

Self-supported Chiral Catalysts for Heterogeneous Asymmetric Catalysis

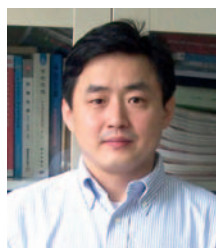
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Abstract: A conceptually new strategy for chiral catalyst immobilization, self-supported catalysts, in heterogeneous asymmetric catalysis is highlighted in the present article. Various homochiral metal-organic polymers with diverse structures have been designed and readily prepared through coordination assembly of modular polytypic/polyfunctional ligands and metal ions without using any supports. These polymers have been successfully employed as chiral catalysts in a variety of heterogeneous asymmetric reactions, including hydrogenation, epoxidation, sulfoxidation, carbonyl-ene reactions, diethylzinc addition, and Michael addition. The self-supported heterogeneous chiral catalysts showed activity and enantioselectivity comparable or even superior to those obtained with their corresponding homogeneous counterparts, and could be readily recovered and reused several times without significant loss of activity or enantioselectivity.

Keywords: Heterogeneous asymmetric catalysis · Self-supported chiral catalysts



Hongchao Guo received his B.Sc. degree (1997) and Ph.D. degree (2002) from China Agricultural University. After spending several years in chemical research at Shanghai Institute of Organic Chemistry, Max-Planck-Institut für Kohlenforschung, University of California at Los Angeles, and University of Illinois at Urbana-Champaign, he joined China Agricultural University as an associate Professor in 2010. His research focuses on Lewis base-catalyzed organic reactions and their application in organic synthesis.



Kuiling Ding received his B.Sc. degree from Zhengzhou University (1985) and Ph.D. degree from Nanjing University (1990) under the supervision of Professor Yangjie Wu. He became an assistant professor at Zhengzhou University in 1990 and full professor at the same place in 1995. During 1993–1994, he was engaged in postdoctoral research with Professor Teruo Matsuura at Ryukoku University (Japan). In the period from 1997 to 1998, he was a UNESCO research fellow with Professor Koichi Mikami at Tokyo Institute of Technology (Japan). He joined the Shanghai Institute of Organic Chemistry in 1999, where he is currently a professor of organic chemistry. His research interests include development of new chiral catalysts and methodologies for asymmetric catalysis.

tivity and catalytic activity, mild reaction conditions, and predictable manipulation, the difficulties associated with recovery and reuse of expensive chiral catalysts and the product contamination caused by metal leaching significantly hinders their practical applications in the synthesis of value-added fine chemicals, particularly in pharmaceutical production.^[4,5] The immobilization of chiral catalysts is considered as one of the most promising solutions to such problems.^[4,5] Multifarious approaches to immobilize homogeneous chiral catalysts for heterogeneous asymmetric reactions have been developed, typically including inert inorganic materials or organic polymers as supports and conducting the reactions in unconventional media such as ionic liquids.^[6–9] However, classical immobilization with various prefabricated supports often resulted in disadvantages such as reduced catalytic activity and/or selectivity as a result of the poor accessibility, random anchoring, or disturbed geometry of the active sites in the solid matrix.

As a new alternative strategy, the use of homochiral metal-organic polymers as heterogeneous catalysts for asymmetric reactions has been successfully developed as an effective tool for chiral catalyst immobilization in the last decade.^[10–18] The basic principle for the immobilization is to use multitopic chiral ligands and metal centers to form functionalized metal-organic assemblies *via* coordination bonds, which generally have an infinitely extended structure and usually are insoluble in certain organic solvents, hence could be used as heterogeneous catalysts. Two types of metal-organic polymers have been developed for this purpose (Scheme 1). The

1. Introduction

Among various catalysts for asymmetric catalysis, complexes of chiral ligands with transition metals as chiral homogeneous catalysts represent a convenient and efficient methodology for accessing a wide range of enantiomerically enriched compounds.^[1–3] Although homogeneous asymmetric catalysis offers many inherent advantages, such as high selec-

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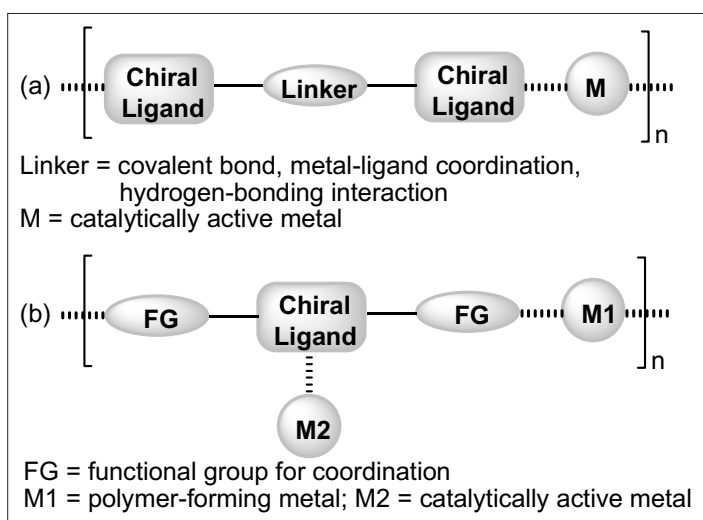
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Scheme 1. Schematic representation of the self-supported chiral catalysts.

