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Journal of Solid State Chemistry 178 (2005) 2486–2490

JOURNAL OF SOLID STATE CHEMISTRY

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Homochiral porous metal-organic frameworks: Why and how?

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Received 7 February 2005; received in revised form 30 May 2005; accepted 2 June 2005
Available online 26 July 2005

Abstract

This paper highlights the most significant recent advances in the synthesis, characterization, and applications of single-crystalline homochiral porous metal-organic frameworks (MOFs). The motivations for the synthesis of homochiral porous solids and the strategies on how they can be designed are provided. The latest examples of chiral separation and Lewis acid heterogeneous asymmetric catalysis using homochiral porous MOFs are presented.

Keywords: Crystal engineering; Asymmetric catalysis

The field of metal-organic frameworks (MOFs), particularly the area of synthesis and characterization of MOFs, has undergone explosive growth over the past decade [1–10]. The great current interest in MOFs has been inspired by their potential in many areas of technological applications. It is important for the researchers in this exciting area of interdisciplinary science to recognize the pros and cons of MOFs. The intrinsic advantages and limitations of MOFs dictate their true potential in each area of technological application. The synthesis of MOFs with permanent porosity represents one of the most significant advances in the area of porous materials over the past decade [11–15]. Because of the great utility of zeolites in heterogeneous catalyses and selective sorptions [16,17], significant efforts have been devoted to exploring the applications of porous MOFs in these areas. In comparison to traditional inorganic zeolites, most MOFs however do not have the thermal and chemical stabilities required by many of the current heterogeneous catalytic processes performed by zeolites. The potential of MOFs in selective sorption applications is also limited owing to their relatively high costs compared to inorganic zeolites. It is thus unlikely that porous MOFs can compete with inorganic zeolites in many areas of applications where inorganic zeolites have excelled.

Although zeolites have been extensively used for the production of numerous chemical intermediates and household products, their applications in enantioselective separations and catalyses have not been realized. Few enantiopure zeolites have been obtained in spite of the significant efforts on developing chiral zeolites over the past few decades [18,19]. None of these enantiopure zeolites have found applications in stereoselective processes. MOFs are on the other hand typically synthesized under very mild conditions, which should allow facile construction of homochiral porous MOFs by judicious choices of chiral constituent building blocks. In ideal scenarios, these homochiral porous MOFs can possess chiral functionalities that are accessible via the open channels or cavities. Such readily accessible, periodically ordered chiral functionalities can be utilized to generate heterogeneous asymmetric catalysts for the economical production of optically pure compounds. Ideal homochiral porous MOFs can combine both the advantages offered by heterogeneous catalysts (including facile catalyst separation and recovery, high stability, and ease of handling), and

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0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.06.013

those offered by their homogeneous counterparts (including homogeneity of active sites, high efficiency, reproducibility, selectivity, and controllability, and mild reaction conditions). Homochiral porous MOFs with desired chiral open channels and pores can also be expected to find applications in enantioselective sorptions/separations. Successful design of homochiral porous MOFs can therefore expand the utility of zeolitic materials into the realm of chirotechnology.

How can one then synthesize homochiral porous MOFs that may be applicable in enantioselective processes? Three distinct approaches have thus far been utilized to construct homochiral solids. In the first approach, chiral MOFs can be built from achiral components. In principle, any MOF can crystallize in a chiral space group as a result of a particular spatial disposition of all the building units. The bulk samples of the MOFs built from achiral components however tend to contain both enantiomorphs and are thus racemic even though the single crystals are chiral [20]. There is only one well-established example where an enantiopure bulk sample of a chiral MOF was obtained from linking achiral building blocks via a homochiral crystallization process [21]. A helical MOF with the composition of $Cd(\mathbf{L_1})(NO_3)_2(H_2O)(EtOH)$, **1**, was obtained by treating achiral [5-(9-anthracenyl)]pyrimidine, $\mathbf{L_1}$, with $Cd(NO_3)_2 \cdot 4H_2O$. Adjacent helices of **1** adopt the same handedness and are linked by interstrand H_2O–nitrate hydrogen-bonding interactions to lead to chiral crystals of **1** (Fig. 1). Moreover, solid-state circular dichroism (CD) experiments indicate that the entire bulk sample of **1** is homochiral. Aoyama et al. further demonstrated that seeding technique could be used to grow crystals of the desired *M*- or *P*-stereochemistry. The application of homochiral crystals of **1** in enantioselective processes was not explored.

