Engineering Chiral Polyoxometalate Hybrid Metal−Organic Frameworks for Asymmetric Dihydroxylation of Olefins

Qiuxia Han,[†,‡] Cheng He,[†] Min Zhao,[†] Bo Qi,[†] Jingyang Niu,[‡] and Chunying Duan*[,†]

[†]State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, People's Republic of China
[‡]School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, People's Republic of China

S *Supporting Information*

ABSTRACT: Chiral metal−organic frameworks (MOFs) with porous and tunable natures have made them feasible for performing a variety of chemical reactions as heterogeneous asymmetric catalysts. By incorporating the oxidation catalyst $[BW_{12}O_{40}]^{5−}$ and the chiral group, L- or D-pyrrolidin-2-ylimidazole (**PYI**), into one single framework, the two enantiomorphs Ni-**PYI**1 and Ni-**PYI**2 were obtained via self-assembly, respectively. The channels of Ni-**PYI**s were enlarged through a guest exchange reaction to remove the cationic chiral templates and were well modulated with hydrophilic/hydrophobic properties to allow molecules of both H_2O_2 and olefin ingress and egress. The coexistence of both the chiral directors and the oxidants within a confined space provided a special environment for the formation of reaction intermediates in a stereoselective fashion with high selectivity. The resulting MOF acted as an amphipathic catalyst to prompt the asymmetric dihydroxylation of aryl olefins with excellent stereoselectivity.

Catalytic asymmetric processes that exhibit high activity, selectivity, and broad substrate generality under mild reaction conditions are indispensable for producing enantiomerically enriched compounds in modern organic synthesis.[1,2] The primary research avenues by which these goals are pursued have successfully delivered vast numbers of new reactions over many decades. On using either chiral metal complexes or chiral small organic molecules to activate the target chemical bonds, these reactions can also be rendered asymmetrically.[3,4] In this case, the combination of both chiral organic molecules and metal complexes in a cooperative catalysis fashion attracted much attention as a powerful method to generate catalysts for prospective practical applications.[5,6] The major challenge in achieving the enhanced catalytic activity and higher level of stereodifferentiation thus goes beyond the synthesis of highly functionalized complexes but includes the judicious selection of appropriate catalytic combinations for compatibility between the chiral organic and the inorganic catalysts.[7]

Metal−organic frameworks (MOFs) are hybrid solids with infinite networks built from organic bridges and inorganic connecting nodes.[8,9] In addition to their potential applications in many diverse areas, chiral MOFs are ideally suited for heterogeneous asymmetrically catalytic conversions, since they can impose size- and shape-selective restriction through readily fine-tuned channels or pores[10,11] and high enantioselectivity through the imbedded, regularly ordered chiral groups.[12,13] In particular, the potential to directly blend both chiral ligands and the metal ions endows MOFs with multiple functionalities and new features that their components do not have.[14,15]

Polyoxometalates (POMs) are well-known catalysts studied in the olefin epoxidation with excellent thermal and oxidative stability toward oxygen donors.[16−18] The introduction of POMs into these hierarchical frameworks at the molecular level possibly increases the stability and corresponding functions, providing a promising way to combine the organic and inorganic catalytic components synergistically.[19−21] One of the important issues in the petroleum industry is that the oxidation reactions using POMs as catalysts often involve reactants in immiscible liquid phases and aqueous oxidizing agents. The attempt to find suitable amphipathic catalysts is an important methodology for organic synthesis in both industrial and academic laboratories.[22,23]

By incorporating a Keggin-type $[BW_{12}O_{40}]^{5−}$ anion, nickel-(II) ions, and an asymmetric organocatalytic group, **PYI**,[24] within one single MOF, herein, we report the design and synthesis of two new enantiomorphs of MOFs, Ni-**PYI**1 and Ni-**PYI**2, for the asymmetric dihydroxylation of aryl olefins (Scheme 1). We envisioned that the unique redox properties of

