

Hybrid organic-inorganic solids for heterogeneous asymmetric catalysis

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This paper provides a short review of recent progress in the design and synthesis of chiral organic-inorganic hybrid solids and their applications in heterogeneous asymmetric catalysis. Homochiral hybrid solids containing catalytic sites can be readily prepared by linking appropriately designed chiral bridging ligands with metal ion or metal cluster nodes. Heterogeneous asymmetric catalysts with enantioselectivity as high as 99.2% and turnover number (TON) as high as 20,000 have been obtained based on these hybrid organic-inorganic solids. The modular nature of the present approach promises to lead to a variety of practically useful heterogeneous asymmetric catalysts for many organic transformations.

KEY WORDS: asymmetric catalysis; coordination networks; heterogeneous catalysis; hybrid solids.

1. Introduction

Heterogeneous catalysis is estimated to be involved in 90% of currently used chemical manufacturing processes, and without a doubt, is a cornerstone of the chemical industry [1]. Heterogeneous catalytic processes not only contribute to the economical production of countless household products but also can help to lead to greener environments. As an example, size-selective heterogeneous catalytic transformation of petrochemicals has been extensively used by the petrochemical industry to improve the quality of gasoline, and thus significantly reduce the pollution from incomplete combustions of fossil fuels [2].

In light of the importance of heterogeneous catalysis in the production of commodity chemicals, there has been significant interest in the development of heterogeneous asymmetric catalysts over the past few decades [3]. Compared to homogeneous asymmetric catalysts, heterogeneous asymmetric catalysts can be readily recycled and reused, and thus lead to significant cost reduction for the production of chiral compounds. The use of heterogeneous asymmetric catalysts can also prevent the leaching of often toxic metals from the catalysts into the organic phase which can present a formidable challenge if the chiral products are to be used as pharmaceutical ingredients.

Several different approaches have been taken to develop recyclable and reusable heterogeneous asymmetric catalysts, including oxide-supported group 8 metals (Ni, Pd, and Pt) with chiral modifiers (such as cinchona alkaloids) [4], and homogeneous asymmetric catalysts immobilized on oxide supports, organic polymer supports, aqueous biphasic systems, room-temperature ionic liquids, supercritical carbon dioxide, and fluoro phases [5,6]. The group 10 metal/chiral modifier systems can have high enantiomeric excesses (ee's) and

turnover numbers (TONs), but their substrate scopes are rather limited. In fact, after 40 years of exhaustive searches, asymmetric hydrogenation of functionalized ketones represents the only successful example. On the contrary, heterogenized homogeneous asymmetric catalysts are in principle not limited to any reaction type, and indeed, many homogeneous asymmetric catalysts have been immobilized on a variety of supports for catalyzing many different reactions including hydrogenation, hydroformylation, isomerization, dihydroxylation, epoxidation, ring-opening of epoxides, allylic substitution, cyclopropanation, Diels-Alder reactions, conjugation additions, and Aldol reactions [5]. Unfortunately, in almost all the cases, either the catalytic activity or enantioselectivity (or both) suffers upon the immobilization of the homogeneous asymmetric catalysts. In some cases, the leaching of the immobilized catalysts is also an issue. Alternative means for the preparation of recyclable, reusable heterogeneous asymmetric catalysts are thus needed before more widespread industrial applications of heterogeneous asymmetric catalysis can be realized. We briefly review here the development of hybrid organic-inorganic solids for applications in heterogeneous asymmetric catalysis.

2. Homochiral hybrid organic-inorganic solids

Recent interest in hybrid metal-organic coordination networks (MOCNs) stems from their potential applications in catalysis, photonics, separation, gas storage, and molecular sensing [7]. In contrast to traditional inorganic zeolites and related inorganic mesoporous materials, which are typically synthesized under harsh conditions and are thus not amenable to the fine-tuning of subtle features such as chemical functionality and chirality [8], hybrid MOCNs are synthesized under mild conditions and in principle allow systematic engineering of desired chemical and physical properties via modifications of their constituent building blocks. Specifically,

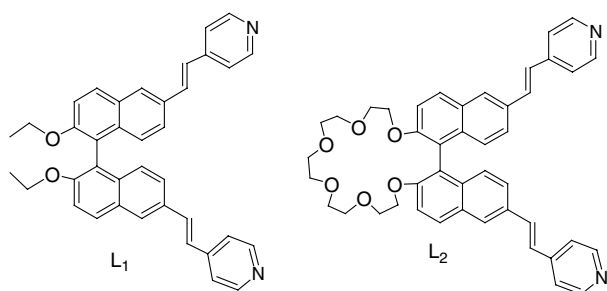
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such a modular approach allows for the construction of chiral solids that possess chiral pockets or functionalities within the open channels or cavities. These homochiral hybrid MOCNs are exploitable for applications in asymmetric catalysis and chiral separations, and represent a new approach toward the design of heterogeneous asymmetric catalysts.

