Homochiral Metal−Organic Frameworks for Heterogeneous Asymmetric Catalysis

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Abstract: Homochiral crystallizations of two enantiomeric metal−organic frameworks (MOFs) Ce−**MDIP1** and Ce−**MDIP2** were achieved by using L- or D-**BCIP** as chiral inductions, respectively, where the chiralities were characterized by solid state CD spectra. Ce−**MDIPs** exhibit excellent catalytic activity and high enantioselectivity for the asymmetric cyanosilylation of aromatic aldehydes; the homochiral Cd−**TBT** MOF having L-**PYI** as a chiral adduct exhibits stereochemical catalysis toward the Aldol reactions.

Recently, there has been increasing interest in creating homochiral porous metal−organic frameworks (MOFs), because chiral MOFs are, beyond the more fundamental search for new topologies, highly attractive for asymmetric catalysis and other applications requiring noncentrosymmetric crystal structures such as nonlinear optical devices.[1−3] Among the essential approaches that exist for the preparation of chiral MOFs,[4] self-resolution crystallization offers great advantages as it does not use chiral components.[5] In the case of the presence of an additional chiral source, such a homochiral crystallization has the potential to result in a given handedness.[6] In several unusual discoveries, the absolute configuration of the bulk crystals is controllable through the chiral induction effect.[7,8] However, this approach has not been successfully used in the preparation of chiral MOFs for enantioselective catalysis yet, because chirality control from run to run is generally quite difficult[7] and the design of highly enantioselective MOF catalysts *via* remote influence by chiral environments of open channels still remains a big challenge.[9,10]

L-Proline and its derivatives are well-known asymmetric organocatalysts, accelerating a variety of enantioselective organic reactions, including C−C bond forming Aldol and Michael reactions under homogeneous reaction conditions.[11,12] By using L- and D-pyrrolidine-2-yl-imidazole (**PYI**)[13] as a chiral adduct, we perform the homochiral crystallization of the two enantiomorphs Ce−**MDIP1** and Ce−**MDIP2**, having one-dimensional channels and coordinatively unsaturated metal sites, resepectively. Asymmetric cyanosilylations of aromatic aldehydes were dispalyed to validate the enantioselectively catalytic performance of the MOFs.

Solvothermal reaction of methylenediisophthalic acid (H₄**MDIP**) and Ce(NO₃)₃·6H₂O in the presence of L-*N*-*tert*-butoxy-carbonyl-2-(imidazole)-1-pyrrolidine (L-**BCIP**) in water gave compound Ce-**MDIP1** in a high yield (60%). Elemental analysis along with powder X-ray analysis of the compound indicated the pure phase of its bulky sample. Circular dichroism (CD) studies of the bulk samples of Ce−**MDIP1** showed clearly positive cotton effects at about 254 nm and negative cotton effects at about 322 nm. The whole spectrum was quite different from those of the chiral adducts L-**BCIP** and **PYI**. Compound Ce−**MDIP1** crystallized in a chiral space group $P2_1$ with one cerium ion, one H**MDIP** ligand, and one water molecule included in an asymmetric unit. Molecules of

Table 1. Results for the Catalytic Cyanosilylation of Carbonyl Substrates in the Presence of Ce−**MDIPs**[a]

| | | ee (%)[b] | |
Entry	Ar	Ce−**MDIP1**[a]	Ce−**MDIP2**
1	phenyl	93	94
2	4-methoxyphenyl	91	97
3	1-naphthyl	98	>98
4	2-naphthyl	>98	>98

[a] Reaction conditions: (CH₃)₃SiCN, 1.2 mmol; aldehyde, 0.5 mmol; Ce−**MDIP** catalysts, 0.01 mmol (2 mol %); room temperature under N₂ for 24 h to ensure high conversion (>95%) of the reaction. [b] The enantiomeric excess (*ee*) was determined by HPLC analysis.