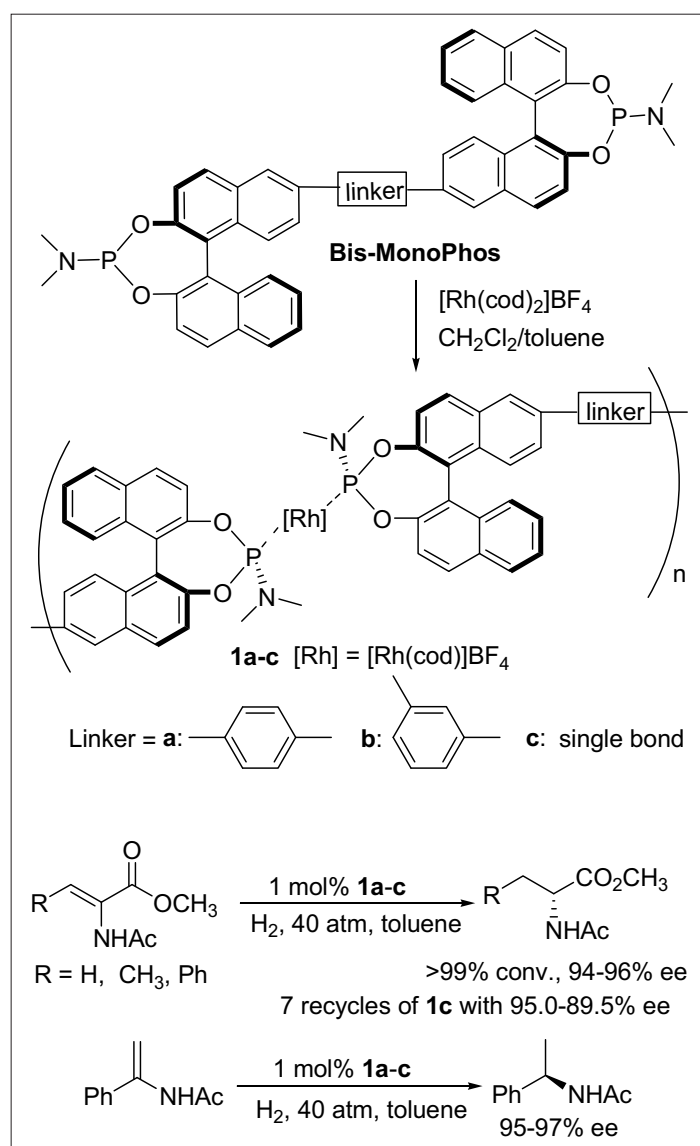
most straightforward way is the use of a linker to combine two molecules of chiral ligands for construction of an enantiopure ditopic (or polytopic) chiral ligand, which is then copolymerized with a catalytically active metal ion to afford a homochiral coordination polymer (Scheme 1a). The linker moiety may be either covalently bonded or have noncovalent interactions such as hydrogen bonding or ligand-to-metal coordination. As an alternative, the chiral bridging ligands are designed to bear two types of orthogonal functional groups, where one serves as the primary functional group to interact with the network-forming metal for the formation of the extended structure, and the other is responsible for attaching a metal for catalysis (Scheme 1b). In the case of the assembly involving the network-forming metal, there are two distinct types of metals, one assisting polymer formation and the other acting as the catalytic center. The two metals may be same or not. This kind of catalyst is generally obtained in a stepwise manner including the generation of the network followed by uploading of catalytically active metals. The active sites are located at the wall or as pendant auxiliaries on the backbones of the resulting solid. Using the above two ways, a homogeneous molecular catalyst can be incorporated into a polymeric solid, acting as the active center to catalyze asymmetric reactions in the chiral environment of the assembly. Depending on the coordination geometry of the metal as well as the bonding preference of the bridging ligand, polymeric structures with 1D chains, 2D layers, or 3D networks can be generated with uniform active sites. By judiciously tailoring the linkers and the chiral units of the polytopic ligand, chiral environment and other useful properties such as porosity can be fine-tuned for the specific application of these homochiral metal-organic assemblies in asymmetric catalysis. Since these homochiral metal-organic assemblies are utilized as immobilized homoge-

neous catalysts without external support, they are named self-supported chiral catalysts. Numerous successful self-supported chiral catalysts have been developed by the way shown in Scheme 1a or 1b for heterogeneous asymmetric catalysis. Herein, self-supported chiral catalysts, developed by the method in Scheme 1a in the author's

laboratory and by others, are discussed as classified by the nature of the linker moiety. Catalysts^[19–28] prepared by the strategy in Scheme 1b will not be covered in this review.