Three distinct approaches have been utilized to construct homochiral solids. In the first approach, chiral hybrid MOCNs can be built from achiral components. The bulk materials however tend to be racemic even though single crystals are chiral. Only in one example has a homochiral solid been obtained via a homochiral crystallization process that utilizes all achiral components [9]. In the second approach, an enantiopure co-ligand can be used to direct homochiral crystallization of an intrinsically chiral hybrid MOCN that is built from achiral metal nodes and bridging ligands [10]. The chirality of these hybrid MOCNs obtained from these two approaches originates from the spatial disposition of their building blocks and is not amenable to fine-tuning [11]. The third and most straightforward approach to construct homochiral porous MOCNs utilizes metal ions or metal clusters as nodes and chiral multifunctional ligands as linkers [12]. In ideal scenarios, functional groups reside inside the MOCNs which are accessible to prochiral substrates and can catalyze organic transformations in an asymmetric fashion.

Lin *et al.* has designed a variety of enantiopure bipyridine, dicarboxylic acid, and bisphosphonic acid bridging ligands based on the readily available atropisomeric 1,1'-binaphthyl framework. Homochiral crystalline hybrid organic-inorganic solids of varied dimensionality have been obtained by combining these chiral bridging ligands with metal ions and metal cluster nodes. For example, periodically ordered homochiral interlocked nanotubes $[\text{Ni}(\text{acac})_2(\text{L}_1)] \cdot 3\text{CH}_3\text{CN} \cdot 6\text{H}_2\text{O}$, **1** and $[\text{Ni}(\text{acac})_2(\text{L}_2)] \cdot 2\text{CH}_3\text{CN} \cdot 5\text{H}_2\text{O}$, **2**, were obtained by treating C2 symmetric 1,1'-binaphthyl-6,6'-bipyridine ligands L_1 or L_2 with $\text{Ni}(\text{acac})_2$ in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solvent mixtures at 70 °C for 2 days (Scheme 1)



Scheme 1

[13]. The bridging bipyridines linked the $\text{Ni}(\text{acac})_2$ units to result in infinite helical chains which assemble into nanotubes via parallel alignment (figure 1). Further interlocking of the nanotubes in **1** lead to chiral pores

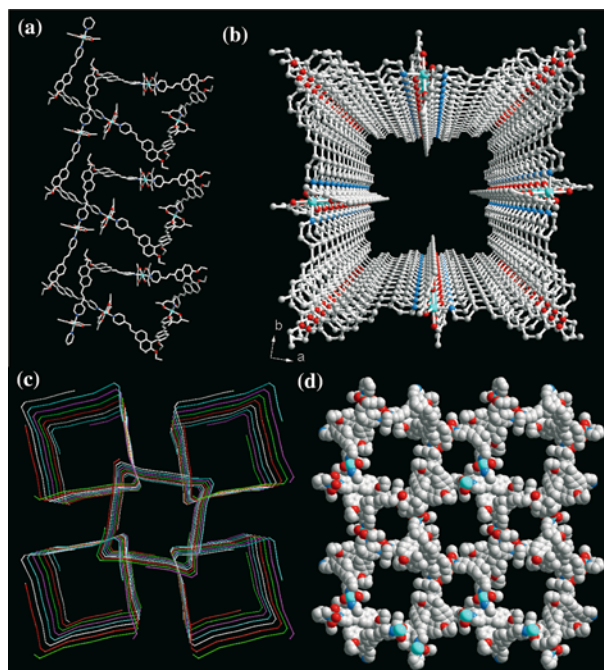
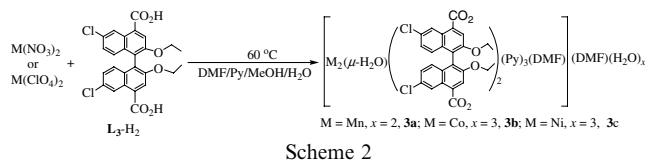


Figure 1. Views of the (a) helical chain (b) nanotube made of five parallel helices (c) interlocking adjacent helices (d) space filling model showing the open channels in the network of $[\text{Ni}(\text{acac})_2(\text{L}_1)]$ in **1** [13].

with 1.7×1.7 nm dimensions that are filled with H_2O and CH_3CN solvate molecules. Both **1** and **2** show framework stability toward the removal of solvent molecules.