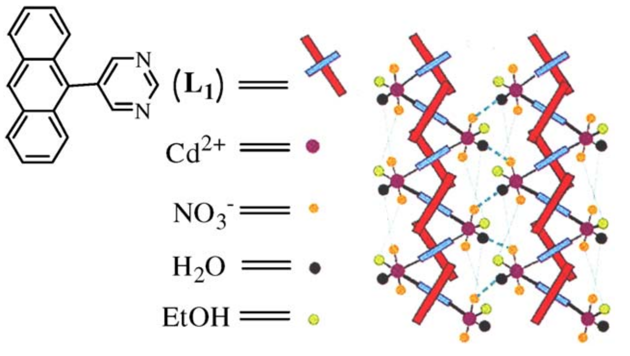

Fig. 1. A view of the homochiral MOF $Cd(\mathbf{L_1})(NO_3)_2 \cdot H_2O \cdot EtOH$ formed by interstrand hydrogen-bonding interactions between coordinated water and nitrate groups.

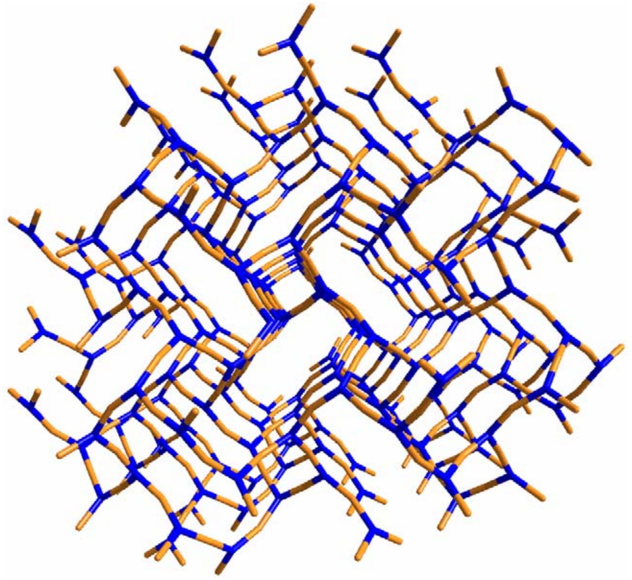

Fig. 2. A view of the chiral (10,3)-a $M_3(btc)_2$ network showing the helical motifs along the cube edge direction. The gold linkers represent M centers while the blue connectors represent btc ligands. The rest of the metal coordination is completed by Py and 1,2-pd ligands.

In the second approach, an enantiopure co-ligand can be used to direct homochiral crystallization of an intrinsically chiral MOF that is built from achiral metal nodes and bridging ligands. As shown above, in the absence of enantiopure co-ligand, the bulk sample of the intrinsically chiral MOF built from achiral building blocks tends to be racemic. Rosseinsky et al. recently demonstrated the use of enantiomerically pure 1,2-propanediol (1,2-pd) co-ligand in directing the formation of homochiral porous networks of the type $M_3(btc)_2$ (where btc is 1,3,5-benzenetricarboxylate) [22]. In the doubly interpenetrated (10,3)-a network $Ni_3(btc)_2(py)_6(1,2\text{-pd})_3 \cdot [11(1,2\text{-pd}) \cdot 8(H_2O)]$, **2**, the coordinating 1,2-pd acts as a chiral template that not only controls the handedness of the helices but also directs the crystal growth to afford homochiral networks with chiral pores and cavities (Fig. 2). Interestingly, X-ray and chiral GC studies indicated that the (*S*)-enantiomer of 1,2-pd preferentially binds to the Ni center even when racemic 1,2-pd is used (with an enantiomeric excess (ee) of ~20%). The solvent molecules in **2** can be carefully removed to afford crystalline samples with both empty chiral pores and vacant coordination sites around the metal centers. The evacuated sample of a related compound $Ni_3(btc)_2(3\text{-pic})_6(1,2\text{-pd})_3 \cdot [9(1,2\text{-pd}) \cdot 11(H_2O)]$, **2a**, has recently been shown to enantioselectively adsorb 1,1′-bi-2-naphthol at a modest capacity of 7.3 wt% and ee of 8.3% [23]. The chirality of the MOFs obtained from these two approaches originates from the spatial disposition of their building blocks, and it is not easy to systematically engineer the chiral pores or functionalities within such solids to enhance the stereoselectivity of a separation or catalytic process.