2. The Covalent Bond as Linker

The design and synthesis of multitopic chiral ligands with diverse geometrical features is a central issue in the generation of homochiral metal-organic polymers. Since there are lots of synthetic tools, using the covalent bond as linker is a powerful method for a ditopic (or polytopic) ligand architecture, which could be constructed by the combination of two molecules of chiral ligands at the both ends of the linker moiety. The homochiral coordination polymer for the self-supported catalyst is obtained by direct alternating copolymerization of the chiral bridging ligands and the metal ions. By this way, the catalytically active metal centers are directly incorporated into the main chain of the resulting homochiral solid. The metal plays a dual role as both



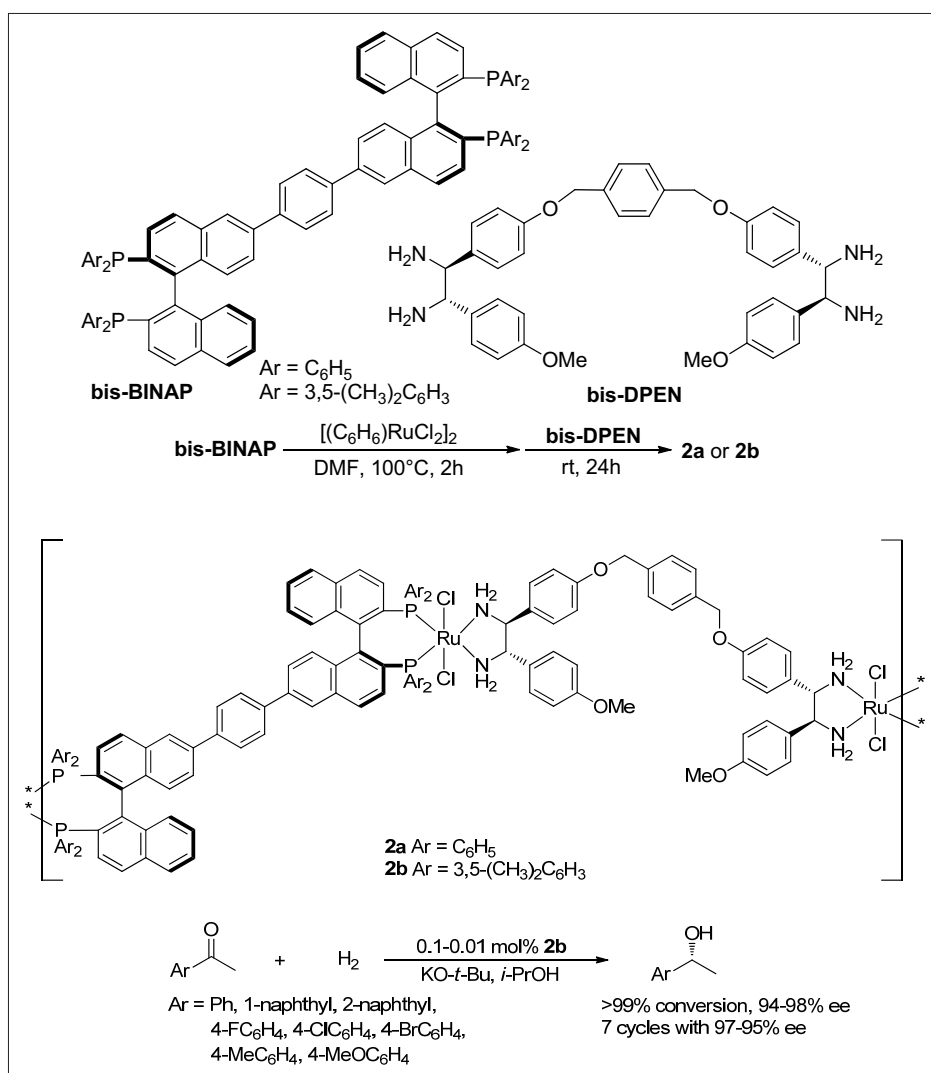
Scheme 2. Heterogeneous enantioselective hydrogenation of dehydro- α -amino acid and enamide derivatives with self-supported MonoPhos/Rh catalysts.

the structural binder and the active site. This strategy has been used in several heterogeneous asymmetric reactions.

2.1 Asymmetric Hydrogenation

Heterogenization of the well-known Feringa's MonoPhos/Rh system for asymmetric hydrogenation has been carried out by using the self-supporting strategy.^[29] The MonoPhos was bridged by using the covalent bond. For Rh(I)-catalyzed asymmetric hydrogenation of functionalized olefins using monophosphoramidite as the ligand, it has been widely accepted that the active species contains two monodentate phosphorous ligand moieties binding to one Rh center. Thus, the incorporation of active P-Rh-P sites into the coordination polymer could be achieved by assembly of an appropriate polytopic phosphorus ligands with a Rh(I) precursor. A solution of [Rh(cod)]BF₄ in dichloromethane was treated with the solution of the ditopic bis-phosphoramidites (Bis-MonoPhos) in toluene to give the Rh-containing polymer **1a-c** as amorphous orange solids. The solids **1a-c** were insoluble in toluene and thus used as heterogeneous catalysts in the asymmetric hydrogenation of β -aryl- or alkyl-substituted dehydro- α -amino acid and enamide derivatives, providing the corresponding amino acid and secondary amine derivatives with 94–97% *ee* in >99% conversion of substrates (Scheme 2). It is noteworthy that all three catalysts gave better enantioselectivity than that of their homogeneous counterpart (95–97% vs 89% *ee*) in the asymmetric hydrogenation of the enamide. In the hydrogenation of methyl 2-acetamidoacrylate, catalyst **1c** was isolated from the reaction mixture by filtration and reused for seven runs with full conversion and a slight decrease in enantioselectivity (95–89.5% *ee*). During the recovery and reuse of a heterogenized catalyst, partial decomposition of the catalyst was observed, probably leading to the deterioration of the catalytic activity and/or enantioselectivity. In order to address this issue, a continuous-flow reactor packed with a self-supported chiral catalyst was set up and used in the heterogeneous asymmetric hydrogenation.^[30] The continuous-flow system was demonstrated to be successful in the asymmetric hydrogenation of methyl α -acetamidobut-2-enoate, and ran continuously for a total of 144 h to afford the hydrogenation product in >99% conversion and constant 96–97% *ee* values.

