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Chapter

Chirality in Porous Functional Materials

Shumaila Ashraf and Bo Wang

Abstract

Recently crystalline porous functional materials have specifically captured the scientist's attention, because of their high surface area coupled with many unique chemical and physical properties. These frameworks can be efficiently tailored to induce chirality for asymmetric catalysis and enantiomeric separation. Chirality can be introduced either through bottom up assembly or by post-synthetic modification. Compared to the traditional chiral catalysts, they are highly stereo-selective, reproducible and environmentally benign. They also have a great potential to be used as asymmetric photo-catalysts with the combination of photoactive group and chiral center in to one molecular architecture, providing the advantages of atomically economic structure design. On account of their high stability, large number of active sites, permanent porosity, easy recovery and reuse, they can be considered as excellent candidates to fabricate efficient and economical green chiral catalysts of commercial interest.

Keywords: asymmetric catalysis, chiral heterogeneous photocatalysis, enantiomeric separation, metal organic frameworks, covalent organic frameworks

1. Introduction

To design a crystalline material that contains both chirality and porosity in to one framework is still a big challenge [1]. There are many inorganic frameworks with chiral crystal structures and some zeolite frameworks like LTJ, ITQ-37, CZP, BEA, SFS and STW have intrinsic chirality but their synthesis is full of challenges [1–3]. So far, different chiral induction methods and chiral structure directing agents has been applied to transfer chirality in inorganic frameworks but all of them have a limited success [1, 4]. In contrast to the traditional chiral materials as mentioned above, there are two emerging classes of chiral porous materials known as metal organic frameworks (MOFs) and covalent organic frameworks (COFs) that can be efficiently tailored to induce chirality for asymmetric catalysis and enantiomeric separation. As compared to the zeolite syntheses, homochiral MOFs/COFs can be efficiently constructed using chiral molecules as primary linkers or as supplementary or auxiliary ligands [5]. Herein, we will focus on recent advances in the syntheses of chiral microporous MOFs and COFs, their different properties and application e.g., enantioselective adsorption [6], chiral chromatographic resolution [7, 8], membrane separation [9], their specific structures and advantages over the traditional chiral materials.

2. Synthesis of porous chiral frameworks

Two aspects are notable while discussing chirality in solid materials; either the components of the framework are chiral, or the arrangement of the components in the solid framework is chiral [10]. For the development of chiral materials different strategies have been used, which include the introduction of chiral ligands or chiral templates, control of the chiral physical environment, and post-synthetic modification of the organic struts or the metal nodes through guest exchange [11, 12]. So the three most commonly used strategies for synthesizing homo-chiral microporous materials are, direct synthesis, chirality induction synthesis and post-synthetic modification [13]. Among these, the most successful strategy is to use enantiopure organic linkers (direct synthesis) or the chiral co-ligands to control the stereochemistry at the metal centers. Below is the detail of these strategies.

2.1 Chiral structures from chiral building blocks

2.1.1 Direct synthesis

In order to synthesize chiral MOFs or COFs for specific applications the term "design synthesis" is usually used, according to which the resulting frameworks components are first carefully designed to utilize them for framework construction. In addition during the synthesis, environment and conditions are also carefully controlled for the efficient construction of solid materials. In general a number of different synthesis methods have been developed and reported so far, which include solvothermal synthesis, ionothermal, microwave assisted synthesis, electrochemical synthesis, mechanochemical synthesis and sonochemical synthesis [14, 15].

Most of the chiral materials are being synthesized using design synthesis by direct or bottom up strategy, in which the homochirality in the resulting framework comes from the starting materials. Such type of the synthesis is also known as "chirality conversion process" [16]. In 2015 Jian Zhang and coworkers synthesized a homochiral MOF "FIR-28" (Fujian Institute of Research) an 8-fold interpenetrating srs-type MOF based on (**Figure 1**). The synthesis was based on direct solvothermal synthesis using the ligand of interest and metal salt, $Zn(NO_3)_2 6H_2O$ [17].
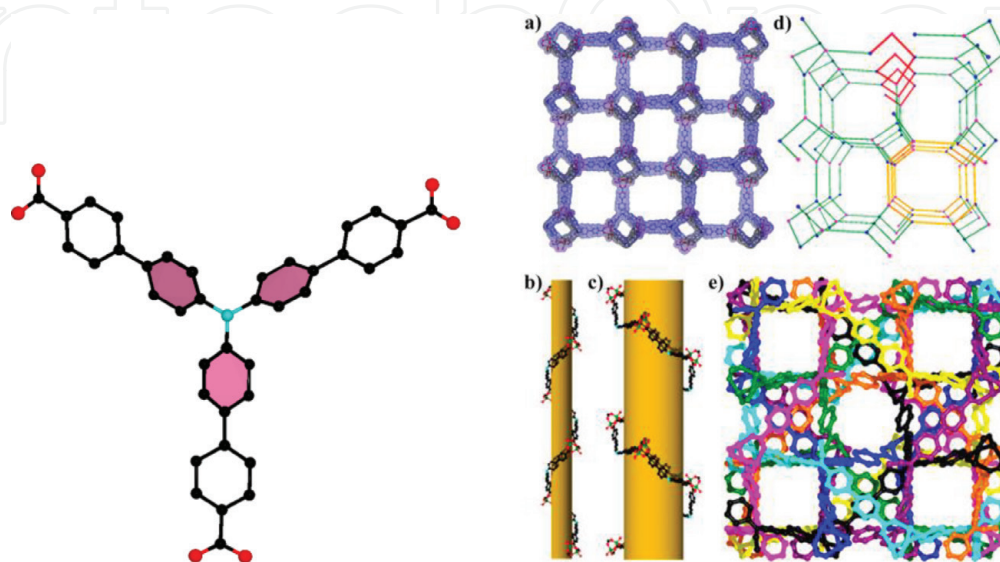

Figure 1.
Structure of the H_3TPA ligand, (a) single framework in FIR-28, (b) P-helix, (c) M-helix, (d) 3-connected srs network in FIR-28, and (e) 8-fold interpenetrating framework of FIR-28.
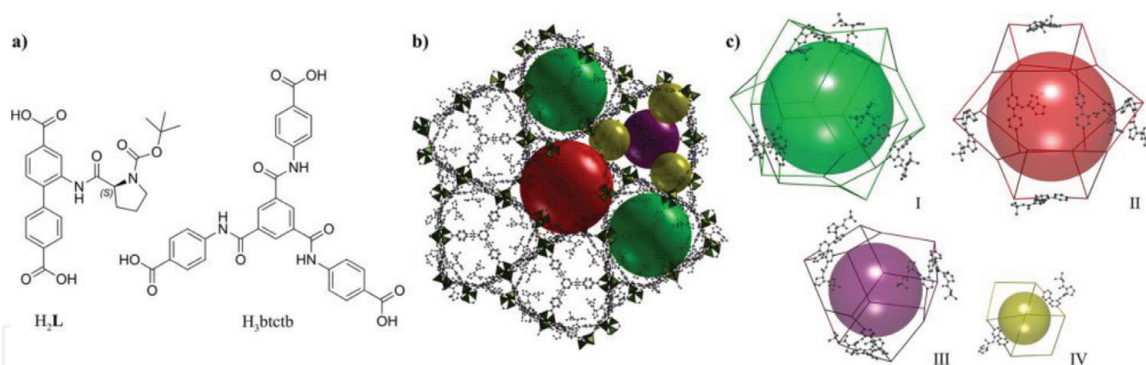
Figure 2.
(a) Linker used for the synthesis of DUT-32-NHProBoc, (b) crystal structure of DUT-32-NHProBoc and (c) simplified representation of four pore types highlighting bordering chiral ligands L₂.