Reactions of enantiopure 6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthylene-4,4'-dicarboxylic acid ($\text{L}_3\text{-H}_2$) with appropriate metal salts in DMF, MeOH and pyridine at 60 °C afforded a series of isostructural homochiral porous 2D metal carboxylates of the general formula $[\text{M}_2(\mu\text{-H}_2\text{O})(\text{L}_3)_2(\text{py})_3(\text{DMF})] \cdot (\text{DMF}) \cdot (\text{H}_2\text{O})_x$ ($\text{M} = \text{Mn}$, $x = 2$; Co , $x = 3$; Ni , $x = 3$), **3a-c** (Scheme 2) [14]. The basic building unit for **3a-c** can be



Scheme 2

viewed as two metal atoms bridged by one H_2O molecule and two carboxylate groups of two different L_3 ligands. Three pyridine and one DMF molecule complete the coordination geometry around the metal atoms. This dimetal carboxylate unit is further linked to four neighboring dimetal cores through the carboxylate groups of four different L_3 ligands. As a result, a 2D neutral rhombohedral grid is constructed that have chiral cavities (figure 2). The ethoxy protected BINOL functionality in the network structure is oriented toward the chiral pores. However, the void space in **3a-c** is

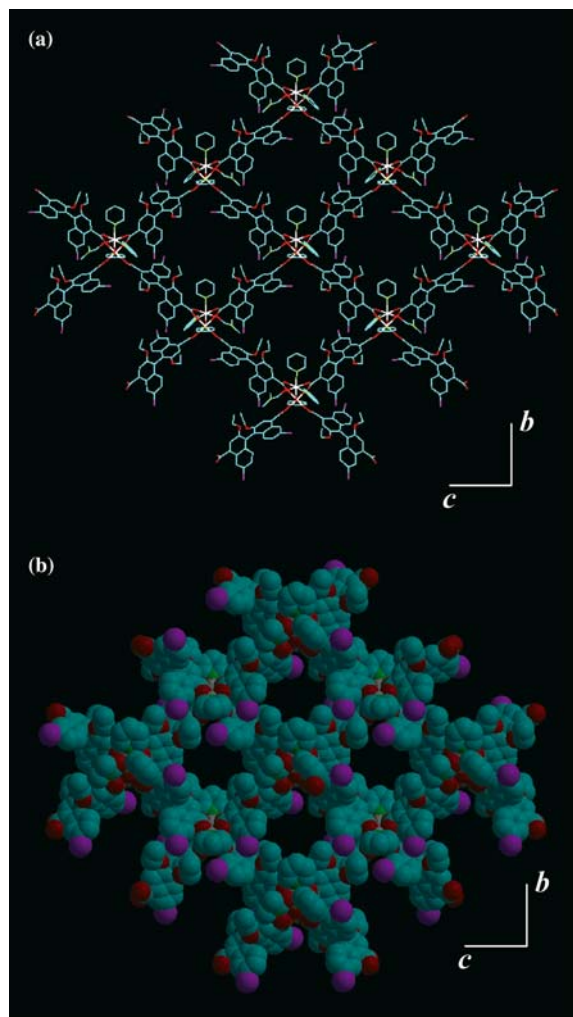


Figure 2. (a) Crystal structure of **3a**, showing 2D rhombohedral grid. (b) Space filling model down the *a*-axis [14].

minimal as the 2D grids have a staggered arrangement with a 7.45 Å layer to layer separation and is occupied by one DMF and two water molecules.

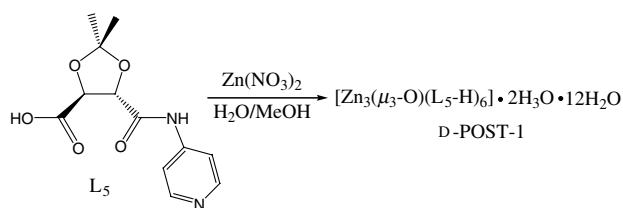
Lin *et al.* has also constructed homochiral 3D MOCNs using chiral bisphosphonic acid [15]. A hydro(solvo)thermal reaction of 2,2'-diethoxy-1,1'-binaphthyl-6,6'-bisphosphonic acid (**L₄-H₄**) with MnCO₃ in a H₂O and MeOH solvent mixture at 110 °C yielded homochiral [Mn(**L₄-H₂**)](MeOH) · MeOH, **4**, which exhibits a 3D network structure and contains chiral cavities. The Mn atom in **4** is five coordinate with one MeOH and four oxygen atoms of four different **L₄-H₂** ligand. The phosphonate groups of **L₄** link adjacent Mn atoms to form [Mn(PO₃H)₂]_∞ chains along *a*-axis (figure 3). These [Mn(PO₃H)₂]_∞ chains are further linked by the bridging **L₄-H₂** groups to form a homochiral 3D network. The 3D framework contains rhombohedral channels with approximate dimensions of 5.3 × 2.7 Å, filled with MeOH guest molecules.

Numerous other crystalline homochiral hybrid organic-inorganic solids have been obtained by the Lin

and other groups over the past few years [12–15]. With their precise structures known from X-ray single crystal determinations, these MOCNs serve as interesting structural models for the design of chiral porous solids containing catalytic sites that can be used for heterogeneous asymmetric catalysis.

