construction of these solids have utilized metal-ligand coordination, hydrogen-bonding interactions and other non-covalent interactions to link their molecular components. Number of such frameworks have been found to exhibit desirable zeolitic properties such as stability and micro-porosity of the framework, guest exchange, gas storage and selective catalytic activity. Recently there has been considerable interest in synthesis of host frameworks with chiral cavities. These solids have potential applications in the separation of enantiomers and in asymmetric catalysis. Especially chiral porous metal-organic frameworks are found to be most reliable catalysts for heterogeneous asymmetric catalysis. Self-assembly of the metal ions linked together by organic bridging ligands lead to the generation of metal-organic frameworks (MOF’s). Various structures with interesting composition and topologies have been produced through judicious choice of chiral ligand and metal coordination to construct chiral porous materials with defined pore size. Synthesis and applications of some of the
chiral porous metal-organic frameworks and the aim of the present investigation are described below.

1.2.1. Homochiral porous MOF’s constructed from achiral ligands

Spontaneous resolution of an achiral compound on crystallization in the absence of any chiral source is of great interest in recent years. There are several examples of achiral molecules including simple metal salts which can crystallize in chiral space group. One of the serious inaccuracies for such systems that although single crystals of such compounds lead to homochiral crystals, in bulk sample it may be racemic. Ayoma and coworkers recently reported an interesting example of homochiral crystallization of that are built from achiral components. They treated Cd(NO$_3$)$_2$·4H$_2$O with achiral 5-(9-antharacenyl pyrimidine) (L$^1$) and a helical coordination polymer with composition of Cd(L$^1$)(NO$_3$)$_2$(H$_2$O)(EtOH) (1) was obtained. The Cd$^{2+}$ center adopts octahedral geometry with two pyrimidine ligands (equatorial cis), water and ethanol (equatorial cis), and two nitrate ions (axial trans). X-ray crystallographic analysis reveals that this coordination polymer crystallizes in monoclinic $P2_1$ space group and exhibit helical nature through metal-ligand coordination. Interestingly, adjacent helices adopt the same handedness and linked by the intrastrand H$_2$O – nitrate hydrogen-bonding interactions. Compound L$^1$ also forms achiral ($Pbca$) trihydrate adduct Cd(L$^1$)(NO$_3$)$_2$·3H$_2$O having nonhelical pyrimidine-Cd$^{2+}$ zigzag chains (Scheme 1). Both chiral and achiral coordination polymers are interconvertable to each other in the solid state upon exchange of volatile ligands. They used the seeding technique to control the chirality of these coordination polymers.
1.2.2. Homochiral porous MOF’s constructed from chiral ligands

One of the easy ways for the synthesis of chiral porous solids is to combine metal salts with well designed chiral ligands. The use of chiral ligand will ensure the chirality in the resulting network structure. Recently, Hosseini and coworkers have designed and synthesized a chiral tecton to coordinate metal centers and generated a perfectly polar 1D network (Figure 1). The ligand (L$^2$) consists of a pyridine group on one end and a C$_2$-symmetric 2, 6-bis (oxazolyl)-pyridine on the other end, and is thus chiral owing to the use of optically active oxazoline groups. Slow diffusion of EtOH solution of Co(II)Cl$_2$ into CHCl$_3$ solution of L$^2$ afforded crystals of X-ray quality. Crystal structure analysis revealed that metal-ligand coordination leads to perfectly polar 1D coordination polymer with chiral voids. These voids are occupied by CHCl$_3$ molecules. It is well known that polar solids have potential applications towards nonlinear optics.
Figure 1. 1D Perfect polar network built from Co(II) and a chiral tecton $L^2$. 
Recently, Kimoon and coworkers have demonstrated the use of homochiral metal-organic porous material for enantioselective separation and catalysis.\textsuperscript{10} The homochiral open-framework solid having the formula of \([\text{Zn}_3(\mu_3-O)(L^3\cdot H)_6]\cdot 12\text{H}_2\text{O}(\text{D-POST})\) was prepared by the reaction of \(\text{Zn}^{2+}\) with enantiopure chiral building block derived from D-tartaric acid. The enantiomorphic L-POST is obtained from the enantiomer of \(L^3\) and the \(\text{Zn}^{2+}\) ion under same condition. In D-POST, three zinc ions are held together with six carboxylate groups of the deprotonated chiral ligand \(L^3\) and bridging oxo group, to form a triangular unit, in which a three-fold axis parallel to the \(c\)-axis passes through the center of the trinuclear unit. The trinuclear units are further interconnected through coordinate covalent bonds between the zinc ions and pyridyl group of \(L^3\) to generate 2D infinite layers consisting of large edge-sharing chair shaped hexagons with triangular unit at each corner (Figure 2).