A Boc-protected proline based homochiral MOF DUT-32-NHProBoc was synthesized by Stefan Kaskel group in 2014. The direct synthesis using proline based linker was not successful, so their group functionalized the ditopic linker (4,4′-biphenyldicarboxylic acid) with a chiral BOC-protected proline functionality (NHProBoc group) in three steps. They used two ligands a tritopic 4,4′,4″-[benzene-1,3,5-triyltris (carbonylimino)] trisbenzoate (btcb₃) and ditopic 4,4-biphenyldicarboxylate (bpdc₂) with Zn(NO₃)₂·4H₂O salt by direct synthesis (**Figure 2**) [18]. Using bottom-up approach, in 2016 a series of thermally stable chiral COFs, CTpPa-1, CTpPa-2 and CTpBD were successfully synthesized that exhibit a two-dimensional eclipsed layered sheet structure (**Figure 3**) [19].

Wei Wang and coworkers used a facile strategy for the direct construction of chiral functionalized COFs, LZU-72 and LZU-76 using chiral pyrrolidine-containing building blocks. They used 4,4′-(1H-benzo [d] imidazole-4, 7-diyl) dianiline as a rigid scaffold in order to attach chiral moieties. As a result chiral pyrrolidine-embedded building block (S)-4,4′-(-(pyrrolidin-2-yl)-1H-benzo [d] imidazole-4,7-diyl) dianiline was accordingly synthesized and used to successfully construct the above mentioned chiral COFs [20].

In 2005 Lin and coworkers synthesized a series of catalytically active chiral MOFs by designing a variety of chiral pyridyl, carboxylates and phosphonate bridging ligands with orthogonal functional groups using readily available chiral 1,1′-bi-2-naphthol (BINOL) [21]. While in 2012 their group synthesized a highly fluorescent chiral MOF from 1,1-bi-2-naphthol (BINOL) based chiral tetracarboxylate bridging ligand and a cadmium carboxylate infinite chain secondary building unit [22].

In 2008 Jian Zhang et al. described unusual integrated homochirality features in six 3D MOFs containing enantiopure building blocks embedded in intrinsically chiral topological quartz net. Direct synthesis using solvothermal method was used to construct these MOF materials from economically cheap ligands; D or L camphoric acid and divalent or trivalent metal ions in the presence of achiral template cations or molecules. Single crystal analysis revealed that all six MOFs have three homochiral features: 3D intrinsically homochiral net (quartz, quartz dual, srs net), enantiopure molecular chirality and homohelicity. It is noteworthy that chirality of molecular building blocks controls the absolute helicity in each case [23]. In 2014 this group further developed a low-cost homochiral MOF platform which was based on the inexpensive D-camphoric acid and formic acid. Size-selective crystallization of these homochiral camphorate metal organic frameworks was used for lanthanide separation. According to their findings, crystallization of these homochiral camphorate metal organic frameworks is highly sensitive to ionic radii of lanthanides and can be used to selectively crystallize a lanthanide element into predesigned MOF [24].
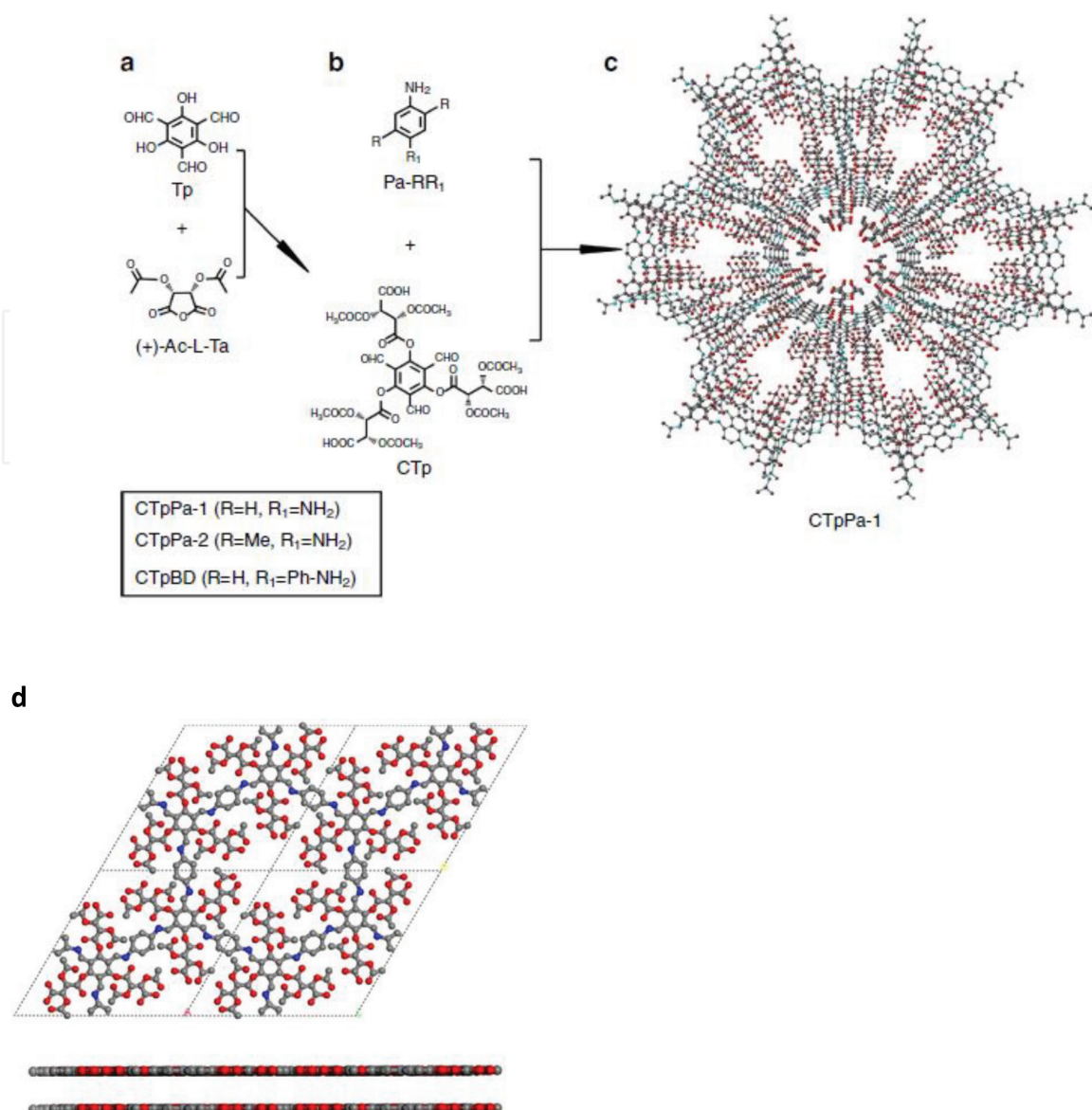
Figure 3.
(a) Synthesis of CTp through the esterification of Tp and (+)-Ac-L-Ta, (b) synthesis of chiral COFs through the condensation of CTp and Pa-RR1, (c) graphical view of CTpPa-1, (d) eclipsed structure of CTpPa-1. C, gray; N, blue, O, red; H omitted for clarity.

In 2014 two chiral micro- and mesoporous MOFs were synthesized using step-wise assembly of triple-stranded heptametallic helicates with six carboxylic acid groups. The mesoporous framework proved to be an efficient recyclable heteroge-neous catalyst when encapsulated with an enantiopure organic amine catalyst. The organocatalyst-loaded framework catalyze the asymmetric direct aldol reactions with significantly in proved stereo-selectivity in comparison to the homogenous organocatalyst [25]. In the past few years, the UiO family of MOFs with linear dicarboxylate organic linkers and $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$ SBUs has particularly been synthesized by direct synthesis method. These MOFs are an ideal platform to design highly efficient MOF catalysts because of their stability in harsh reaction conditions and broad range of solvents [26, 27].