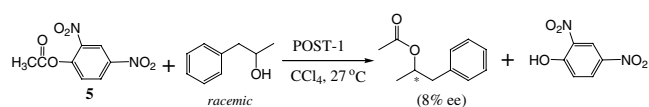
3. Homochiral MOCNs as heterogeneous asymmetric catalysts

Fujita *et al.* [16] and Aoyama and coworkers [17] first explored the utility of hybrid organic-inorganic solids as Lewis acids for heterogeneous catalysis. Interesting size selectivity of the substrates was observed with these MOCNs, but no asymmetric induction could be achieved with these achiral solids. Kim *et al.* reported the first example of asymmetric catalysis using a crystalline homochiral MOCN [18]. Enantiopure bridging ligand **L₅** with both carboxylic and pyridyl functional groups was derived from readily available D-tartaric acid, and treated with Zn(NO₃)₂ in H₂O/MeOH solvent mixture to give porous and chiral [Zn₃(μ₃-O)(**L₅-H**)₆] · 2H₂O · 12H₂O (**D-POST-1**) (Scheme 3) [18].



Scheme 3

D-POST-1 possesses a layer structure with large chiral 1D channels of ~13.4 Å in dimension along the *c*-axis (figure 4). Three of six pyridyl groups in each trinuclear unit ([Zn₃(μ₃-O)(**L₅-H**)₆]²⁻) are coordinated to the zinc ions of three neighboring trinuclear units, the other three extrude into the channel without any interactions with the framework. A charge neutrality argument and other data indicated that two of the three dangling pyridyl groups have been protonated. Interestingly, the dangling pyridyl groups in **D-POST-1** were used to catalyze kinetic resolution of *rac*-1-phenyl-2-propanol via transesterification of **5**. The reaction of **5** with a large excess of *rac*-1-phenyl-2-propanol in the presence of **D-POST-1** produces the corresponding esters with ~8% ee in favor of *S*-enantiomer (Scheme 4). Although the ee value is very modest, this is the first observation of asymmetric induction by modular porous materials.



Scheme 4

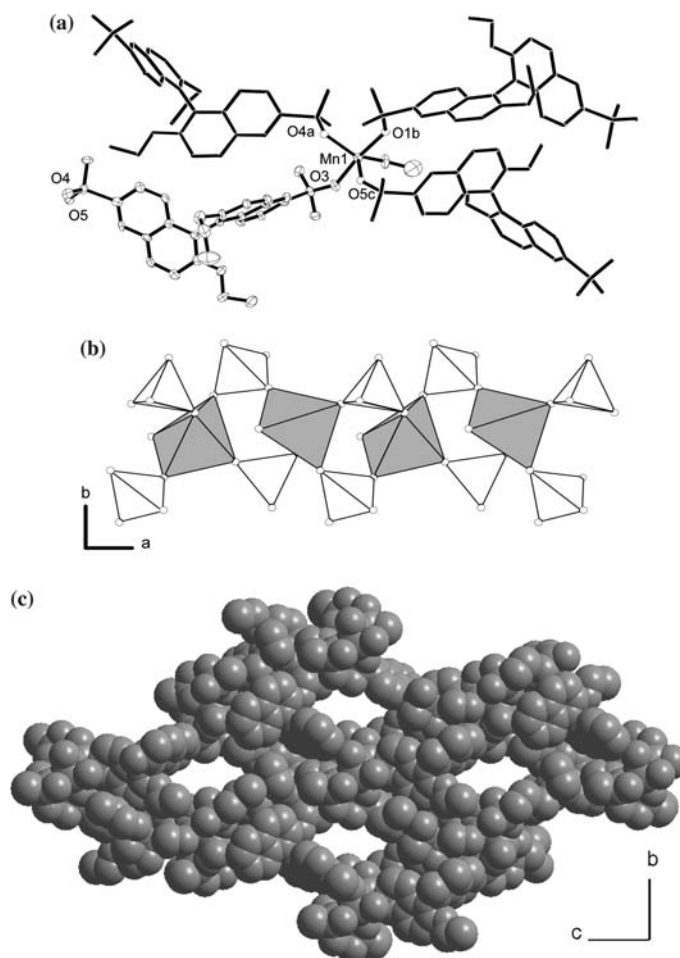
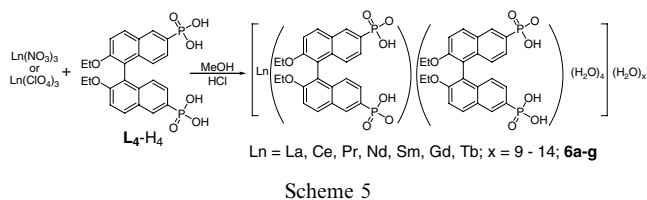


Figure 3. (a) Coordination environment of **4**. (b) View of the infinite $[\text{Mn}(\text{PO}_3\text{H})_2]$ chains along a -axis. (c) Space filling model of **4** [15].

Lin *et al.* prepared a series of homochiral porous lamellar lanthanide bisphosphonates with a generic formula of $[\text{Ln}(\text{L}_4\text{-H}_2)(\text{L}_4\text{-H}_3)(\text{H}_2\text{O})_4] \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, x = 9\text{--}14$, **6a–g**) (Scheme 5) [19].