The third and most reliable strategy to generate homochiral MOFs utilizes metal ions or metal clusters as nodes and chiral multifunctional ligands as linkers.

The use of chiral bridging ligands will ensure the chirality in the resulting network structures. In ideal scenarios, chiral pores with desired chemical and shape selectivities can be generated and used for highly enantioselective sorption or separation processes. Alternatively, desirable chiral functional groups can be periodically incorporated into the MOF structures and be accessible to prochiral substrates to therefore catalyze organic transformations in an asymmetric fashion. Many chiral bridging ligands have been utilized to construct numerous homochiral MOFs, but only those showing potential in enantioselective applications are highlighted below.

Kim et al. reported the first example of asymmetric catalysis using a crystalline homochiral MOF [24]. An enantiopure bridging ligand with both the carboxylic and pyridyl functional groups (**L$_2$**) was derived from readily available D-tartaric acid and treated with $Zn(NO_3)_2$ to give chiral porous $[Zn_3(\mu_3\text{-O})(\mathbf{L_2}\text{-H})_6]\cdot 2H_3O\cdot 12H_2O$ (D-**POST-1**) (Fig. 3). D-**POST-1** possesses a layer structure with large chiral 1D channels of ~13.4 Å in dimension along the *c*-axis. Dangling pyridinium groups of **L$_2$** are present in D-**POST-1** and located along the open channels. These dangling pyridinium groups were used to catalyze the kinetic resolution of *rac*-1-phenyl-2-propanol via a transesterification process. The acetate of 1-phenyl-2-propanol was produced with a modest ee of ~8% in favor of *S*-enantiomer in the presence of D-**POST-1**. No information was however provided on how the enantioselectivity was achieved by the pyridinium units which are in fact quite remote from chiral core of the tartrate ligand.

The Lin group has taken a systematic approach toward designing homochiral porous MOFs for chiral separation and asymmetric catalysis [25–33]. Lin et al. first reported a series of homochiral porous lamellar lanthanide bisphosphonates with a general formula of $[Ln(\mathbf{L_3}\text{-H}_2)(\mathbf{L_3}\text{-H}_3)(H_2O)_4]\cdot xH_2O$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, $x = 9 - 14$, **3a–g**). **3a–g** contain large chiral asymmetric channels with largest dimensions of 12 Å (Fig. 4), and exhibit reversible dehydration and framework stability [25]. Ammonia-treated **3e** was used for bulk chiral separation of *trans*-1,2-cyclohexanediamine with a modest ee of ~13.6%. Although Compound **3e** was an active heterogeneous chiral Lewis acid catalyst for several organic transformations, including cyanosilylation of aldehydes, ring opening of meso-carboxylic anhydride, and Diels-Alder reactions, no enantioselectivity was observed for all these reactions probably as a result of the highly symmetrical coordination environment around the catalytically active Sm centers.

In order to enhance the enantioselectivity, Lin et al. has designed chiral bridging ligands containing orthogonal functional groups. Metal-connecting units can link these chiral bridging ligands to form extended network structures via the primary functional groups. The orthogonal secondary chiral functionalities periodically decorating the porous MOF can then be used to generate asymmetric catalytic sites which are accessible to the substrates via the open channels or cavities. Lin et al. successfully utilized this strategy to prepare noncrystalline chiral porous zirconium phosphonates for applications in asymmetric diethylzinc additions to aromatic aldehydes at up to 72% ee [30], asymmetric hydrogenation of b-keto esters at up to 95% ee [31], and asymmetric hydrogenation of aromatic ketones at up to 99.2% ee [32].