2.1.2 Different ligands used for direct construction of crystalline chiral materials

Different chiral ligands have been used for the direct synthesis of chiral micro-porous frameworks, some of them are given in **Figure 4**.
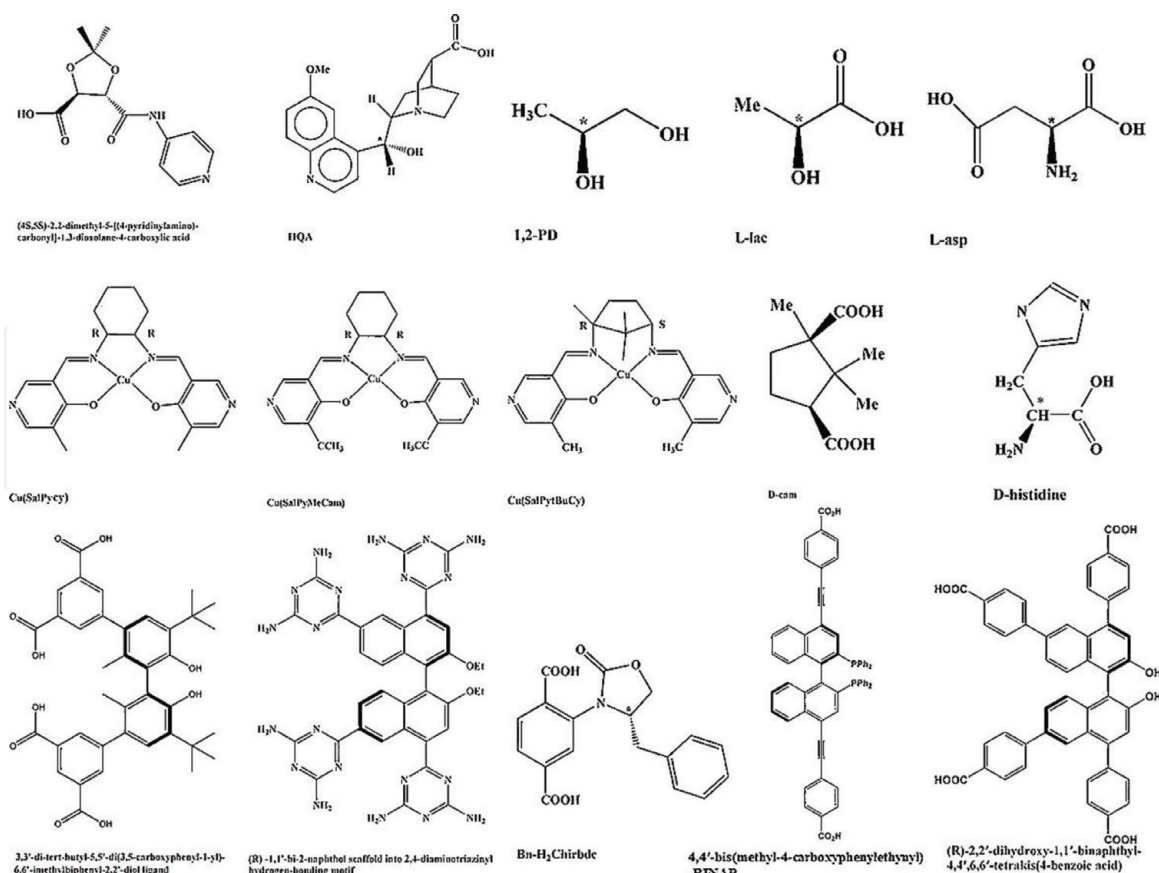
Figure 4.
Different chiral ligands used to construct chiral porous materials.

2.2 Chiral structures from achiral building blocks

In order to prepare a chiral crystalline material from achiral building units different strategies have been applied including, chiral templating, chiral induction, solvent effects, and chiral additive effects. The key feature in all of these processes is the transfer of chiral information from a chiral species to the nucleus of growing crystallite. For successful crystallization of chiral frameworks, such information transfer needs to be very specific, and probably requires quite strong directional bonding to the substrate crystal. That's the reason templating is rather a disappointing method of forming chiral crystals from achiral building blocks because it might cause framework collapse once the template is thermally removed [5].

In this chapter we will discuss some of the techniques that have been used by different research groups to synthesize chiral MOFs and COFs. One of the important aspects that should be kept in consideration is that the bulk sample must be homochiral. Different bulk measurement techniques have been developed and used so for, such as circular dichroism (CD) spectra, VCD spectrum, or multiple single-crystal for checking the homochirality of the bulk material [28, 29].

2.2.1 Chirality induction synthesis

In comparison to the direct synthesis, a little progress has been achieved in asymmetric crystallization of enantiopure or enantioenriched materials through chiral induction using achiral precursors. There is great deal of similarity between chiral induction by enantiopure additives and asymmetric catalysts used by organic chemists to synthesize chiral molecules. Although there is no direct proofs of how a chiral solvent or a chiral additive plays its role of induction, recent examples of chiral induction

Formula of chiral material	(BMIM)$_2$[Ni(HTMA)$_2$(H$_2$O)$_2$	[(CH$_3$)$_2$NH$_2$][In(thb)$_2$]·(DMF)$_x$	Mn$_3$(HCOO$_4$(adc)	NaZnPO$_4$·H$_2$O
Name or zeolite structure code	SIMOF-1 (St Andrews ionothermal MOF-1)	ATF-1P and ATF-1M (ATF, anionic tetrahedral framework)	Mn-1D and Mn-1L	CZP (chiral zeolite phosphate)
Key structural features	Anionic MOF with ionic liquid cation as template/guest	Anionic MOF with 2-fold diamond topology.	Neutral MOF with honeycomb channels	Anionic zeolite-type inorganic framework
Chiral symmetry	$P4_32_12$ and $P4_12_12$	$P4_122$ and $P4_322$	$P3_121$ and $P3_221$	$P6_122$ and $P6_522$
Chiral induction agents (CIA)	Chiral ionic liquid BMIM L-aspartate or BMIM D-aspartate	(−)-Cinchonidine for $P4_122$ or (+)-cinchonine for $P4_322$	D-Camphoric acid for Mn-1D with 32 symmetry; L-camphoric acid for Mn-1L with 31 symmetry; DL-camphoric acid for racemic Mn-1D/Mn-1L; L-glutamic acid for Mn-1D	(−)-Uridine 5′-phosphate (ump) for $P6_122$
What if CIA is not used?	Formation of achiral material with different structure (SIMOF-2)	Racemic twins	A different crystal structure, Mn (adc)	Racemic
Solvent	BMIM L-aspartate or BMIM D-aspartate	DMF or DEF	Mixed DMF and ethanol	Water
Crystallization temperature	110°C	120°C	120°C	80°C

Table 1.
A summary of asymmetric crystallization induced by chiral additives or solvents.

by additive/solvents (**Table 1**) suggest that chemical bonding interaction between additives and cationic metal sites might be the reasons of induced chirality [5].

A more recent discovery of chiral induction by Zhang et al. supports the above proposed mechanism that the chiral induction is likely to involve the coordinate bonding between framework metal sites and chiral additives. In 2010 their group explored the enantioselective effect of inexpensive asymmetric molecular catalysts such as enantiopure organic acid (camphoric acid) and naturally occurring amino acid (glutamic acid) for asymmetric crystallization of 3D crystalline porous materials from achiral building units. In this case, the absolute chirality of chiral MOF [Mn$_3$(HCOOH)$_4$]$^{2+}$ is determined by the chirality of D- or L-camphoric acid. Instead of chiral induction effect, it's more like an auxiliary chiral ligand effect (**Figure 5**). It is suggested that chirality control is attained through cooperative binding between enantiopure chiral reagents and achiral structural building units and that the enantiopure chiral reagents control the absolute chirality of crystals by participating in nucleation and crystallization processes but they are later on replaced by achiral ligands in the resulting crystals. **Scheme 1** illustrates solvothermal synthesis of crystals of (+)-[Mn$_3$(HCOOH)$_4$(adc)] (denoted by D) and (−)-[Mn$_3$-(HCOOH)$_4$(adc)] (L) [30].