the chiral adduct were not found in the crystals. Each cerium ion was coordinated by five oxygen atoms corresponding to five monodentate carboxyl groups, two oxygen atoms from one bidentate carboxyl group, and one water molecule. The H**MDIP** ligands linked the metal ions through the carboxyl groups forming a noninterpenetrating 3D network containing chiral channels with a 10.5 × 6.0 Å² cross section along the *a*-axis. The cerium ions having removable coordinated water molecules were well-positioned within the channels. They were able to interact with potential guest molecules that enter the framework channels, suggesting Ce−**MDIP1** had the potential to functionalize as an actively heterogeneous catalyst.[14]

The asymmetric cyanosilylation experiments were employed with a 1:2.4 mol ratio of the selected aromatic aldehyde and cyanotrimethylsilane in CH₃CN at room temperature through a heterogeneous manner. As shown in Table 1, the loading of only a 2 mol % ratio of Ce−**MDIP1** (0.01 mmol) catalyst leads to the almost complete conversion of (*S*)-2-phenyl-2-(trimethylsilyloxy)acetonitrile corresponding to benzaldehyde and excellent stereochemical performance with an *ee* value up to 91%.[15] Ce−**MDIP1** thus represents the first example of MOF-based heterogeneous asymmetric catalysts for that important reaction, providing a convenient route to canhydrins. Also, the catalysis efficiency of Ce−**MDIP1** is comparable to the best prior result for metal−organic framework catalysts (Supporting Information Table S1).[16] Noticeably, the removal of Ce−**MDIP1** by filtration after only 4 h completely shut down the reaction, affording only 10% additional conversion upon stirring for another 7 h. These experiments unambiguously demonstrate that Ce−**MDIP1** is a true heterogeneous asymmetric catalyst. The solids of Ce−**MDIP1** can be easily isolated from the reaction suspension by simple filtration alone and can be reused at least three times with a slight decrease in the reactivity and enantioselectivity. The index of XRD patterns of the Ce−**MDIP1** bulky sample filtered off from the catalytic reaction evidences the maintenance of the crystallinity. Infrared spectroscopy of the catalyst impregnated with a dichloromethane solution of

benzaldehyde exhibited one broad C−O stretch at 1685 cm^{-1}. The red shift from 1692 cm^{-1}(free aldehyde) suggested the absorbance of benzaldehyde and possible activation of the substrate in the channels of Ce−**MDIP1**.

Similarly, a chirality induction effect was observed with D-**BCIP**, which resulted in the formation of another enantiomorph, Ce−**MDIP2**. Ce−**MDIP2** also crystallized in the chiral space group $P2_1$ with cell dimensions similar to those of Ce−**MDIP1.** The CD spectrum of bulk crystals of Ce−**MDIP2** exhibited Cotton effects exactly opposite to those of Ce−**MDIP1** (Figure 1c), indicating that the homochiral crystallization is controllable through chiral induction. Without the chirality induction effect, such an observation is highly unlikely.
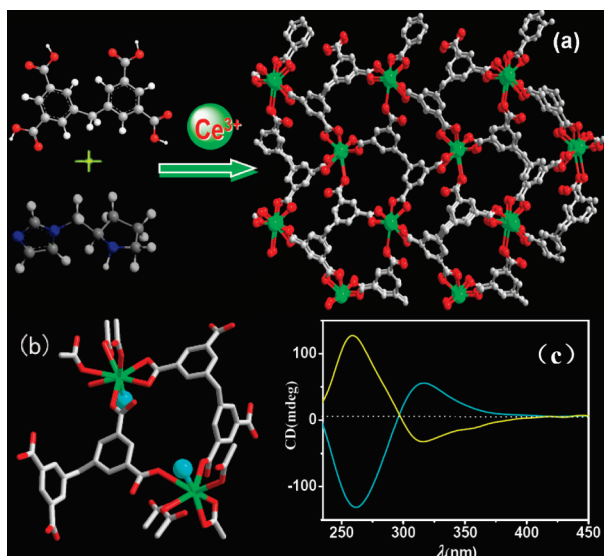

Figure 1. Crystal structure of Ce−**MDIP1** showing the positions of the removable coordinative molecules and the metal ions exposed within the 1D channels (a) and (b); the cyan balls show the removable coordinated water molecule, and the red, gray, and green spheres represent the oxygen, carbon, and cerium atoms, respectively. H atoms and lattice water molecules are omitted for clarity. (c) CD spectra of bulk crystals of Ce−**MDIP1** (yellow line) and Ce−**MDIP2** (cyan line), respectively, showing the opposite Cotton effects of the two compounds.