Very recently, the Lin group successfully synthesized a crystalline chiral porous MOF for highly enantioselective diethylzinc additions to aromatic aldehydes. A homochiral MOF $[Cd_3Cl_6(\mathbf{L_4})_3]\cdot 4DMF\cdot 6MeOH\cdot 3H_2O$, **4**, (where **L$_4$** is (*R*)-6,6′-dichloro-2,2′-dihydroxy-1,1′-binaphthyl-4,4′-bipyridine) crystallizes in the triclinic *P*1 space group with three Cd atoms, six chloride atoms, and three **L$_4$** ligands in each unit cell [33]. The Cd(II) centers in **4** are doubly bridged by the chlorides to form 1 D zigzag $[Cd(\mu\text{–}Cl)_2]_n$ chain SBUs (Fig. 5a). Each Cd(II) center in the 1D zigzag chain further coordinates to two pyridyl groups of the **L$_4$** ligands and connects adjacent 1D $[Cd(\mu\text{–}Cl)_2]_n$ SBUs to form a non-interpenetrating 3D network with very large chiral channels of ~1.6 × 1.8 nm cross-section that are

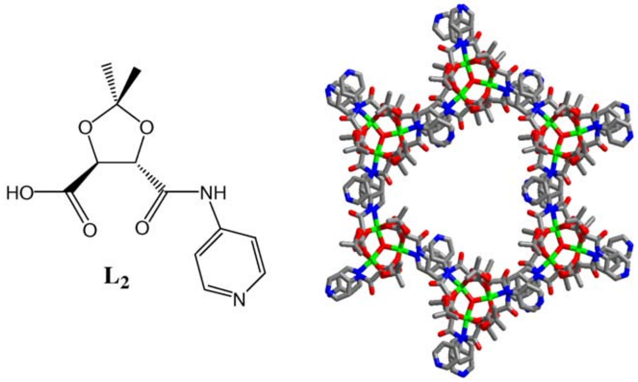

Fig. 3. The hexagonal framework of chiral $[Zn_3(\mu_3\text{-O})(\mathbf{L_2}\text{-H})_6]\cdot 2H_3O\cdot 12H_2O$ (D-**POST-1**).

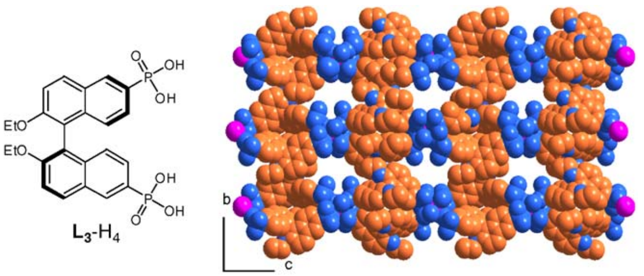

Fig. 4. A space-filling model view of lamellar structure of $[Gd(R\text{-}\mathbf{L_3}\text{-H}_2)(R\text{-}\mathbf{L_3}\text{-H}_3)(H_2O)_4]\cdot 12H_2O$, **3e**.

oriented along the crystallographic *a*-axis (Fig. 5b). PLATON calculations (21) indicate that **4** contains 54.4% (2044.2 Å^3 out of 3760.8 Å^3 per unit cell) void space that is accessible to the solvent molecules. X-ray powder diffraction demonstrated that the framework structure of **4** was maintained upon the removal of all the solvent molecules. The evacuated sample of **4** possesses permanent porosity with a specific surface area of 601 m^2/g and a pore volume of 0.26 mL/g.

Homochiral MOF **4** was utilized in heterogeneous asymmetric catalysis by taking advantage of the chiral dihydroxy groups that are readily accessible through the large open cannels. Treatment of **4** with excess $Ti(O^iPr)_4$ led to an active catalyst (designated as **4** · Ti) for the diethylzinc addition reactions (Fig. 6). Specifically, **4** · Ti catalyzes the addition of diethylzinc to 1-naphthaldehyde to afford (*R*)-1-(1-naphthyl)propanol with complete conversion and 93% ee. This level of ee rivals that of the homogeneous analog under similar conditions (94% ee). **4** · Ti also catalyzes the addition of diethylzinc to a range of other aromatic aldehydes with complete conversion and ee values comparable to those of the homogeneous analog. No secondary alcohol product was obtained when 1-naphthaldehyde was treated with diethylzinc in the presence of the supernatant from a mixture of **4** and $Ti(O^iPr)_4$ under otherwise identical conditions, indicating that the present catalyst system is heterogeneous in nature. Furthermore, control experiments with a series of dendritic aldehydes of varying sizes (from 0.8 to 2.0 nm) demonstrate that **4** · Ti is a true heterogeneous asymmetric catalyst and both diethylzinc and aromatic aldehyde are accessing the (BINOLate)-$Ti(O^iPr)_2$ sites via the open channels to generate the chiral secondary alcohol product. **4** · Ti represents the first highly enantioselective asymmetric catalyst derived from a homochiral MOF.