Most notably, large 1D chiral channel exists along the \(c\)-axis with side length of \(\sim 13.4\ \AA\). The solvent access area of D-POST estimated to be \(\sim 47\%\) and these voids are occupied by 47 water molecules per unit cell. The presence of accessible chiral pores in D-POST allows enantioselective inclusion studies. Enantioselective inclusion of chiral metal complexes was studied by using racemic \([\text{Ru}(2,2'^{-}\text{bipy})_3]\text{Cl}_2\) and ethanol suspension of L-POST. Such enantioselective inclusion of chiral metal complexes in porous materials is unprecedented. The pyridyl groups in D-POST were used to catalyze transesterification reactions. Although the enantiomeric excess in the product of transesterification was rather low (\(\sim 8\%\)), the enantioselectivity is unprecedented because this asymmetric induction was observed for reaction promoted by a modular porous material (Scheme 2). This creative work triggered interest in using the chiral metal-organic porous materials for asymmetric catalysis. The success of asymmetric catalysis with this kind of porous metal-organic frameworks was realized only very recently.\textsuperscript{6c}
Figure 2. (a) Chiral ligand $L^3$, (b) Trinuclear building unit in POST-$L^3$, (c) trigonal channels of D-POST, (d) hexagonal framework of POST-$L^3$ that formed from trinuclear building units.

Scheme 2

Lin and coworkers have designed a variety of chiral bridging ligands based on atropisomeric $1,1'$-binaphthyl framework. These chiral bridging ligands with twisted di carboxylate group leads to 1D, 2D and 3D MOFs. When enantiopure $2,2'$-
dihydroxy-1,1'-binaphthylene-6,6'-dicarboxylic acid ($H_2L_4$) was treated with various metal salts under slightly basic conditions, 1D homochiral MOF's 2-6 with interesting topologies were obtained (Scheme 3). They stated that heterogenation of Noyori's catalysts could be achieved by insitu formation of chiral porous hybrid solids such as 8 and 9 through the reaction of zirconium tert-butoxide with chiral bisphosphine/Ru complexes functionalized with phosphonic acid groups, 7 (Scheme 4). Nitrogen adsorption measurements demonstrated that these hybrid solids are highly porous with rather wide pore size distributions. The total BET surface areas of the solids ranges from 328 to 475 m$^2$g$^{-1}$ with microporous surface area of 60-161 m$^2$g$^{-1}$ and pore volumes of 0.53-1.02 cm$^3$g$^{-1}$. The heterogeneous catalysts 8a and 8b show exceptionally high activity and enantioselectivity in the hydrogenation of aromatic ketones, 10. With 0.1 mol % of catalyst 8a enantioselectivity up to 99% has been achieved. Interestingly, these porous binaphthol derived Zr phosphonate catalysts provide enantioselectivity superior to that of the parent homogeneous counterpart, the binap/RuCl$_2$/dpen (dpen = 1,2-diphenylethlenediamine) system developed by Noyori et al.$^{12}$ The two other catalysts 9a and 9b are also used for the asymmetric hydrogenation of $\beta$-keto esters (12) with good enantioselectivities.

Scheme 3
$7a \ R^1 = P(O)(OH)_2, \ R^2 = H$

$7b \ R^1 = H, \ R^2 = P(O)(OH)_2$

$8a \ L-L = (R,R)$-dpen

$8b \ L-L = (R,R)$-dpen

$9a \ L = DMF$

$9b \ L = DMF$

Scheme 4
1.2.3. Homochiral porous MOF’s constructed from chiral reduced Schiff base ligands

Transition metal complexes with chiral Schiff base ligands are known for some time and found applications towards asymmetric catalysis, nonlinear optics and supramolecular chemistry. Recently tremendous research efforts have been devoted to the synthesis and structural analysis of metal complexes with chiral reduced Schiff bases. Because of their greater flexibility generated by reduced Schiff base -CH₂-NH- backbone and the influence of ligand chirality often leads to novel supramolecular networks by self assembly process. It is well known that, the conformational changes in flexible ligands coordinated to metal ions can generate different but closely related network architectures. The conformationally flexible reduced Schiff base ligands are ideal choice for this purpose. These metal complexes have also potential applications towards solid state conversion, DNA cleavage activity and in asymmetric catalysis.