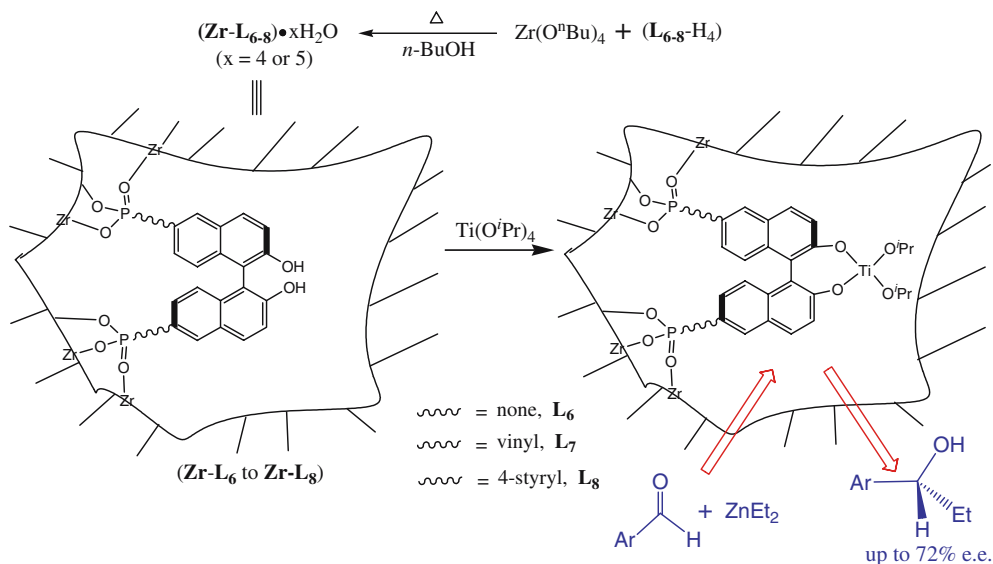
Scheme 5

6a–g adopt 2D lamellar structures with square anti-prismatic Ln center that have four H_2O molecules and four oxygen atoms of the phosphonate groups of four different binaphthylbisphosphonates in the coordination sphere (figure 5). **6a–g** contain large chiral asymmetric channels with largest dimensions of 12 Å, and exhibit reversible dehydration and framework stability. Compound **6e** 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.

Unfortunately, there is essentially no enantioselectivity for all these reactions. Such a lack of enantioselectivity was a direct consequence of the highly symmetrical coordination environment around the catalytically active Sm centers.

In order to improve the enantioselectivity, Lin *et al.* designed chiral porous Zr phosphonates with pendant chiral dihydroxy groups [20]. Amorphous chiral porous zirconium phosphonates **Zr-L₆** to **Zr-L₈** were obtained by refluxing BINOL-derived bisphosphonic acids **L_{6–8}** with $\text{Zr}(\text{O}^i\text{Bu})_4$ in $n\text{-BuOH}$, and have been characterized by powder X-ray diffraction, solid-state CP-MAS ^{31}P NMR, IR, TGA, adsorption measurements, circular dichroism spectroscopy, and microanalyses. These zirconium phosphonates have empirical formulae of $(\text{Zr-L}_{6-8}) \cdot x\text{H}_2\text{O}$ ($x = 4$ or 5), and exhibit BET surface areas ranging from 431 to 586 m^2/g . In combination with $\text{Ti}(\text{O}^i\text{Pr})_4$, these zirconium phosphonates have been used to heterogeneously catalyze the additions of diethylzinc to a wide range of aromatic aldehydes with high conversions and ee's of up to 72% (Scheme 6).

In a conceptually different approach, Sasai *et al.* prepared heterogeneous aluminum-bridged polymers **7** of chiral aluminum–lithium–bis(binaphthoxide) com-