An early example of chiral induction of porous solids by additives involves the use of chiral alkaloids to induce the absolute chirality of a microporous indium dicarboxylate. In 2008 a series of MOFs, ATF-1, ATF-1P or ATF-1M; (ATF anionic tetrahedral framework; P and M denotes handedness) were synthesized using
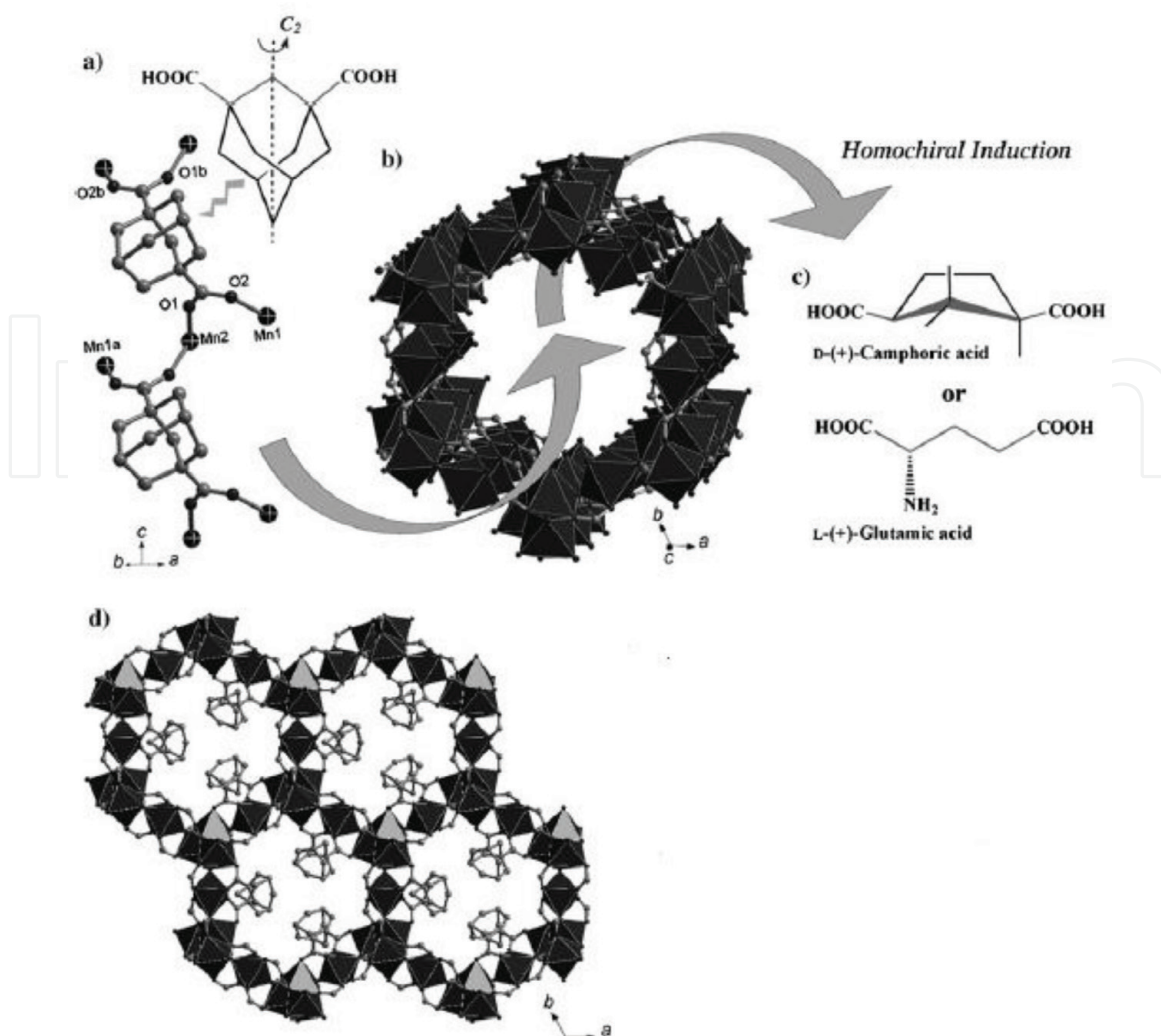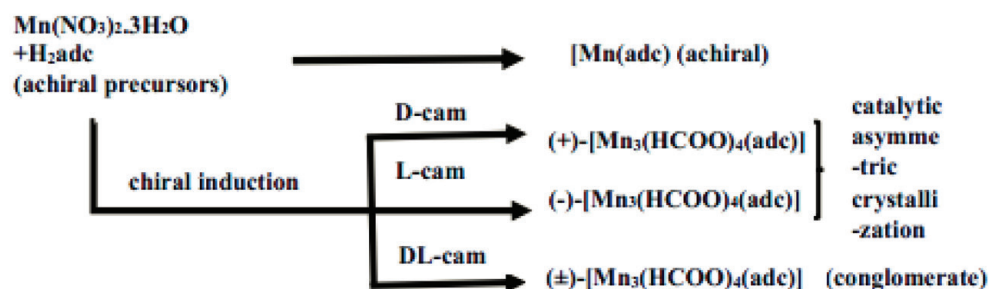
Figure 5.
(a) $[Mn(adc)]_n$ chain based on achiral adc ligand with μ_4 coordination; (b) porous $[Mn_3(HCOOH)_4]_n^{2+}$ channel based on inorganic Mn—O—Mn connectivity; (c) two types of enantiopure catalysts used for the synthesis and chiral induction of 1D; the direction of arrows show the possible mechanism of chiral induction. D-camphoric acid initially controls the absolute chirality of $[Mn_3(HCOOH)_4]_n^{2+}$ frameworks but is later displaced by adc. (d) 3D hybrid framework of 1D, showing the achiral $[Mn(adc)]_n$ chains attached to the wall of the nanosized channels.

solvothermal reactions of $In(NO_3)_3 \cdot xH_2O$ and ligand H_2thb with (or without) cinchonidine or cinchonine in two different solvents (1, DMF; 2, DEF) instead of using chiral solvents, chiral spectator solutes (−)-cinchonidine or (+)-cinchonidine were used to induce the chirality (**Figure 6**) [16].

In 2005 a 2D layered coordination polymer $Co(PDC) \cdot (H_2O)_2$ have been developed, which was comprised of two helical chains using an achiral ligand, pyridine-2,5-dicarboxylic acid (H_2PDC). Its synthesis did not involve any chiral reactant or solvent or any other auxiliary agent. Surprisingly, the resultant crystals were not racemic as investigated by the observation of strong signals in vibrational circular dichroism (VCD) spectra. Chirality might come from spatial organization of achiral building blocks in crystalline frameworks [31].

Recently a series of nine chiral 2D-COFs have been synthesized using (R)- or (S)-1-PEA as a chirality inducing catalyst, through imine condensations of Tp with diamine or triamine linkers, as indicated in **Figure 7**. Among these COFs, CCOF-TpTab exhibited greater enantioselectivity towards chiral carbohydrates in fluorescent quenching. After post-synthetic modification of the enaminone groups with Cu(II) ions, the solid was converted in to a recyclable heterogeneous catalyst which can be used for asymmetric Henry reaction of nitroalkane with aldehydes [32].