The self-supported strategy was also used to incorporate BINAP-RuCl₂-DPEN moieties into a linear polymer by a programmed self-assembly of two different multitopic ligands with Ru(II) metallic ions.^[31] The bis-BINAPS were treated sequentially with [(C₆H₆)RuCl₂]₂



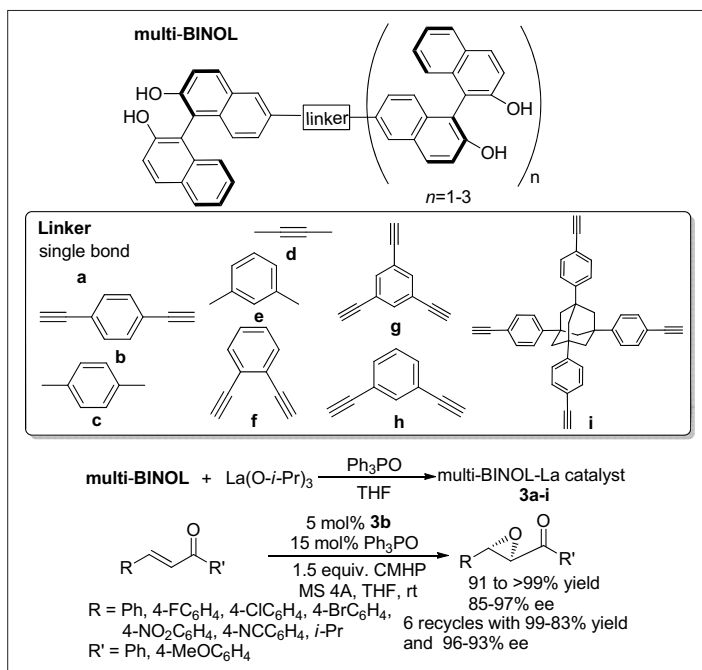
Scheme 3. Heterogeneous enantioselective hydrogenation of ketones with self-supported Noyori's catalyst.

and the chiral bridging bis-DPEN, to give the heterogenized Noyori-type catalysts **2a** and **2b**, respectively, by a spontaneous heterocoordination. Using 0.1 mol% of **2b** as a heterogeneous catalyst, the asymmetric hydrogenation of a variety of aromatic ketones was carried out in isopropanol at room temperature with potassium *tert*-butoxide as the base, providing the corresponding products in 100% conversion with 94–98% *ee* (Scheme 3), which are comparable to those obtained by using the homogeneous counterpart of **2**. Even using 0.01 mol% of **2b** in the hydrogenation of acetophenone, the hydrogenation still proceeded smoothly without significant loss of yield or enantioselectivity (95% *ee*). In contrast, 0.1 mol% of **2a** only gave a moderate 78% *ee* in the hydrogenation of acetophenone under the otherwise identical conditions. Once the hydrogenation was finished, the catalyst could be isolated from the reaction mixture by simple filtration under an Ar atmosphere (Ru leaching in product <0.1 ppm), and reused seven times with nearly unchanged enantioselectivity and yield.

The analogous heterogenized Noyori-type catalysts from achiral bis-BIPHEP in combination with the chiral bis-DPEN and Ru(II) salt have also been prepared by a similar procedure.^[32] Using the resulting chiral solid as a heterogeneous catalyst, up to 87% *ee* of the product was obtained in the asymmetric hydrogenation of aromatic ketones. The catalyst was reused four times in the hydrogenation of acetophenone with some decline of selectivity and activity.