Scheme 6

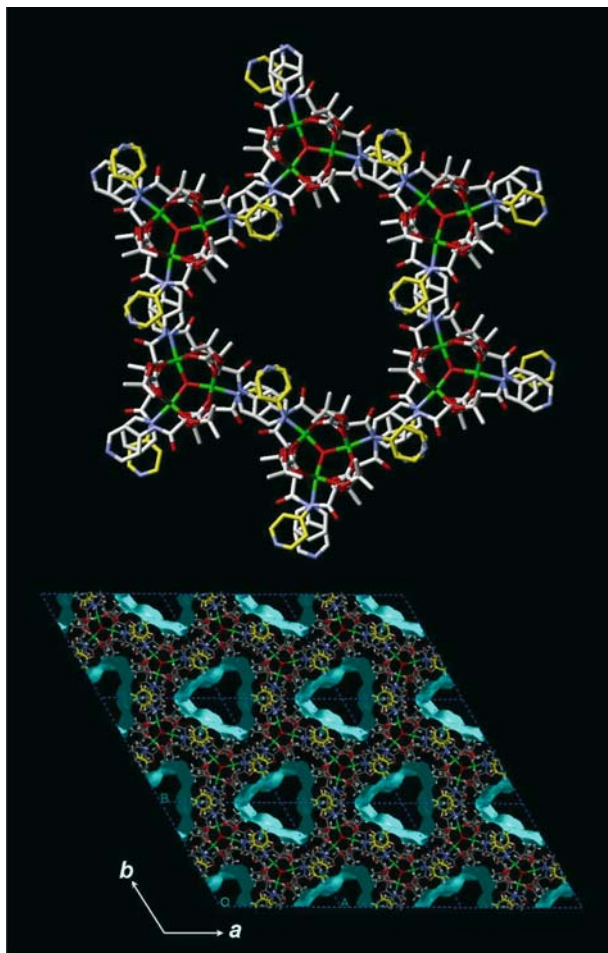


Figure 4. (Top) The hexagonal framework of **D-POST-1** that is formed with the trinuclear SBU. (Bottom) The chiral trigonal channels of **D-POST-1** as viewed down the *c*-axis [18].

plexes (ALB) by simply mixing a known bis(BINOL) ligand [21] with LiAlH₄ and BuLi (Scheme 7) [22]. These

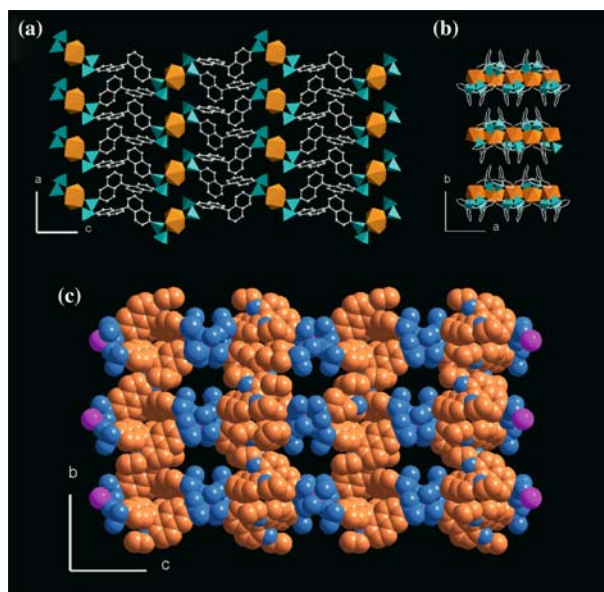
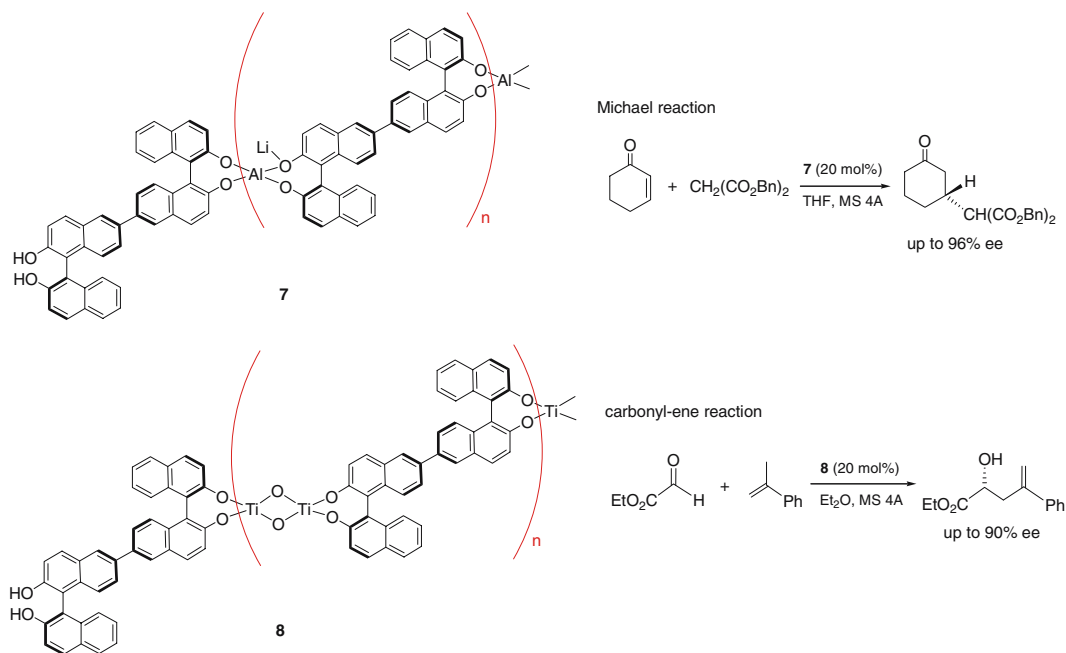


Figure 5. 2D structure of $[\text{Gd}(\text{R-L}_4\text{-H}_2)(\text{R-L}_4\text{-H}_3)(\text{H}_2\text{O})_4] \cdot 12 \text{H}_2\text{O}$, (a) along *a*-axis (b) showing interdigitation of binaphthyl rings from adjacent layers (c) space-filling model [19].

chiral hybrid organic–inorganic solids are efficient catalysts for a Michael reaction between 2-cyclohexenone and dibenzyl malonate with high conversion and ee values of up to 96% (only 2% lower than the homogeneous ALB catalyst). An analogous Ti-bridged hybrid polymer **8** was also prepared and used for catalyzing a carbonyl-ene reaction with up to 96% ee. Both of these heterogeneous catalysts have been recycled and reused up to five times with some deterioration of conversion and enantioselectivity.