Scheme 1.
Illustration of four crystallization processes showing that camphorate ligand not only controls the absolute chirality of crystals, but also enables and catalyzes the growth of chiral crystals.
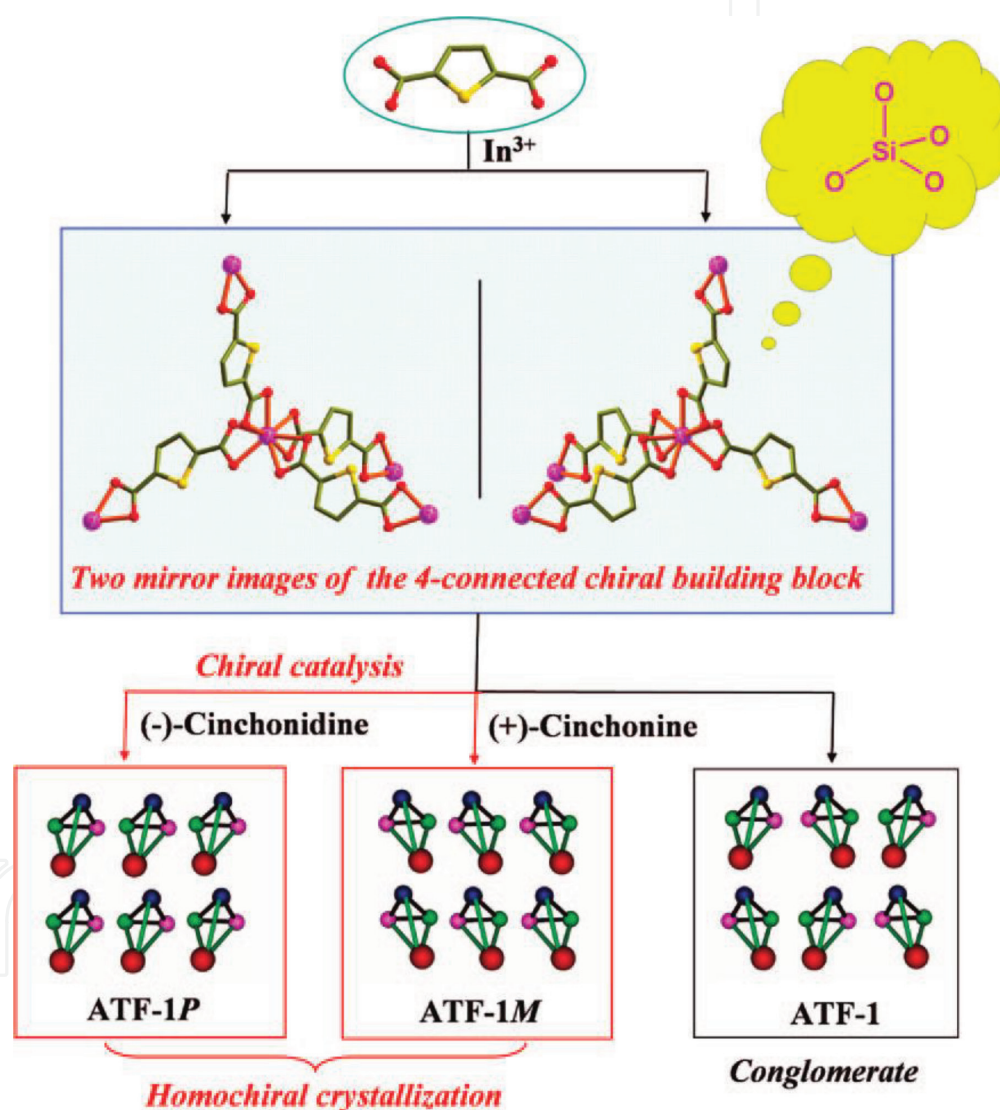

Figure 6.
Schematic illustration of the generation of conglomerate (ATF-1) or bulk homochirality (ATF-1P and ATF-1M) induced by (−)-cinchonidine or (+)-cinchonine from the basic 4-connected building block with achiral precursors.

2.3 Post-synthetic functionalization

MOFs and COFs can be modified to improve their catalytic properties through covalent and coordinate covalent PSM. A variety of active and chiral functional groups can be tethered to metal nodes and organic ligands to convert MOFs and COFs in to catalytically active materials. Through PSM, a single MOF can be
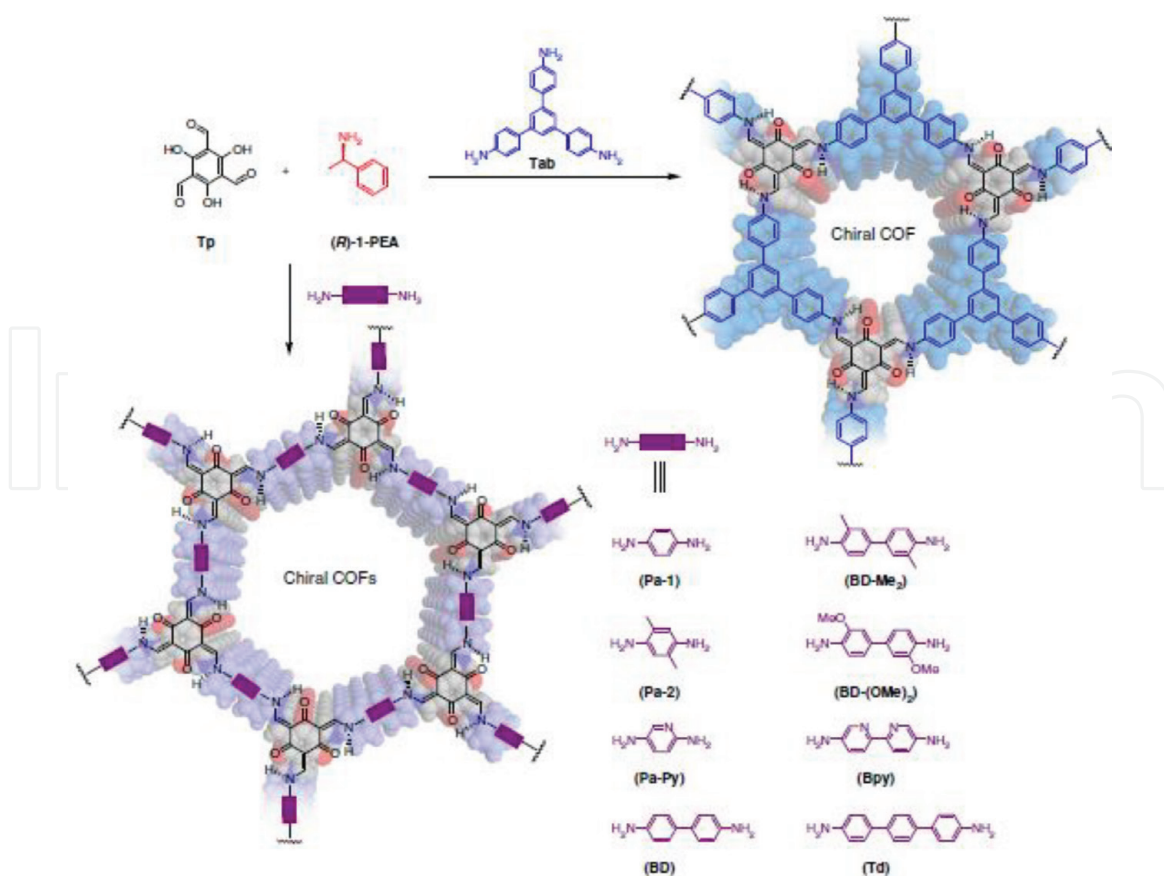
Figure 7.
Schematic demonstration of the synthesis of CCOFs. These CCOFs are synthesized from achiral precursors by chiral catalytic induction.

modified with several combinations of functional groups and thereby tested as a catalyst for different reactions [33].

