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 difficult9 and the design of highly enantioselective MOF catalysts has been 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 enantiomers Ce–MDIP1 and Ce–MDIP2, having one-dimensional channels and coordinatively unsaturated metal sites, respectively. Asymmetric cyanosilylations of aromatic aldehydes were displayed to validate the enantioselectively catalytic performance of the MOFs.

Solvochemical reaction of methylenedisopthalic acid (HMDIP) 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 P21, with one cerium ion, one HMDIP ligand, and one water molecule included in an asymmetric unit. Molecules of the preparation of chiral MOFs,4 self-resolution crystallization offers optical devices.1

The asymmetric cyanosilylation experiments were employed with a 1:2.4 mol ratio of the selected aromatic aldehyde and cyanomethylsilane 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)acetoni-trile 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 carboxylic acids. 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, allowing 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

Table 1. Results for the Catalytic Cyanosilylation of Carbonyl Substrates in the Presence of Ce–MDIPs

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>Ce–MDIP1 ee (%)</th>
<th>Ce–MDIP2 ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>phenyl</td>
<td>93</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>4-methoxyphenyl</td>
<td>91</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>1-naphthyl</td>
<td>98 &gt;98</td>
<td>98 &gt;98</td>
</tr>
<tr>
<td>4</td>
<td>2-naphthyl</td>
<td>&gt;98</td>
<td>&gt;98</td>
</tr>
</tbody>
</table>

*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.

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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 P2₁ 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.](image1)

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 ν(N–H) stretching band at 3074 cm⁻¹, revealing the incorporation of Pyi in the MOF. CD studies of the Cd–TBT bulk samples showed the homochirality with a positive cotton effect centered at 358 nm. Single crystal structural analysis revealed that Cd–TBT crystallizes in the chiral space group P2₁. It comprised two structurally similar parts that interpenetrate each other. In each part, the pseudotetrahedral Cd²⁺ ion was coordinated by three bidentate chelating carboxylate groups from three HTBT bridging ligands and a nitrogen atom of an imidazole ring as a terminal one. The Cd²⁺ ion and the HTBT anion bridge each act as a three-connected node to produce a 2D honeycomb network. The rhombus channels with dimensions of 4.0 × 6.5 Å² (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. Catalysis activities of Cd–TBT in asymmetric aldol reactions between various aromatic aldehydes and cyclohexanone 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 Å² 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 may partially originate from the restricted movement of the substrates on the MOF’s exterior coupled with multiple chiral inductions.

![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.](image2)

| Table 2. Aldol Reactions between Aldehydes and Cyclohexanone* |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| **entry** | **Ar** | **Yield (%)** | **ee (%)** | **Yield (%)** | **ee (%)** |
| 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. |

* 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. ¥ Isolated yield based on aldehydes. ¥ Value represents the major isomer. n.d. = not determined.

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**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.

**References**