2.2 Enantioselective Epoxidation

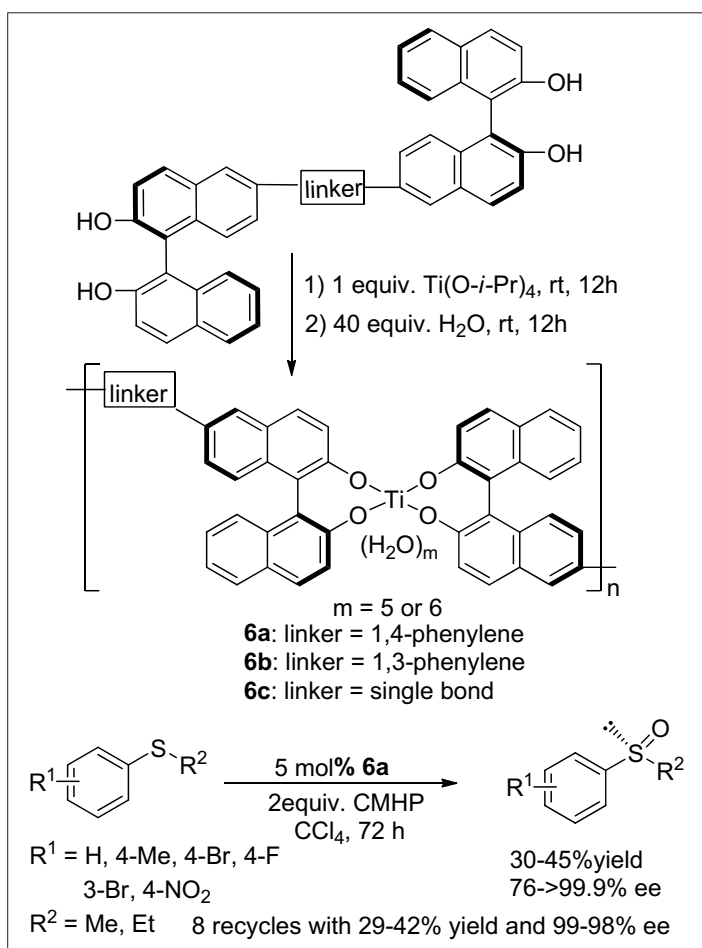
The heterogenization of Shibasaki's BINOL/La(III) catalyst for the enantioselective catalysis of epoxidation of α,β -unsaturated ketones was achieved by using the poly-BINOL/La(III) assemblies as the heterogeneous catalysts **3a-i**, which were prepared by the treatment of various multi-BINOL ligands containing diversified linker geometries with a THF solution of La(O-*i*-Pr)₃ in the presence of triphenylphosphine oxide.^[33] The chiral catalysts were amorphous precipitates and used in the enantioselective epoxidation of α,β -unsaturated ketones with cumene hydro-



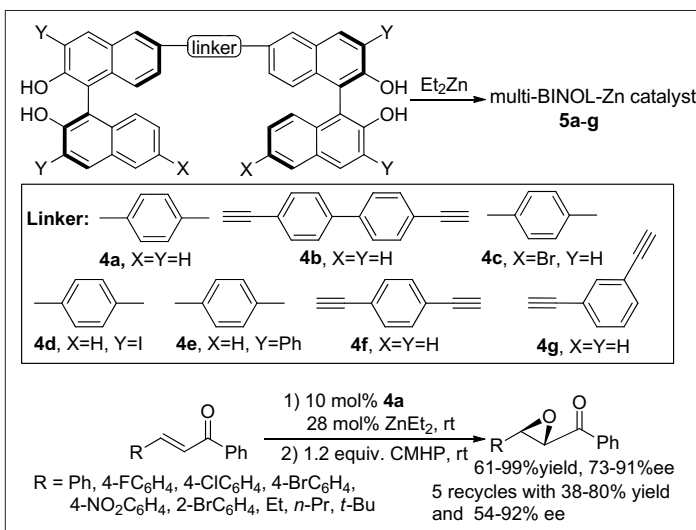
Scheme 4. Heterogeneous asymmetric epoxidation of α,β -unsaturated ketones using self-supported Shibasaki's BINOL/La(III) catalysts.

peroxide (CMHP) as the oxidant (Scheme 4). In the presence of 5 mol% **3b**, the oxidation reactions proceeded smoothly in THF at room temperature, providing the corresponding products in 91–99% yields with 85–97% *ees*, which are comparable

to those obtained using the homogeneous counterpart. The linker moieties of the bridging ligands exhibited a significant impact on the enantioselectivity and activity of the reactions. In the reaction of chalcone (R = R' = Ph), the enantioselectivity varied



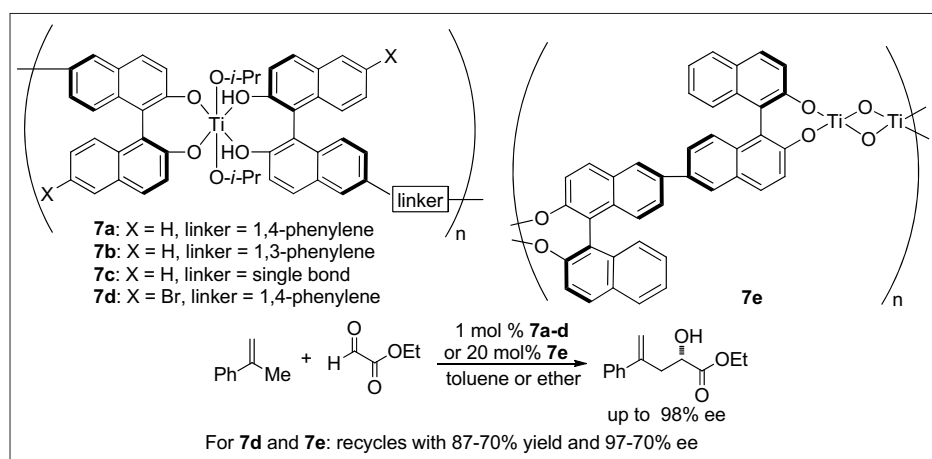
Scheme 6. Self-supported BINOL-Ti catalysts for heterogeneous catalysis of asymmetric sulfoxidations.