To further investigate the catalytic performance of the MOFs assembled with the chiral adduct L-**BCIP**, compound Cd−**TBT** was produced by a hydrothermal reaction using cadmium perchlorate, 1,3,5-tris(4-carboxyphenyl)benzene and L-**BCIP** as the original reactants. IR spectroscopy of Cd−**TBT** showed the N−H stretching band at 2974 cm^{-1}, revealing the incorporation of **PYI** in the MOF.[17] CD studies of the Cd−**TBT** bulk samples showed the homochirality with a positive cotton effect centered at 385 nm. Single crystal structural analysis revealed that Cd−**TBT** crystallizes in the chiral space group $P2_1$. It comprised two structurally similar parts that interpenetrate each other. In each part, the pseudotetrahedral Cd^{2+} ion was coordinated by three bidentate chelating carboxylate groups from three H**TBT** bridging ligands and a nitrogen atom of an imidazole ring as a terminal one. The Cd^{2+} ion and the H**TBT** anion bridge each acted as a three-connected node to produce a 2D honeycomb network. The rhombus channels with dimensions of 4.0 × 6.5 Å^2 (Figure 2) are constructed through tumbling one 2D sheet to another in an interpenetration manner. Molecules of **PYI** locate above or beneath the 2D interpenetration layer with the potential catalytic active sites N−H of pyrrolidine exposed.[17] Catalysis activities of Cd−**TBT** in asymmetric aldol reactions between various aromatic aldehydes and cyclohexanone
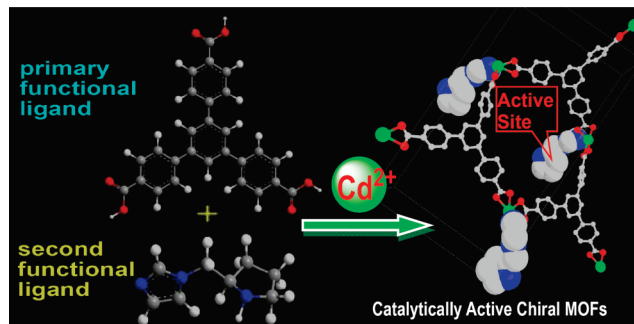

Figure 2. Schematic representation of the construction of compound Cd−**TBT**. The catalytically active units were drawn in the space-filling diagram. The framework was drawn in a ball/stick diagram. The green, red, blue, and gray balls represent the Cd, O, N, and C atoms, respectively.

Table 2. Aldol Reactions between Aldehydes and Cyclohexanone^a

		Cd−TBT		L-PYI	
entry	Ar	Yield (%)^b	ee (%)^c	Yield (%)^b	ee (%)^c
1	2-nitrophenyl	42	60	92	25
2	3-nitrophenyl	77	61	93	25
3	4-nitrophenyl	97	58	98	21
4	1-naphthyl	8	n.d.	6	n.d.

^{a} Reactions conditions: 25 °C for 10 days in a 1:1 solution of methanol and water using 0.5 mmol of aldehyde and 5 mmol of cyclohexanones with about 0.025 mmol (5 mol %) of catalyst. ^{b} Isolated yield based on aldehydes. ^{c} Value represents the major isomer. n.d. = not determined.

were assessed and shown in Table 2. The same sequence of catalytic activities corresponding to Cd−**TBT** in a heterogeneous manner and free **PYI** in a homogeneous manner suggested that the aldol reactions were mainly prompted by the chiral adduct L-**BCIP**, rather than the structural motifs of the MOF. Also, structural simulations of the substrates demonstrated that the rhombus channel of 4.0 × 6.5 Å^2 was not large enough to encapsulate molecules of **PYI** and the substrates. In this case, the better enantioselection in the case of the heterogeneous catalyst than that of the corresponding **PYI** and its derivatives in the homogeneous manner[13] may partially originate from the restricted movement of the substrates on the MOF's exterior coupled with multiple chiral inductions.

Supporting Information Available: Crystal data (CIF) experimental details and the general procedure of catalysis reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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