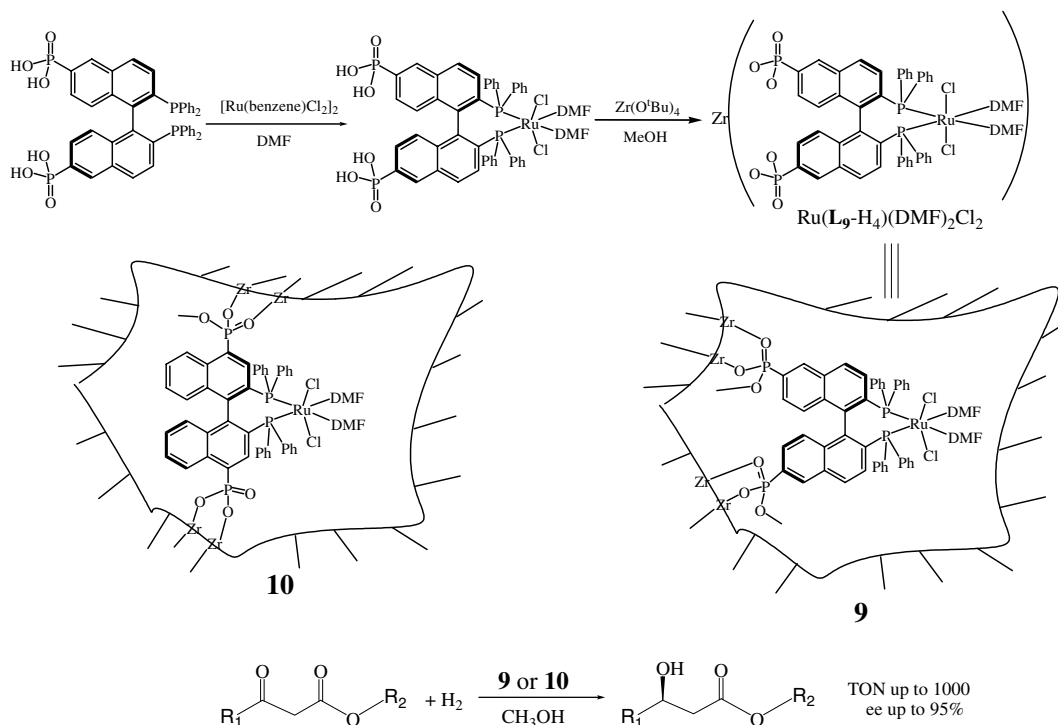
In order to obtain heterogeneous asymmetric catalysts with both high activity and enantioselectivity, Lin *et al.* prepared Zr phosphonates containing 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP)



Scheme 7

groups [23]. Homogeneous Ru and Rh–BINAP complexes are well studied and known to enantioselectively catalyze the reduction of many unsaturated substrates [24]. Two different BINAP derivatives 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl-6,6'-bis(phosphonic acid) (L_9 -H₄) and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl-4,4'-bis(phosphonic acid) (L_{10} -H₄) were

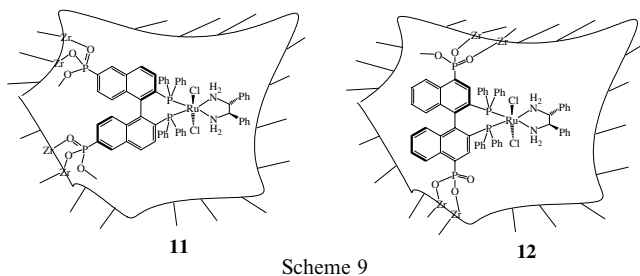
used to prepare Zr phosphonates (Scheme 8). Ru(II) complexes of L_9 -H₄ and L_{10} -H₄ were first prepared by treating $[Ru(\text{benzene})Cl_2]_2$ with 1 equiv of L_9 -H₄ and L_{10} -H₄ in DMF at 100 °C, which were then refluxed with $Zr(O^tBu)_4$ in MeOH to give solids formulated as $Zr[Ru(L_9)\text{-DMF})_2Cl_2] \cdot 2MeOH$, (**9**) and $Zr[Ru(L_{10})\text{-DMF})_2Cl_2] \cdot 2MeOH$ (**10**), respectively (Scheme 8).