Scheme 5. Self-supported BINOL/Zn catalysts for asymmetric epoxidation of α,β -unsaturated ketones.

between 82% and 95%, depending on the length or spatial orientation of the linker in the poly-BINOLs, indicating the supramolecular structures of the assemblies have a significant influence on the catalytic processes. While the catalyst **3b** containing 1,4-diethynylbenzene linker afforded 97% *ee*, the catalyst **3d** bearing the shorter ethynyl linker only resulted in 82% *ee*. By simple filtration, catalyst **3b** can be readily recovered and reused for six cycles without significant loss of enantioselectivity (from 96% to 93%).

Chiral self-supported BINOL-Zn catalysts have also been developed for the heterogeneous asymmetric catalysis of epoxidation of enones.^[34] The self-supported catalysts **5a–5g** were obtained as white amorphous solids by treatment of the multi-BINOL ligands **4a–4g** bearing linear or bent linkers with two molar equivalents of diethylzinc in hexane/Et₂O. The solid catalysts are virtually insoluble in all organic solvents tested. Using **5a** as a heterogeneous chiral catalyst, the enantioselective epoxidations of α,β -unsaturated ketones with cumene hydroperoxide (CMHP) as the oxidant were performed in Et₂O to give the corresponding products in 61–99% yield and 73–91% *ee* (Scheme 5). Upon completion of the epoxidation, the solid catalyst **5a** was easily isolated from the reaction mixture by filtration under argon, and reused for five runs in the epoxidation of chalcone. Unfortunately, a considerable loss of reactivity (80%–38% yield) and enantioselectivity (92%–54%) after the second run was observed for unknown reasons.



Scheme 7. Self-supported BINOL-Ti catalysts for enantioselective carbonyl-ene reaction 7a-e.

2.3 Enantioselective Sulfoxidation

Ti-Poly-BINOL homochiral metal-organic polymers were applied in the heterogeneous asymmetric catalysis of sulfoxidation reaction.^[35] The bridged BINOL ligands were treated with $\text{Ti}(\text{O}-i\text{-Pr})_4$ in a 1:1 molar ratio in CCl_4 , followed by addition of 40 equivalents of water (relative to ligand), providing the homochiral Ti-Poly-BINOL polymers **6a-c** as amorphous orange or red powders. Using 5 mol% of the self-supported catalysts **6a-c**, the oxidation of a variety of aryl alkyl sulfides with CMHP as the oxidant was carried out in CCl_4 to afford the corresponding chiral sulfoxides in 96–99.9% *ee* and around 40% yield (Scheme 6). Filtration was performed

in air to recover the solid catalyst **6a**, which was reused in the sulfoxidation reaction of thioanisole for eight cycles that covered a period of more than one month. After eight runs, the enantioselectivity remained at the same level as that in first run (99% *ee*) and no significant deterioration in activity was observed.

2.4 Carbonyl-Ene Reaction

Sasai^[36] and Ding^[35,37] independently developed several homochiral bis-BINOL Ti polymers as the heterogeneous catalysts for the asymmetric carbonyl-ene reaction. The chiral titanium-bis-BINOL polymers **7a-e** (**7a-d** from Ding's lab, and **7e** from Sasai's lab) were prepared

as amorphous solids by treatment of the bridged bis-BINOLs with $\text{Ti}(\text{O}-i\text{-Pr})_4$ in dichloromethane. Using the polymer **7** as the immobilized catalysts, the carbonyl-ene reaction of α -methylstyrene with ethyl glyoxylate was performed under the optimized conditions, giving the α -hydroxyester in high yield and excellent enantioselectivity (up to 98% *ee*) (Scheme 7). The nature of linkers between the two BINOL units in the bis-BINOL ligands has notable impact on the enantioselectivity of the catalysis, presumably as a result of the differences in the supramolecular structures of the assemblies. Sasai's catalyst **7e** could be recovered by simple filtration and reused up to five consecutive runs with yields ranging from 66% to 88% and the *ee* values from 88% to 92%. Ding's catalyst **7d** can also be reused for five times, with a gradual decline in yields (87 to 70%) and *ee* values (97 to 70%).