Kimoon Kim and coworkers reported the first example of modifying an achiral MOF "MIL-101(Cr)", built from Cr^{3+} trimer SBUs and BDC [34] in to an active chiral catalyst. They modified MIL-101 (Cr) in to two chiral MOFs CMIL-1 and CMIL-2, by replacing the coordinated solvent with L-proline derivatives, [(S)-N-(pyridine-3-yl)-pyrrolidine-2-carboxamide] or [(S)-N-(pyridine-4-yl)-pyrrolidine-2-carboxamide respectively. The resulting chiral MOFs termed as MOPMs exhibited improved catalytic activities in asymmetric aldol reactions, including much higher enantioselectivity in comparison to free L-proline ligands [35].

2.3.1 Pore surface engineering

In 2014 the first example of pore surface engineering of stable imine linked COF was reported. Pore surface engineering allows a general principle for designing catalytic COFs and molecular design of COF skeletons by controlling the density and composition of the functional groups on the pore walls. Mesoporous imine-linked porphyrin COF [HC≡C]-X-H$_2$P-COF was used as a scaffold. Using the click reaction of this COF with pyrrolidine azide in the presence of a CuI catalyst in toluene-tert-butanol at 25°C yielded the corresponding [Pyr] X-H$_2$P-COFs (as illustrated in **Figure 8**). Pyrrolidine derivatives are renowned organocatalysts for Michael addition reaction [36, 37]. Engineering pyrrolidine units onto the pore walls generates aqueous organocatalytic COFs with a number of striking catalytic features, including enhanced activity, good recyclability, and high capability to perform transformation. The catalytic activity depends upon the density of the active sites on the pore walls [38].
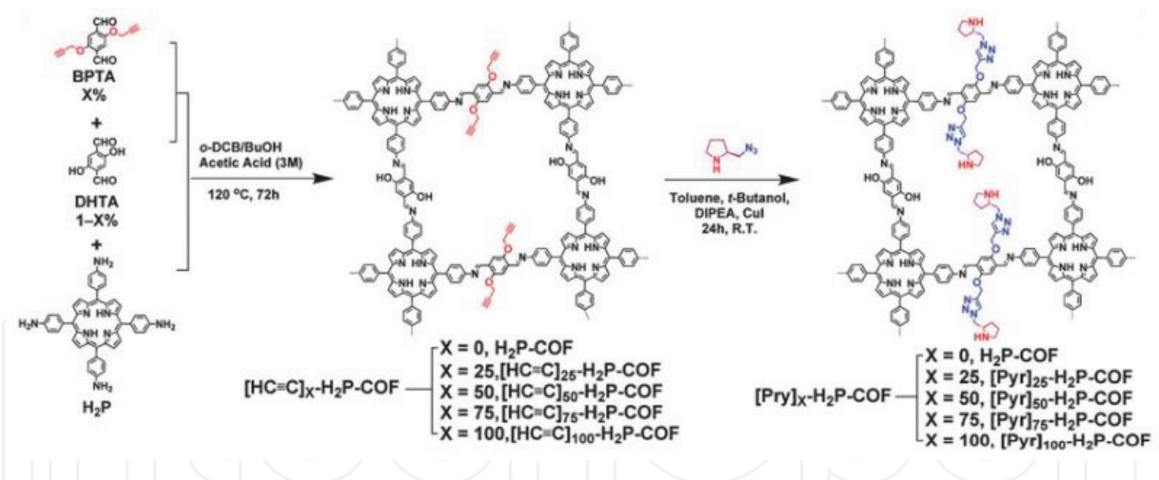
Figure 8.
The general strategy for the pore surface engineering of imine-linked COFs by a condensation reaction and click chemistries (the case for X = 50 was exemplified).

Recently Yong Cui and coworkers synthesized two isostructural 2D Zn (salen)-based CCOFs (chiral covalent organic frameworks) by co-condensation of chiral 1,2-diaminocyclohexane and trisalicylaldehydes alkyl groups. Chiral salen ligands such as (R,R)-1,2-cyclohexanediamino-N,N′-bis-(tert-butyl-salicylidene) are well-known ligands for asymmetric catalysis [39]. By post-synthetic metal exchange, the framework of these CCOFs can be modified for asymmetric catalysis. Their group postsynthetically exchanged Zn^{2+} ions with Cr, Fe, Mn and Co, and analyzed the improvement of efficiency in asymmetric catalysis, stereoselectivities and recyclability of catalyst [40].

3. Solvent-assisted ligand exchange (SALE)

Like molecular homogenous catalysts, MOFs allow for almost the same level of structural rectification, while their large surface area, permanent porosity, and heterogeneous nature facilitate rapid purification and better catalytic activity [26, 41–44]. Among all the chiral MOFs with improved stereo-selective catalysis reported so far, the most privileged examples are all directly crystallized from efficient chiral ligands, including, BINOL- and salen-based derivatives, but it is challenging to synthesize and grow large single crystals for structural elucidation and to prepare highly stereo-selective catalysts comparable or even extraordinary to their homogeneous counterparts [45–48]. Solvent-assisted linker exchange (SALE) have been proved to be incredibly effective for the synthesis of MOFs that are difficult to approach de-novo [33, 49–53]. According to this strategy crystals of a template MOF are placed in the excess solution of secondary linker, as the reaction proceeds the new linker replaces the original MOF linkers while the daughter framework retains the original MOF topology. In addition to the incorporation of desired linker, SALE also proved to be an effective method to incorporate many interesting properties in to the framework like, introduction of catalytically active moieties, incorporation of free carboxylic acid groups by functionalizing defect sites, and enhance proton conductivity as well as photochemical H_2 production. In 2015 Yong Cui and coworkers employed a genius approach of synthesizing chiral MOFs using direct synthesis and then by employing SALE they post-synthetically modified one of the chiral VO salen based MOF-2 in to mixed linker salen based MOF-2^{Cr} by exposing MOF-2 to a DMF/MeOH solution of [CrL₂Cl] at 60°C for 8 h which led to the partial replacement of units with

[Cr(salen)Cl] (2Cr) [12]. Chiral vanadium and chromium salen complexes are famous for their asymmetric catalysis of different types of organic reactions [54–56].

4. Properties and application of chiral porous frameworks

Homo-chiral microporous materials proved to be not only promising candidates for heterogeneous asymmetric catalysis but also enantioselective adsorbents or separators for the production of optically active organic compounds. Therefore the exploration of homo-chiral microporous materials towards the adsorption and diffusion of enantiomeric molecules is essential and important to promote these materials for chiral resolution [1]. Properly designed microporous MOFs and COFs with uniform, periodically aligned active sites have shown great potential in catalyzing shape-, size-, chemo-, region-, and stereo-selective organic transformations as well as fabricating optically active hybrid materials and devices.

4.1 Role of different MOFs in enantioselective adsorption and separation

In 2000 Kim el al. reported the synthesis of a homochiral metal organic framework (D-POST-1) that allows the enantioselective inclusion of metal complexes in its pores and catalyzes a trans-esterification reaction in an enantioselective manner. D-POSt-1 built up by the oxo-bridged tri-nuclear metal carboxylates clusters and enantiopure chiral ligand derived from D-tartaric acid. This was the first example of a porous homochiral MOF to be used for enantioselective adsorption. Presence of the pyridyl groups exposed in the channels also provides D-POST-1 with unique opportunities in catalysis and allows for the chemical modification of the channel environment. Its pore size and catalytic efficiencies can also be modulated by N-alkylation of N-pyridyl group. Treatment of ester-2 and ethanol with suspension of POST-1 (0.1 equivalents) in carbon tetrachloride at 27°C for 55 h provided ethyl acetate in 77% yield [57]. No or little trans-esterification occurs without POST-1 or with N-methylated POSt-1, respectively (**Figure 9**).