Scheme 5

Vittal and coworkers have reported an interesting example of 3D homochiral porous metal-organic framework using the chiral reduced Schiff base N-(2-hydroxybenzyl)-L-alanine (H₂sala). Reaction of H₂sala with Zn(OAc)₂ in presence of NaOH gave a crystalline powder, [Zn₂(Sala)₂(H₂O)₂] (14). X-ray crystal analysis of this complex revealed that Zn(II) adopts distorted square pyramidal geometry and the apical position is occupied by a water molecules. These metal
coordinated water molecules are intermolecularly hydrogen bonded to carboxylate groups and a 3D hydrogen bonded network with chiral channels is produced (Figure 3). Topochemical conversion of these hydrogen bonded network generate porous 3D homochiral MOF \([\text{Zn}\{\text{sala}\}_n]\) (15) (Scheme 5; Figure 4). A homochiral 3D Cu(II) MOF that is isostructural to 15 was also obtained in a topochemical conversion. This work represents the “solid state supramolecular synthesis” of MOF. Same authors very recently reported an intriguing example of porous helical coordination polymer with water helical chains inside the channels.\textsuperscript{16h}

**Figure 3.** 3D Hydrogen bonded structure of \([\text{Zn}_2\{\text{Sala}\}_2(\text{H}_2\text{O})_2]\) (14) with chiral channels.
Ray and coworkers recently reported a self-assembled chiral capsule of an octameric Cu(II) complex by using chiral reduced Schiff base N-(2-hydroxybenzyl)-L-histidine (H₂hist) (Figure 5). X-ray analysis shows that unit cell contains two slightly different cup shaped cyclic tetramers. These cyclic tetramers are on the top of each other, thus forming a capsule bound through eight hydrogen bonding interactions between the imidazole NH groups of one tetramer and nonbonded carboxylate-oxygen atoms of the other tetramer. This capsule has four guest pyridine molecules trapped inside the cavity, in which two of the pyridine molecules are held with a combination of hydrogen bonds and Cu(II) coordination.\(^\text{16g}\)
1.3. Aim of the present investigation

Due to the significant applications of organic and inorganic (or coordination polymers) porous materials in diverse fields, there have been extensive research attention towards design of new host-guest systems for practical applications. The organic porous solids are designed by considering molecular shape, symmetry, and intermolecular interactions such as hydrogen bonding, weaker halogen···halogen, electrostatic and van der Waals interactions. On the other hand, inorganic porous solids are designed primarily by considering metal-ligand coordination, coordination geometry, chemical structure of the organic ligand, metal to ligand ratio, and the coordinating nature of the anions. Recently, significant research efforts have been devoted to combine the above two approaches. Although numerous chiral porous materials are known with hydrogen bonded organic and metal-organic frameworks, there has been shortage of chiral porous solids with organic-inorganic hybrid materials assembled through hydrogen bonds.

While some metal complexes of Schiff bases derived from salcylaldehyde and (R) or (S) α-methylbenzylamine are known, no complex of its reduced analogues is reported. We have attempted to synthesize and structurally characterize the copper(II) complexes with bidentate chiral reduced Schiff bases HL to HL. Hydrogen bonding capability and patterns of these ligands play a key role in the formation of various types of molecular assemblies. The results and interesting features are summarized in Scheme 6. The details of these investigations form the subject matter of this thesis.
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Chapter 5

1. Selective inclusion of chloroalkanes
2. Enantio-specific inclusion of chiral 1,2-dichloroethane rotamers
3. Chiral voids

Chapter 2

1. Chiral host-guest system
2. Stabilisation of guest molecules via O-H···O interactions

Chapter 3

1. Helical self-assembly via activated C-H···O interactions
2. Retains this feature in solvated and unsolvated forms

Chapter 4

1. Perfect polar host and guest alignment
2. Enantio-specific inclusion of 1,2-dichloroethane rotamers
3. Enantio-specific inclusion of 1,2-dibromoethane rotamers
4. Chiral channels

Scheme 6
Chapter 1

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1.4. References


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Chapter I

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