Scheme 1. Synthetic Procedure of Ni-PYI1, Showing the Guest Exchange and the Potential Amphipathic Channel for the Asymmetric Olefin Dihydroxylation
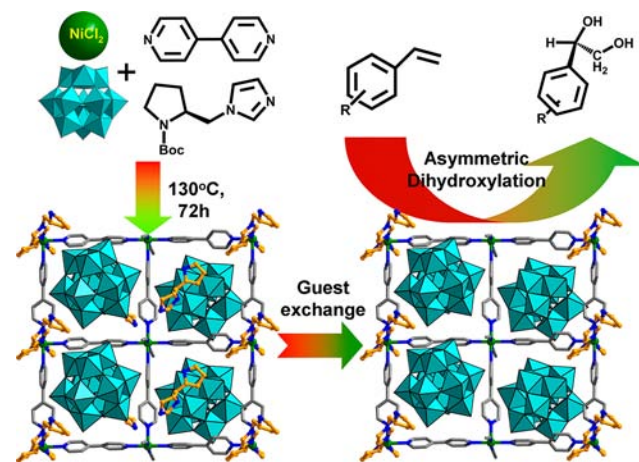
$[BW_{12}O_{40}]^{5-}$ with its oxygen-enriched surface provided a sufficient driving force for the transformation of catalytic precursors to the active intermediate of the epoxidation.[25,26] In addition, the chiral **PYI**s potentially acted as cooperative catalytic sites to forge a crucial reaction center that enhanced the activities of the oxidants and drove the catalysis in an asymmetrical way.[27,28] In the meantime, the hydrophilic/hydrophobic properties of the MOFs consolidated by the organic ligands and the POM anions was beneficial for the amphipathic catalysis of the epoxidation processes.[29,30]

Solvothermal reaction of $Ni_2H[BW_{12}O_{40}]$ and 4,4′-bipyridine with L-*tert*-butoxycarbonyl-2-(imidazole)-1-pyrrolidine (L-**BCIP**) gave Ni-**PYI1** in a yield of 60%. Elemental analyses and powder X-ray analysis (XRD) indicated the pure phase of its bulk sample. Single-crystal structural analysis revealed that Ni-**PYI1** crystallized in the space group C_2.[31] Each of the two crystallographically independent Ni(II) ions connected four 4,4′-bipyridine bridges alternatively to produce a 2D sheet. In addition, the $[BW_{12}O_{40}]^{5-}$ anions were imbedded within the polygons of the sheets (Figure S2, Supporting Information). The nickel(II) ions were coordinated in octahedral geometries with four nitrogen atoms from four bpy ligands forming the equatorial plane and with either two imidazole N atoms or two acetonitrile N atoms occupying the axial positions, respectively (Figure 1b). These coordinated **PYI** molecules were located
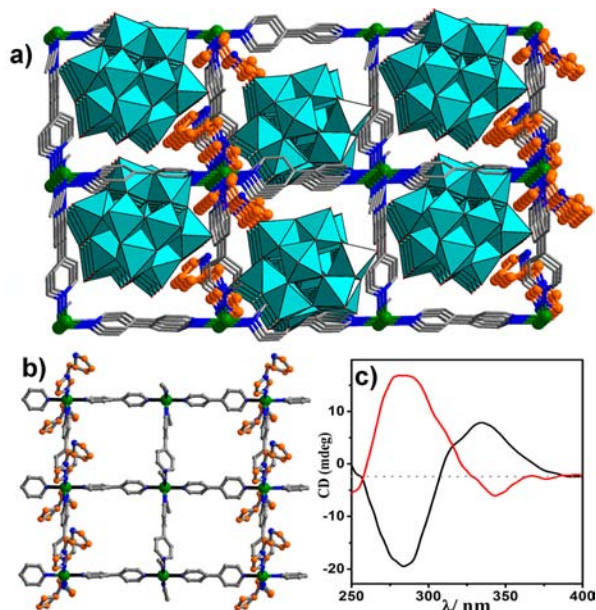

Figure 1. (a) Crystal structure of Ni-**PYI1** showing the stacking pattern of the gridlike sheets and the 1D channels along the *a* axis with $[BW_{12}O_{40}]^{5-}$ anions imbedded. (b) 2D network of Ni-**PYI1** displaying the coordination environments of Ni(II) ions. (c) CD spectra of the crystalline powders Ni-**PYI1** (black) and Ni-**PYI2** (red), respectively, showing the opposite Cotton effects.

above or beneath the 2D layer with the butoxycarbonyl of L-**BCIP** being removed in the reaction simultaneously and the pyrrolidine N atoms being protonated. Hydrogen bonds were found between the protonated pyrrolidine N atoms and the imbedded $[BW_{12}O_{40}]^{5-}$ anion with N(9)···O(19A) and N(9)···O(22) separations of about 3.24 and 3.27 Å, respectively (symmetry code A: $^3/_2$ - x, $-^1/_2$ + y, 1 − z) (Figure S4, Supporting Information). Interacting with $[BW_{12}O_{40}]^{5-}$ through hydrogen bonds, the sheets were further stacked in a

parallel fashion with both the active sites of the chiral directors and the oxidation catalysts aligned in the channels (Figure 1a). It is postulated that this kind of structure would render the formation of the reaction intermediate of ethanediols coexisting with the chiral sites and the hydroperoxy group in a well-defined stereoselective fashion.