In summary, there has been significant progress in the synthesis of homochiral MOFs over the past few years. Chiral MOFs of diverse topologies and functionalities can be prepared using three distinct strategies. The facile tunability of such a molecular building block approach should allow precise engineering of chiral functionalities within chiral porous MOFs. Although still at its infancy stage, chiral porous MOFs have already shown very high catalytic activity and enantioselectivity in several organic transformations. Practically useful heterogeneous asymmetric catalysts can thus be envisioned from such a molecular building block approach, which promises to lead to a breakthrough in the burgeoning field of chirotechnology.

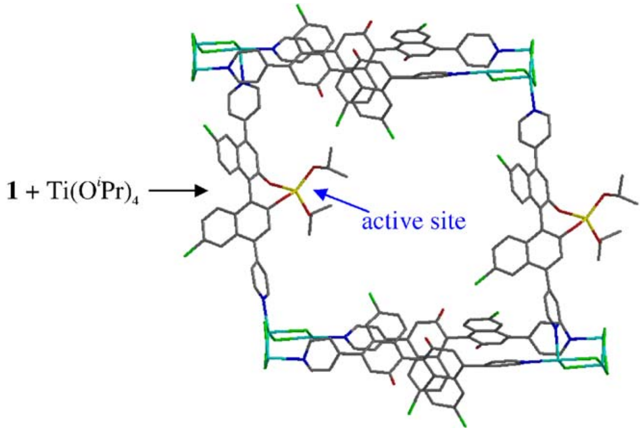

Fig. 6. A schematic representation of the active $(BINOLate)Ti(Oz^iPr)_2$ catalytic sites in the open channels of **4** · **Ti**.

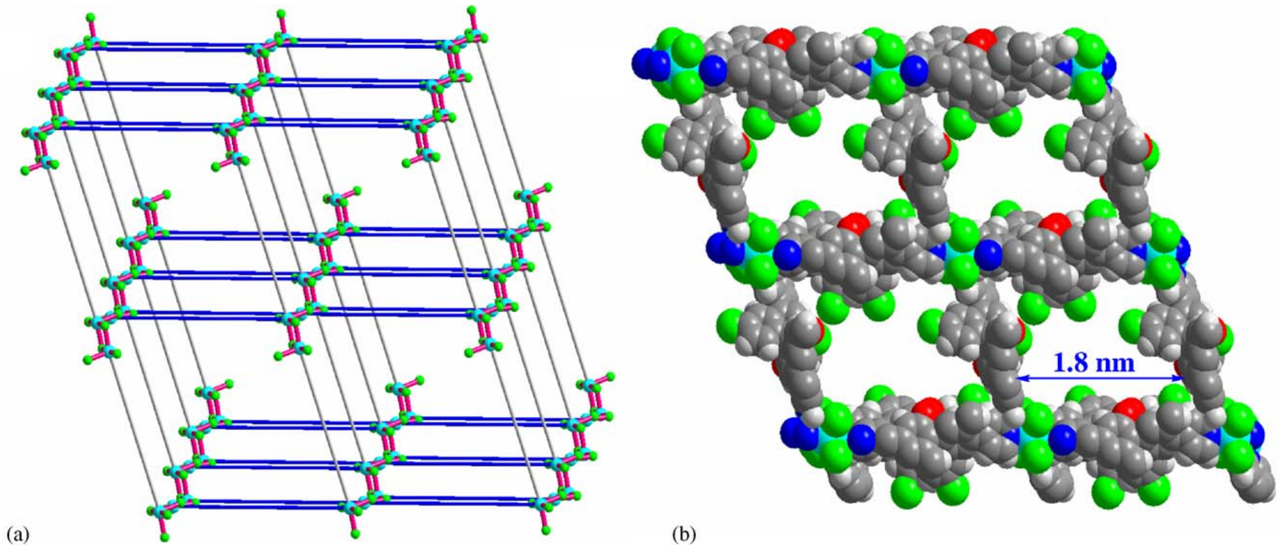

Fig. 5. (**a**) Schematic representation of the 3 D framework of **4** as viewed slightly off the crystallographic *a*-axis. (**b**) Space-filling model of **4** as viewed down the crystallographic *a*-axis showing the large chiral 1D channels (~1.6 × 1.8 nm).

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