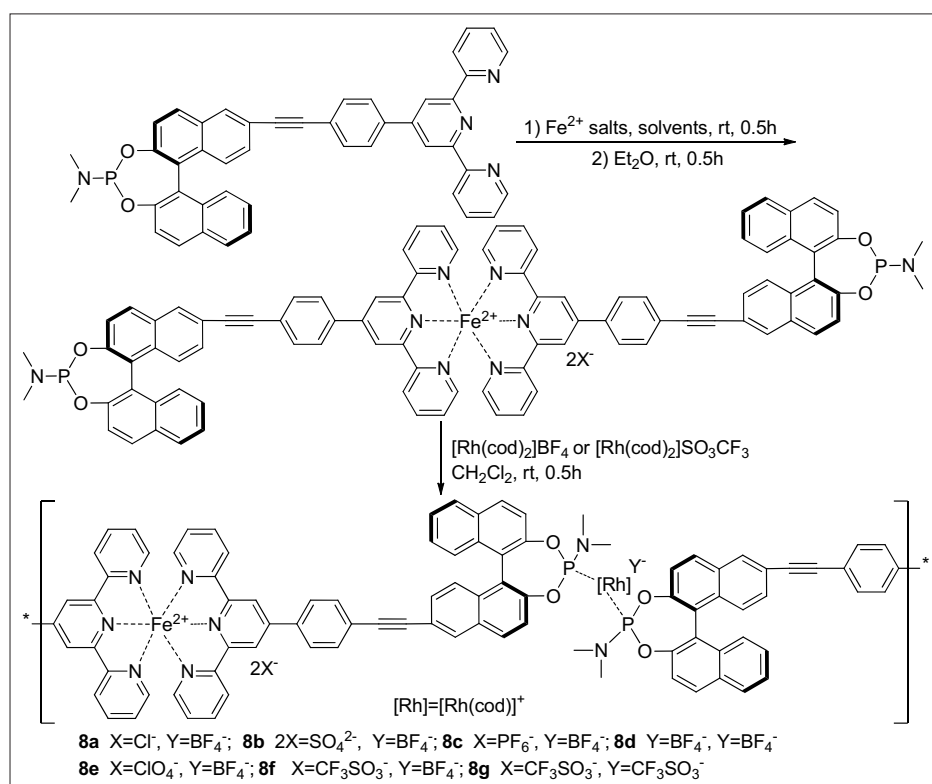
2.5 Other Reactions

Besides our work, Harada and Nakatsugawa reported the use of self-supported Ti-catalysts from the assembly of tris-BINOL ligands and $\text{Ti}(\text{O}-i\text{-Pr})_4$ for the heterogeneous asymmetric addition of diethylzinc to aldehydes.^[38] Sasai and coworkers used the self-supported Al-catalyst from the assembly of bis-BINOL ligands and LiAlH_4 for the heterogeneous enantioselective Michael reactions.^[36]

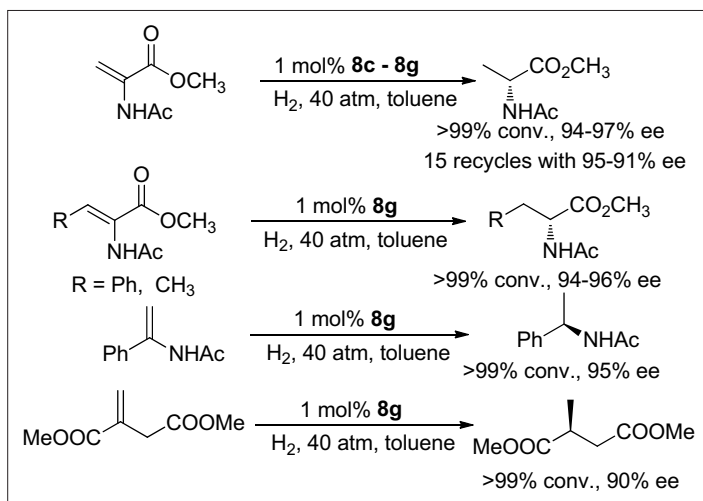
3. The Metal-Ligand Coordination as Linker

Sometimes, the preparation of covalent multitopic ligands is somewhat tedious. The use of noncovalent self-assembly, frequently metal coordination or hydrogen bond, as a practical alternative to covalent-based chemistry, is very helpful in the construction of a ditopic (or polytopic) ligand. The chiral ligand is required to bear two types of orthogonal functional groups, which might result in bimetallic assemblies upon sequential or one-pot reaction(s) with two different metals ions. The self-supported catalysts through this strategy are generally obtained by simultaneous generation of the bridging ligand and uploading of catalytically active metals to form extended structure.

By using the above strategy, an immobilized Feringa's MonoPhos/Rh catalyst containing two types of metal centers was elegantly constructed.^[39] In this case, a bifunctional heteroditopic ligand was designed to bear two orthogonal metal-ligating units (2,2':6',2''-terpyridine unit and Feringa's MonoPhos) (Scheme 8), which was readily synthesized with a copper-free Sonogashira coupling reaction as the key step. A class of chiral bimetallic



Scheme 8. Supramolecular bimetallic assemblies obtained by orthogonal metal coordination interactions.



self-supported catalysts **8a–8g** was formed by sequential treatment or one-pot reaction of bifunctional heteroditopic ligands with Fe(II) and Rh(I) salts. With 1 mol% of **8g** as the heterogeneous catalyst, asymmetric hydrogenation of α -dehydroamino acid, enamide, and itaconic acid derivatives were carried out in toluene at room temperature under 40 atm of H_2 to give the corresponding products with full conversion in 90–97% *ee*. The enantioselectivities obtained with the heterogeneous catalysts are comparable or even superior to those obtained with their homogeneous counterpart (MonoPhos)₂/Rh(I) (Scheme 9). Upon completion of the reaction, the catalyst could be easily recovered by filtration. In the asymmetric hydrogenation of methyl α -acetamidoacrylate, the catalyst **8e** and **8g** could be reused more than ten times without

obvious loss in the enantioselectivity or activity. In particular, catalyst **8g** was recycled for 15 runs with only slightly deteriorated enantioselectivity (95–91% *ee*).