Most importantly, there are isolated **PYI** molecules that are protonated and occupy the pores of channels. They can be expediently replaced by soaking the crystals of Ni-**PYI1** in a dichloromethane solution containing diethylamine (Figure S7, Supporting Information).[32] As a result, channels of Ni-**PYI1** were enlarged with accessible pores of about 1230 Å³, as calculated from PLATON analysis.[33] Unlike the hydrophobic channels within most MOFs, these channels in the guest-exchanged Ni-**PYI1** were consolidated by the hydrophilic $[BW_{12}O_{40}]^{5-}$ anions and the hydrophobic organic ligands. Consequently, both the aryl olefin and the oxidant H_2O_2 could take part in ingress and egress through these amphipathic channels to interact with each other as well as the catalytically active sites in the channels.

The transformation of the asymmetric dihydroxylation was examined initially by using styrene and aqueous hydrogen peroxide (15%) as oxidant in CH_2Cl_2, along with *ex*-Ni-**PYI1** (0.7% mol ratio) in a heterogeneous manner at 40 °C, as shown in Table 1. The result revealed the successful execution of our

Table 1. Yields and Enantiomeric Excess (ee) Values of the Asymmetric Dihydroxylation about the Aryl Olefins[a]
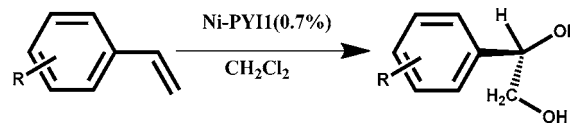
entry	substrate	conversion (%)[b]	ee (%)[c]
1	styrene (**1**)	75	>95
2	2-chlorovinylbenzene (**2**)	76	67
3	3-chlorovinylbenzene (**3**)	79	>95
4	4-chlorovinylbenzene (**4**)	75	>95
5	3,5-di-*tert*-butyl-4′-vinylbiphenyl (**5**)	<10	nd

[a]Reaction conditions: olefin, 55 mmol; *ex*-Ni-**PYI1**, 0.04 mmol; H_2O_2 (15%), 15 mL; CH_2Cl_2, 5 mL; 40 °C; 60 h. [b]The conversions were determined by ^1H NMR spectroscopy of crude products. [c]The ee value was determined by chiral HPLC on a Chiralcel OD-H column.

MOF design, showing excellent enantioselectivity (ee > 95%) for (R)-phenyl-1,2-ethanediol. In addition, the removal of *ex*-Ni-**PYI1** by filtration after 30 h shut down the reaction, and the filtrate afforded only 5% additional conversion after stirring at 40 °C for another 30 h. These observations suggested that *ex*-Ni-**PYI1** was a true heterogeneous catalyst. Solids of *ex*-Ni-**PYI1** could be isolated from the reaction suspension by simple filtration alone. In addition, the catalysts could be reused at least three times with moderate loss of activity (from 75% to 68% of yield) and a slight decrease in the selectivity (ee values from >95% to 90%). The index of XRD patterns of the *ex*-Ni-**PYI1** bulky sample filtered off from the catalytic reaction evidenced the maintenance of the crystallinity (Figure S8, Supporting Information). The use of such a catalyst can be extended to other chlorovinylbenzene substrates with comparable activity and asymmetric selectivity (Table 1).

In contrast to the smooth reactions of the substrates **1**−**4**, the asymmetric dihydroxylation catalytic reaction in the presence of bulky olefin **5**, 3,5-di-*tert*-butyl-4′-vinylbiphenyl,