Xiong et al. prepared a new enantiopure chiral ligand HQA-(6′-methoxy-(8S,9R)-cinchonan-9-ol-3-carboxylic acid) from quinine, "an off-the-shelf anti-malarial alkaloid" and utilized it to synthesize a homo-chiral MOF [Cd(QA)$_2$]. The enantioselective separation activity of this MOF was investigated by solvothermal reaction of the powder sample of Cd(QA)$_2$ in the racemic 2-butanol solution at 100°C for 3 days. As a result, a crystalline sample of ((S)-2butanol)@[Cd(QA)$_2$ was analyzed by the single-crystal X-ray diffraction that revealed the inclusion of (S)-2-butanol in to the chiral cavity. The *ee* value of 2-butanol desorbed from ((S)-2butanol)@[Cd(QA)$_2$ was assessed to be approximately 98.2%. When larger racemic 2-methyl-1-butanol was used, the *ee* value of (S)-2-methyl-1-butanol obtained was reduced to only 8.2%. Such differences in selectivity for chiral molecules of different size suggest that an appropriate match between pore dimension and the size of chiral guest is the crucial factor for enantioselective adsorption [58].
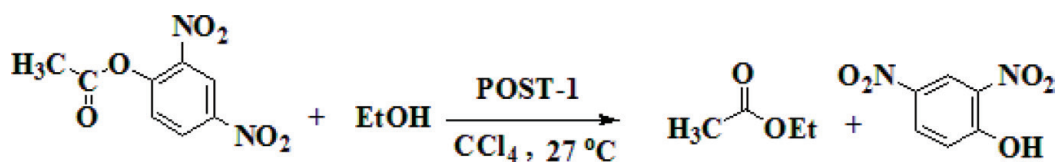
Figure 9.
Trans-esterification in the presence of POST-1.

Although several porous materials such as activated carbon, silica gel, zeolites, and various polymer resins proved to be useful stationary phases in gas chromatography, liquid chromatography and electro-chromatography, MOFs are far less explored for these applications. In 2007, Fedin and Bryliakov et al. reported the first example of utilizing a homochiral 3D porous Zn-MOF "$Zn_2(bdc)(L-lac)(DMF)$" in chiral liquid chromatography (LC) column for resolution of racemic mixtures of chiral alkyl aryl sulfoxides [59, 60].

In 2006 Rosseinsky and coworkers synthesized microporous chiral MOF [Ni_2 (L-asp)$_2$(bipy) using cheap and readily available amino acid (aspartic acid). Nine chiral diols, having very close functionalities were enantioselectively adsorbed on this chiral MOF at 278 K, which showed that a good match of size and shape between small chiral guest and chiral pore of the homochiral framework is the decisive factor for chiral resolution application. 2-Methyl-2,4-pentanediol demonstrated the highest enantiomeric excess of 53.7%, attributable that both hydroxyl groups of (S)-2-methyl-2,4-pentanediol are involved in hydrogen bonding within the chiral channels [61].

Nowadays membrane separation offers great potential owing to the outstanding prevalence over the traditional methods, such as low-energy consumption, large processing capacity, and a continuous mode of operation. Due to their well-defined porosity and stability, zeolites and mesoporous MOF membranes have attracted a huge interest in engineering applications, such as gas and liquid separations, membrane reactors and chemical sensors. However, it's still very challenging to synthesize these materials with required chirality, which is the core for chiral separation.

In 2012, first homochiral MOF membrane 'Zn-BLD' ($Zn_2(bdc)(L-lac)(dmf)$) was fabricated on a porous zinc oxide substrate through a reactive seeding technique. This membrane was used for the enantioselective separation of important chiral compounds especially drug intermediates which was a new step towards the potential development of sustainable and highly efficient chiral separation technique. Intriguingly, homochiral MOF membranes are expected to possess high enantioselectivity as a result of their open chiral channels or cavities and high permeation flux due to high porosity and low mass transfer resistance. Zn-BLD exhibits enantioselective separation of racemic MPSs with preferential adsorption ability to (S)-(MPS over (R)-MPS. At the feed concentration of 5 mmol L^{-1}, an *ee* value of 33.0% for R-MPS over S-MPS was obtained which was attributed to the different interactions of the two enantiomers with the Zn-BLD inner pores. Such a highly enantioselective separation approach brings advanced materials science to the forefront of a major society need [62].

In 2012, a highly sensitive chiral MOF sensor '**1**' with greatly enhanced enantioselectivity towards chiral amino alcohols in fluorescent quenching was built from 1,1′-bi-2-naphthol (BINOL) derived chiral tetracarboxylate bridging ligand and a cadmium carboxylate infinite chain secondary building unit. **1** shows higher sensitivity towards chiral amino acids with unprecedentedly high SV constants of up to 31,200 M^{-1} and an impressive enantioselectivity, with an enantiomeric quenching ratio [KSV(S)/KSV(R)] of 3.12 for 2-amino-3-methyl-1-butanol. Conformational rigidity of BINOL as well as pre-concentration of the quencher inside the cavities of **1** are the main factors for greatly enhanced detection sensitivity. The confinement effect of MOF cavities for chiral discrimination of analyte and the conformational rigidity of the sensing sites can be utilized to design new MOF materials for future sensing devices [22].

4.2 Metal-organic frameworks with designed chiral recognition sites

A vast majority of MOFs are prepared by using modular assembly, in which organic struts and inorganic joints are connected in three dimensional networks. Such type of modular assemblies results in the formation of two types of domains in

the frameworks, (i) sorting domain [63], whereby the pore apertures act as sieves based on size- and shape-selectivity or (ii) a coverage domain [64] wherein the internal pore surfaces interact non-specifically with guest molecules as a consequence of non-covalent binding forces. In 2010 team of Omar M. Yaghi and J. Fraser Stoddart employed a novel approach known as designer approach, to design active domains [65] with in the MOFs. By using the designer approach their team has successfully constructed new type of distribution domain, the active domains, where an ordered distribution of guests throughout the MOF is maintained by highly specific stereoelectronic control and these active domains are capable of stereoselective molecular recognition. In their reported work, they incorporated the dilocular (two chiral elements) struts (SS)-2 and (RR)-2 containing optically active dilocular bis-binaphthyl [22] crown-6, into (SS)-MOF-1020 and (RR)-MOF-1020 respectively. Such a precise placement of optically active organic struts inside MOF, pave the way well for the advancement of a range of exquisitely engineered chiral stationary phases for carrying out the separation of enantiomers by HPLC [66].

4.3 MOFs in asymmetric catalysis

4.3.1 Brief history and general requirements for MOF-based asymmetric catalysts

MOFs serve as heterogeneous asymmetric catalysts and their role in asymmetric catalysis was first demonstrated by Fujita et al. in 1994 who synthesized a crystalline porous coordination polymer catalyst for cyanosilylation of aldehydes [67]. Afterwards Aoyama and co-workers developed Ti complex based amorphous microporous solid catalyst for stereoselective Diels Alder reaction [68]. Although it was proposed that the incorporation of catalytically active units in the MOFs can promote the field of asymmetric catalysis but there was no proper report on asymmetric catalysis promoted by structurally well-characterized metal organic systems until 2000. The first homochiral MOF, "POST-1" exhibiting catalytic activity for an asymmetric chemical reaction was reported by Kim and coworkers [57]. Lin and coworkers in 2001 reported the first asymmetric catalysis promoted by metal ions at the nodes of framework [69]. In 2005 their group also adopted a systematic strategy to use privileged chiral ligands, such as BINOL for chiral MOFs used in catalytic asymmetric transformations [21]. In short there are many groups who have been working on the development of homochiral MOF based catalysts since 2005 to present noticeably Lin and coworkers, Hupp and Nguyen et al. and Kim and coworkers [47, 63, 68]. There are some general requirements to be fulfilled by homochiral MOF based catalysts, including close proximity of catalytic centers and chiral induction sites, large accessible pores/channels that allow facile diffusion of substrates and products, and ability to maintain structural integrity during the catalytic process. Due to stringent requirements for successful applications in asymmetric heterogeneous catalysis, the MOF based chiral catalysts are still scarce in literature and this area needs a lot of development [41].