Scheme 8

N_2 adsorption measurements indicated that **9** and **10** possess high porosity and surface areas. For **9**, $A_{\text{BET}} = 475 \text{ m}^2/\text{g}$ with microporous surface area of $161 \text{ m}^2/\text{g}$ and pore volume of $1.02 \text{ cm}^3/\text{g}$, and for **10** $A_{\text{BET}} = 387 \text{ m}^2/\text{g}$ with microporous surface area of $154 \text{ m}^2/\text{g}$ and pore volume of $0.53 \text{ cm}^3/\text{g}$. Both **9** and **10** are very effective heterogeneous catalyst for asymmetric hydrogenation of keto esters. **9** catalyzes hydrogenation of β -keto esters with complete conversion and high ee's ranging from 91.7% to 95.0%. Direct couple plasma spectroscopy indicated that no leaching of Ru has occurred during the catalytic reactions. The heterogeneous nature of these reactions is confirmed by the lack of catalytic activity of the supernatants of **9** and **10**. **9** was also reused in asymmetric hydrogenation of methyl acetoacetate for five cycles with complete conversion and no significant deterioration of enantioselectivity.

Lin *et al.* also designed an even more active and enantioselective heterogeneous catalyst for the hydrogenation of aromatic ketones [25]. Treatment of Ru(II) complexes of $\text{L}_9\text{-H}_4$ and $\text{L}_{10}\text{-H}_4$ with diphenylethylenediamine (DPEN) followed by refluxing with $\text{Zr}(\text{O}^t\text{Bu})_4$ in MeOH afforded the porous chiral solids of Zr phosphonates $\text{Zr}[\text{Ru}(\text{L}_9)(\text{DPEN})\text{Cl}_2] \cdot 4\text{H}_2\text{O}$ (**11**) and $\text{Zr}[\text{Ru}(\text{L}_{10})(\text{DPEN})\text{Cl}_2] \cdot 4\text{H}_2\text{O}$ (**12**) (Scheme 9) [25].



Scheme 9

N_2 adsorption measurements established porosity of **11** and **12** and both of them have been used for enantioselective hydrogenation of aromatic ketones. For example, when 0.1 mol% of **12** in isopropanol was used, acetophenone was hydrogenated to 1-phenylethanol with complete conversion and 96.3% ee. **11** has a lower ee of 79.0%, a value similar to the parent homogeneous Ru-BINAP-DPEN catalyst (~80% ee) for the same reaction. Control experiments with homogeneous catalysts showed that the enhanced ee observed for **12** over its parent homogeneous Ru-BINAP-DPEN catalyst is a result of the bulky substituent effects on the 4,4'-positions [26]. Table 1 lists the series of substrates tested that all show complete conversion and high ee's in the range of 90.6–99.2%. TON of as high as 20,000 has been achieved with solid **12**. **12** could be readily recycled and reused for asymmetric hydrogenation of 1-acetophenone for up to eight times. These solids thus

Table 1
Heterogeneous asymmetric hydrogenation of aromatic ketones

Substrate	Solid loading	KO ^t Bu	11 e.e.%	12 e.e.%
Ar = Ph, R = Me	0.1%	1%	79.0 (81.3) ^a	96.3 (97.1) ^a
Ar = 2-naphthyl, R = Me	0.1%	1%	82.1	97.1
Ar = 4'- ^t Bu-Ph, R = Me	0.1%	1%	91.5	99.2
Ar = 4'-MeO-Ph, R = Me	0.1%	1%	79.9	96.0
Ar = 4'-Cl-Ph, R = Me	0.1%	1%	59.3	94.9
Ar = 4'-Me-Ph, R = Me	0.1%	1%	79.5	97.0
Ar = Ph, R = Et	0.1%	1%	83.9	93.1
Ar = Ph, R = <i>cyclo</i> -Pr	0.1%	1%	—	90.6
Ar = 1-naphthyl, R = Me	0.1%	1%	95.8	99.2
	0.02%	0.4%		98.9
	0.005%	0.02%		98.8(70%) ^b
	0.005%	0.02%		98.6 ^c

^aHomogeneous reactions; ^b70% conversion; ^c40 h reaction time.

represent highly active and enantioselective heterogeneous catalysts.

4. Concluding remarks and outlook

This paper summarizes the latest developments in the design of chiral hybrid organic-inorganic solids for applications in heterogeneous asymmetric catalysis. Chiral MOCNs of diverse topologies and functionalities have been prepared via a modular approach. The facile tunability of such molecular building blocks should allow precise engineering of chiral functionalities within these chiral porous MOCNs, which is intrinsically superior to the traditional approaches used for the heterogenization of homogeneous asymmetric catalysts. Although still at its infancy stage, chiral hybrid organic-inorganic solids have already shown very high catalytic activity and enantioselectivity in the hydrogenation of keto esters and aromatic ketones. Practically useful heterogeneous asymmetric catalysts can thus be envisioned from such a molecular building block approach, which will potentially lead to a breakthrough in the burgeoning field of chirotechnology.

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