gave less than 10% of conversion under the same reaction conditions. The negligible adsorption by immersing ex-Ni-**PYI**1 into a solution of substrate **5**, coupled with the fact that the molecule size of **5** is larger than that of the channels,[34] revealed that the substrate **5** is too large to be adsorbed in the channels. It is suggested that the asymmetric dihydroxylations indeed occur in the channels of the MOF, not on the external surface. It is also found that when L-**PYI** and its hydrochloride salt were used as catalysts, the reaction become inert under similar conditions. In addition, employing $Ni_2H[BW_{12}O_{40}]$ and L-**PYI** as homogeneous catalysts gave a conversion of 45% and an ee value of 15%, which are far lower than those with ex-Ni-**PYI**1 as catalyst. The higher conversion in the case of the ex-Ni-**PYI**1 system can possibly be attributed to the suitable distribution of pairs of the chiral **PYI** moiety and $[BW_{12}O_{40}]^{5-}$ oxidant that provides effective contacts with substrates at the same time. The hydrolysis experiments demonstrate that the 0.7 mol % loading of ex-Ni-**PYI**1 lead to the diol product in a conversion of 87% from the racemic 2-phenyloxirane. It seems that Ni-**PYI**1 is really a synergistic catalyst, enabling the concurrence of the catalytic oxidation and hydrolysis reactions.[35,36] As the diols obtained through the hydrolysis of the racemic 2-phenyloxirane do not exhibit any stereoselectivity, the enantioselectivity of the dihydroxylation can thus be mainly attributed to the asymmetric behavior of the epoxidation.[37,38] From a mechanistic point of view, the formation of hydrogen bonds between the pyrrolidine N atom and the terminal oxygen atoms of the $BW_{12}O_{40}{}^{5-}$ first activated the corresponding $W=O_t$ to generate an active peroxide tungstate intermediate with H_2O_2, ensuring the smooth progress of the reaction. At the same time, the hydrogen bonds also enforced the proximity between the conventional electrophilic oxidant and the chiral directors to provide additional steric orientation, driving the catalysis to occur in a steroselective manner.[39] The fact that the $W=O_t$ bonds (greater than 1.71 Å) for both O(22) and O(19) of the hydrogen-bonded terminal oxygen atoms were about 0.03 Å (on average) longer than other $W=O_t$ bonds gave preliminary crystallographic evidence to support this hypothesis (Table S2, Supporting Information).

Circular dichroism (CD) of the bulk sample of Ni−**PYI**1 presented Cotton effects at 284 ($\theta = -19.5°$) and 340 nm ($\theta = 7.90°$) (Figure 1c). The whole spectrum was quite different from that of the chiral precursor L-**BCIP**, which showed a positive cotton effect at 268 nm.[40] The difference in absorption in the spectral region for the charge-transfer bands might be indicative of the homochirality of the framework.[41] The use of D-**BCIP** resulted in the formation of other enantiomorph, Ni-**PYI**2. It crystallizes in the same chiral space group C_2 with the same cell dimensions as for Ni-**PYI**1.[42] The CD spectrum of Ni-**PYI**2 exhibited Cotton effects opposite to those of Ni-**PYI**1, as expected for a pair of enantiomers with a mirror-image relationship between each other. Solids of Ni-**PYI**2 exhibited similar catalytic activities but gave products with opposite chiralities in the asymmetric dihydroxylation of styrene.

To further investigate the synergistic interactions between the chiral amine and the inorganic POM, the reference MOF Ni-**BPY** was assembled using the same starting components with similar stoichiometries but different pH value (yield of 65%) (Scheme S1, Supporting Information). It crystallized in the space group $P2_1$ and was comprised of $[Ni_2H_{1.5}(bpy)_5(H_2O)_{1.5}(Cl)_{0.5}]^{5+}$ and $[BW_{12}O_{40}]^{5-}$ in an asymmetric unit.[43] Both nickel ions reside in octahedral geometries with the equatorial plane defined by the four

nitrogen atoms of bpy ligands. A terminal oxygen of the POM and one water molecule (for Ni(1)) or partially occupied water molecule or chloride (for Ni(2)) were on the axial positions, respectively. As 4-connected nodes, the nickel ions were linked together to form a 2D metal−organic gridlike sheet. These 2D sheets were stacked along the crystallographic c axis and were parallel to each other through the interactions between $[BW_{12}O_{40}]^{5-}$ and the nickel(II) centers, giving rise to 1D channels along the a axis with a cross section of about 9.7 × 12.4 Å^2 (Figure 2). Since Ni-**BPY** possessed the similar
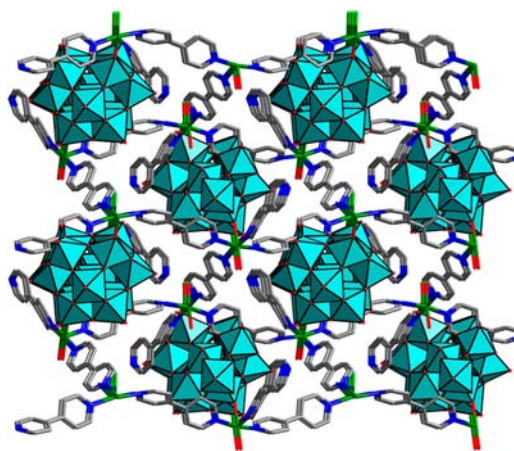

Figure 2. Crystal structure of Ni-BPY showing the stacking pattern of the gridlike sheet and the 1D channels along the a axis with $[BW_{12}O_{40}]^{5-}$ anions imbedded.

channels constructed by the same organic linkers and the same POM anions without any chiral directors, it is thus an excellent reference for investigating the catalytic activity of Ni-**PYI**s in the same dihydroxylation reaction.