4.3.2 Some examples of MOF-based catalysts

Although it's difficult to quote all the examples of MOF based heterogeneous catalysts since their discovery in 2000 until now, but we will try to discuss some of the recent examples in this chapter.

Chiral manganese salen complexes are highly effective asymmetric catalysts for olefin epoxidation. In 2006, Albrecht-Schmitt and coworkers synthesized a paddle-wheel-stabilized MOF using Mn salen complex and H_2bpdc ligand. The MOF-based catalyst confers higher stability, easier separation, recyclability, and substrate size selectivity, as compared to free catalyst [47].

In 2010 Tanaka et al. prepared Cu paddle wheel based chiral MOF (R)-3 and employed this MOF as a catalyst for the kinetic resolution of styrene oxide in the presence of different alcohols. They observed that the kinetic resolution was very sensitive to the structure of alcohols, with MeOH showing the highest conversion and enantioselectivity while bulkier alcohols e.g., EtOH, i-PrOH and t-BuOH, the conversion as well as enantioselectivity was decreased. They proposed a suitable mechanism and explained the reason for the high activity of (R)-3 in the presence of methanol. According to their analysis in the presence of methanol, evacuated MOF is transformed in to 2D in which the substrate is accessible to the Cu active site through diffusion. A pronounced color change was observed from black to green in MeOH during the transformation [45].

Network structure dependent catalytic activity of two chiral Cd MOFs was demonstrated by Lin and coworkers in 2007. They synthesized two Cd MOFs, **1** and **2**, using two different salts $Cd(NO_3)\cdot4H_2O_2$ and $Cd(ClO_4)\cdot6H_2O_2$ with (R)-6,6′-dichloro-2,2′-dihydroxy-1,1′-binaphthyl-4,4′-bipyridine respectively. They tried to generate heterogeneous asymmetric catalysts by activating Lewis acidic metal centers (namely, $Ti(OiPr)_4$) with the chiral dihydroxy groups that are present as the orthogonal secondary functionalities in the porous solids **1** and **2**. Treatment of **1** with $Ti(OiPr)_4$ led to an active catalyst (**1**.Ti) that efficiently catalyzes the addition of diethylzinc to aromatic aldehydes while mixture of **2** and $Ti(OiPr)_4$ under similar conditions did not show the catalytic activity. The absence of catalytic activity with the **2**/$Ti(OiPr)_4$ system is a consequence of the steric hindrance around the chiral dihydroxy groups which prevents the substitution of two isopropoxide groups by the binolate functionality [70]. Lin group made a number of remarkable efforts in developing MOF based active catalysts. In 2010 their group demonstrated a systematic design of eight mesoporous isoreticular CMOFs using copper paddle-wheels and 1′-1,1′-bi-2-naphthol with similar structures but channels of different sizes. By using post-synthetic functionalization with $Ti(OiPr)_4$ they generated chiral Lewis acid catalyst which proved to be highly efficient for conversion of aromatic aldehydes in to chiral secondary alcohols, through addition of alkylzinc or diethylzinc. By slight alteration in BINOL based likers, the size of the channels were modified, which alters the diffusion rates of the organic substrates [48].

Yong Cui and coworkers synthesized a homochiral MOF using an enantiopure 2,2′-dihydroxy-1,1′-biphenyl ligand with $Zn(NO_3)_2\cdot6H_2O$ through solvothermal reaction. Through one proton exchange of the dihydroxyl group with Li(I) ions, the framework proved to be a highly efficient and recyclable heterogeneous catalyst for asymmetric cyanation of aldehydes with up to >99% *ee* [44].

5. Applications of chiral covalent organic frameworks

COFs are among some of the emerging classes of advanced materials which have been greatly seeking the attention of not only chemists but also material scientists. Since the seminal work of Yaghi and coworkers, this class of materials has been through a great deal of progress to serve them for industrial applications. Among its various other applications the most important are their use in enantioselective separations and catalysis. So far, only few chiral COFs have been successfully constructed due to their challenging synthesis and the key bottleneck of creating chiral COFs is the inherent discrepancy between the symmetry for crystalline structures and asymmetry for chiral functionalities. According to the context of this chapter we will briefly try to highlight some examples of CCOFs which played an efficient role in chiral separations and asymmetric catalysis.

5.1 CCOFs in enantioselective separation

Owing to the large surface area, permanent porosity, high solvent and thermal stability, COFs are considered as good candidates to be used for enantiomeric separation of small molecules, especially of biological or pharmacological interest. Yan and coworkers in 2016 synthesized three CCOFs namely, CTpPa-1, CTpPa-2 and CTpBD and then using in situ growth, they fabricated chiral COF bound capillary columns. These chiral COF capillary columns displayed high resolution for the separation of (±)-1-phenylethanol, (±)-1-phenyl-1-propanol, (±)-methyl lactate, and (±)-limonene, which can be efficiently separated within 5 min under excellent repeatability and reproducibility [19].

In 2018 the first chiral 3D COF was constructed by imine condensation of a 2-fold symmetric TADDOL-derived tetraldehyde with a tetrahedral tetra (4-anilyl) methane and transformed in to amide linked COF after post-synthetic oxidation of imine linkages. Both the imine linked COF as well a post-synthetically modified imide linked COF, served as highly reproducible chiral stationary phases for HPLC [71].

5.2 Chiral COFs in asymmetric catalysis

COF is an emerging field of material chemistry and needs a lot of development. The ordered nano-channels and periodic layers in COFs make these materials sustainable open catalytic nano-reactors, but their low stability has prohibited their practical application. Among various other groups working on development of CCOFs, Donglin Jiang and his group has achieved a remarkable progress in this regard. In 2015 they synthesized a mesoporous imine based COF "TPB-DMTP-COF" with improved crystallinity and high chemical and thermal stability, by the incorporation of methoxy groups in to the pore walls. They post-synthetically modified this achiral COF in to two distinct CCOFs by engineering the channel walls with chiral centers and organocatalytic species. The resulting crystalline, metal free catalysts presented activity, enantioselectivity, recyclability and environmental benevolence, a set of characteristics that has remained challenging to engineer in heterogeneous catalysis [72].

6. Conclusion

This chapter summarizes the recent advances in the development of chiral microporous materials, with special emphasis to metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). We discussed some of the synthetic strategies in details and highlighted the current status of chiral microporous materials in enantioselective separation and asymmetric catalysis. Since there is a lot of development needed to be done in this area, as it can open up new doors to the synthesis of advanced green energy materials and catalysis.

Acronyms and abbreviations

MOF	metal organic framework
COF	covalent organic framework
CCOFs	chiral covalent organic frameworks
FIR	Fujian institute of research
H₃TPA	tris(4-carboxylphenylduryl)amine
BOC	tert-butyloxycarbonyl

DUT	Dresden University of Technology
SBUs	secondary building units
H$_2$adc	adamantane-1,3-dicarboxylic acid
PEA	phenyl-ethylamine
Tp	1,3,5-triformylphloroglucinol
Tab	1,3,5-tri(4-aminophenyl)benzene
PSM	postsynthetic modification
MPSs	methyl phenyl sulfoxides
BINOL	1,1′-bi-2-naphthol

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