4. The Hydrogen Bond as Linker

Hydrogen bonding is one of the most important tools in the design and fabrication of complex molecules and functional systems. Therefore, using hydrogen-bonding as the linker moiety for the homochiral coordination polymer is feasible. The key issue here is to combine one complementary or self-complementary hydrogen-bonding recognition motif onto the chiral ligand for the construction of multitopic ligands. By the hydrogen-bonding interaction, a bridging chiral ligand

Scheme 9. Heterogeneous asymmetric hydrogenations catalyzed by homochiral bimetallic assemblies **8**.

was formed to undergo self-assembly with the metal ion. The metal ion behaves as both the linker and the catalytic center.

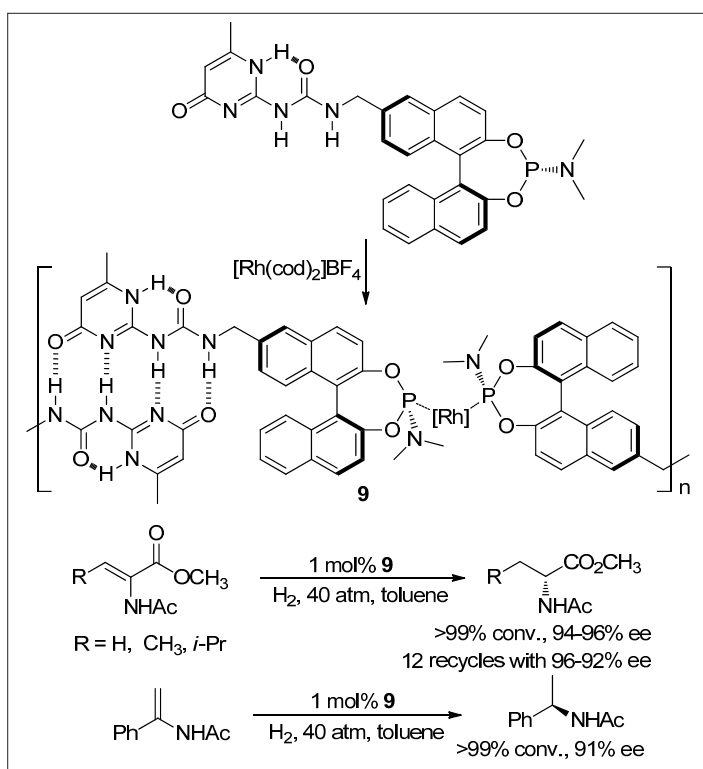
Ureido-4[1H]-ureidopyrimidone, which is among the most commonly used self-complementary hydrogen-bonding units, was tethered on a MonoPhos ligand motif as hydrogen-bonding unit to afford the ditopic chiral ligand.^[40] The formed ligand was treated with [Rh(cod)₂]BF₄ to generate the supramolecular metal-organic polymer **9** as a yellow solid which is insoluble in nonpolar organic solvents such as toluene (Scheme 10). With 1 mol% of **9** as the chiral catalyst, the heterogeneous hydrogenation of dehydroamino acid derivatives and *N*-(1-phenylvinyl)acetamide was carried out in toluene at 25 °C under 40 atm of H_2 to afford the products in 91–96% *ee* with >99% conversion of substrates. Both the selectivity and activity of the catalysis are comparable to the catalytic performance of its homogeneous counterpart. The catalyst **9** could be recovered by simple filtration and reused in the hydrogenation of (*Z*)-methyl 2-acetamidobut-2-enoate ten times to afford the corresponding product with uniformly full conversion and nearly constant enantioselectivity (96–92% *ee*).

5. Summary

Various homochiral metal-organic polymers with diverse structures have been designed and readily prepared through coordination assembly of modular polytopic/polyfunctional ligands and metal ions in the past ten years. These polymers have been successfully used as self-supported chiral catalysts in several types of heterogeneous catalytic asymmetric reactions. Particularly, some self-supported chiral catalysts have showed highly catalytic activity and excellent enantioselectivity that are comparable or even superior to those obtained using their corresponding homogeneous counterparts. These catalysts can be easily recovered and reused several times without significant loss of activity or enantioselectivity. The salient features of self-supported chiral catalyst – the remarkable asymmetric induction, the high catalytic activity and the enormous chemical and structural diversity – suggest that it could find extensive application in heterogeneous asymmetric catalysis.

Acknowledgments

The authors are grateful to their coworkers who have contributed to this research. Their names are listed in the references. K. D. is grateful for the financial support of this work from the Major Basic Research Development Program of China (grant no. 2010CB83300) and the Chinese Academy of Sciences.



Scheme 10. Homo-chiral supramolecular metal-organic assembly for the heterogeneous catalysis of asymmetric hydrogenations.

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