Catalytic activities of Ni-**BPY** in the asymmetric dihydroxylation experiments were carried out under the same conditions by using styrene and aqueous hydrogen peroxide (15%). As shown in Table 2, the ∼0.7% mole ratio loading of the catalyst caused significant catalytic efficiency with conversion of up to 60% of the diol (entry 6). The catalytic reaction did not exhibit any obvious enantioselectivity. It should be concluded that the activity of Ni-**BPY** in the catalytic dihydroxylation arises from the oxidative catalysis activity of $[BW_{12}O_{40}]^{5-}$, whereas the stereoselectivity in the reactions was dominated by the presence

Table 2. Yields and ee Values of the Dihydroxylation of Styrene[a]

entry	cat.	yield (%)[b]	ee (%)[c]
1	Ni-**PYI**1	75	>95
5	Ni-**PYI**2	71	<−95
6	Ni-**BPY**	60	
7	Ni-**BPY**/L-**PYI**	70	16
8	Ni-**BPY**/D-**PYI**	73	−20

[a]Reaction conditions: styrene, 55 mmol; catalyst 0.04 mmol H_2O_2 (15%), 15 mL; CH_2Cl_2, 5 mL; 40 °C; 60 h. [b]The conversions were determined by ^{1}H NMR spectroscopy of the crude products. [c]The ee values were determined by chiral HPLC on a Chiralcel OD-H column.

of the chiral directors and the chiral environment of the channels, like those of Ni-**PYIs**.

Experiments on the asymmetric dihydroxylation also revealed that the presence of excess chiral adduct L-**PYI** in the aforementioned control reaction (entry 7) led to an increased conversion but a slightly lower enantioselectivity (ee of 16%) of the product. It seems that the formation of hydrogen-bonding interactions between the protonated pyrrolidine rings absorbed within the pores and the $[BW_{12}O_{40}]^{5-}$ anions could form a novel mode for activation of the oxidant and improve the catalytic activity. However, under the unconfined conditions, these interactions occur in multiple ways with differing orientations of the ammonium salt and the $[BW_{12}O_{40}]^{5-}$ anion, which is likely to be deleterious to the enantioselectivity. In contrast, in the case of Ni-**PYIs** as catalysts, the interactions between them are confined and fixed orientationally. In other words, the enantioselectivities of Ni-**PYIs** are superior to those of simply mixing the corresponding MOFs with the chiral adduct originating from the integration of POM and chiral directors into a single MOF.[30,44]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving crystal data, experimental details, and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for C.D.: cyduan@dlut.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(31) Data for Ni-**PYI1**: $C_{38}H_{52}BN_{11}NiO_{42}W_{12}$, M_r = 3610.63, monoclinic, space group $C2$, a = 25.266(3) Å, b = 11.490(1) Å, c = 22.880(2) Å, β = 90.49(1)°, V = 6642(1) Å³, Z = 4, 18459 total reflections, 11426 unique reflections (R_{int} = 0.034), final R1 (with I > $2\sigma(I)$) = 0.038, wR2 (all data) = 0.0792, S = 1.021.

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(42) Data for Ni-**PYI2**: $C_{38}H_{52}BN_{11}NiO_{42}W_{12}$, M_r = 3610.63, monoclinic, space group $C2$, a = 25.187(4) Å, b = 11.483(2) Å, c = 22.862(4) Å, β = 90.37(1)°, V = 6612(2) Å³, Z = 4, 18571 total reflections, 11366 unique reflections (R_{int} = 0.048), final R1 (with I > $2\sigma(I)$) = 0.0490, wR2 (all data) = 0.1073, S = 1.003.

(43) Data for Ni-**BPY**: $C_{50}H_{45.50}BCl_{0.50}N_{10}Ni_2O_{42}W_{12}$, M_r = 3810.62, monoclinic, space group $P2_1$, a = 13.414(1) Å, b = 14.924(1) Å, c = 20.062(1) Å, β = 102.67(1)°, V = 3918.5(2) Å³, Z = 2, 18409 total reflections, 10227 unique reflections (R_{int} = 0.0621), final R1 (with I > $2\sigma(I)$) = 0.0576, wR2 (all data) = 0.1412, S = 1.000.

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