Chiral porous metal-organic frameworks with dual active sites for sequential asymmetric catalysis

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Metal-organic frameworks (MOFs) are a class of organic–inorganic hybrid materials built from metal-connecting nodes and organic-bridging ligands. They have received much attention in recent years owing to the ability to tune their properties for potential applications in various areas. Properly designed MOFs with uniform, periodically aligned active sites have shown great promise in catalysing shape-, size-, chemo-, regio- and stereo-selective organic transformations. This study reports the synthesis and characterization of two chiral MOFs (CMOFs 1 and 2) that are constructed from Mn-salen-derived dicarboxylic acids [salen is (R, R)-N, N'-bis(5-tert-butylsalicylidene)-1,2-cyclohexanediamine], bis(4-vinylbenzoic acid)-salen manganese(III) chloride (H2L4) or bis(benzoic acid)-salen manganese(III) chloride (H2L3) and [Zn4(m4-O)(O2CR)6] or [Zn5(H2O)2(m3-OH)2(O2CR)8] secondary building units (SBUs), respectively. The SBUs in CMOF-1 are connected by the linear ditopic Mn-salen-derived linkers to construct a fourfold interpenetrated isoreticular MOF (IRMOF) structure with pcu topology. In CMOF-2, the Mn-salen centres dimerize in a cross-linking way to form a diamondoid structure with threefold interpenetration. CMOF-1 was examined for highly regio- and stereo-selective tandem alkene epoxidation/epoxide ring-opening reactions by using the Mn-salen and Zn₄(μ₄-O)(carboxylate)₆ active sites, respectively. Our work demonstrated the potential utility of chiral MOFs with multiple active sites in the efficient synthesis of complex molecules with excellent regio- and stereo-controls.

Keywords: chiral; crystal engineering; metal-organic framework; asymmetric catalysis; hybrid solid; sequential catalysis

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Metal-organic frameworks (MOFs) have attracted a great deal of interest from the scientific community in recent years (Evans & Lin 2002; Kitagawa et al. 2004; Férey et al. 2005; Ockwig et al. 2005; Bradshaw et al. 2007; Cohen 2012; Cui et al. 2012). Compared with traditional inorganic materials such as zeolites or mesoporous solids (Lee et al. 2006; Egeblad et al. 2008), MOFs are synthesized under mild conditions, thus allowing systematic design and tuning of their structures and properties at the molecular level (Lin 2005, 2007; Ma et al. 2009a). In the past 15 years, MOFs have been molecularly engineered for a variety of applications, such as nonlinear optics (Evans & Lin 2002; Wang et al. 2012), separation (Chen et al. 2006; Pan et al. 2006; Xiang et al. 2011; Li et al. 2012), gas storage (Rowsell & Yaghi 2005; Dincă & Long 2008), chemical sensing (Allendorf et al. 2008; Chen et al. 2009; Lan et al. 2009; Han et al. 2010; Xie et al. 2010; Kreno et al. 2012), biomedical imaging (Rieter et al. 2008; deKrafft et al. 2009; Lin et al. 2009a; Della Rocca et al. 2011), drug delivery (Rieter et al. 2008; Lin et al. 2009a; Horcajada et al. 2010; Huxford et al. 2010; Taylor-Pashow et al. 2010) and heterogeneous catalysis (Seo et al. 2000; Kesani & Lin 2003; Wu et al. 2005; Banerjee et al. 2009; Wang et al. 2009, 2011a, b; Ma et al. 2010a, b; Song et al. 2010; Falkowski et al. 2011). In particular, with their highly ordered, crystalline structures that can be determined unambiguously by single-crystal X-ray crystallography, MOFs provide an ideal platform to study single-site catalysis with solid materials (broadly defined as ‘heterogeneous catalysis’ in this study). MOF catalysts combine advantages of both homogeneous and heterogeneous catalysts. On the one hand, MOF catalysts have uniform active sites as homogeneous catalysts, which provide excellent selectivities of and control over the catalytic processes; on the other hand, the heterogeneous nature of MOF catalysts facilitates the separation, recovery and reuse of the catalytic material, thus significantly reducing the costs for catalyst replacement and product purification. The molecular nature of MOF catalysts also allows systematic engineering of the active sites and/or open channel sizes, enabling detailed delineation of the structure–property relationships in MOF catalysts.

High porosity and large channel sizes are required in MOF catalysts for them to efficiently transport substrates and products in and out of the MOF framework. As MOF porosity increases to a certain extent (more than 60–70% void space as calculated by PLATON) and, in particular, as the MOF open channels become larger (usually greater than 1.5 nm), the MOF structure can significantly distort to lose its porosity upon solvent removal, a phenomenon commonly referred to as breathing of MOFs (Serre et al. 2002; Llewellyn et al. 2008; Férey & Serre 2009; Neimark et al. 2010). However, as the asymmetric catalytic processes are carried out in solution, the large open channels of these MOFs are maintained in the catalytic cycles. Because of the breathing effect, the traditional gas sorption method to quantify the porosity of a solid is not suitable for MOFs with large channel sizes. New methods are needed to assess or even quantify the substrate/product diffusion through the MOF channels. Lin et al. recently developed a dye uptake protocol, in which large dye molecules in solution replace the gas molecules in gas sorption measurement as probes to assess the pore volume and sizes, in order to quantify the porosity of highly porous MOFs with large open...
channels (Ma et al. 2010a). A luminescence quenching study was also carried out recently to quantitatively determine the diffusion coefficients of probe molecules through the channels of a phosphorescent MOF (Wang & Lin 2011).

Chemical stability of MOFs is another major concern regarding MOF catalysis. Different metal-connecting nodes/linking functionality exhibit different chemical stabilities. Among the most common metal-carboxylate cluster secondary building units (SBUs), a general stability trend holds in the order of $\text{Zn}_4(\mu_3-O)(\text{O}_2\text{C}R)_6 < \text{Cu}_2(\text{sol})_2(\text{O}_2\text{C}R)_4 < \text{Zr}_6(\mu_3-O)_4(\mu_3-\text{OH})_4(\text{O}_2\text{C}R)_{12}$ (Eddaoudi et al. 2002; Cavka et al. 2008; Ma & Lin 2008, 2010a; Li et al. 2009; Lin et al. 2009b; Wu et al. 2009; Guillerm et al. 2010; Song et al. 2010; Falkowski et al. 2011; Schaate et al. 2011; Wang et al. 2011a; Kim & Cohen 2012). An MOF catalyst should be designed in such a way that its stability is compatible with the condition under which the catalytic reaction is performed.

Although a large number of MOFs have been examined as heterogeneous catalysts, most of these reactions are Lewis acid-catalysed transformations that can be readily catalysed by zeolites (Lee et al. 2009). Given the lower thermal, chemical and mechanical stabilities of MOFs, MOFs will unlikely compete with zeolites in these catalytic reactions (Lee et al. 2009). Heterogeneous asymmetric catalysis represents an interesting and important area where MOFs can outshine zeolites or other porous materials. Although significant efforts have been devoted to the synthesis of chiral zeolites or other porous materials in the past several decades, little progress has been made in this area. Only a few enantiopure zeolites are reported to date, and none of them have found practical applications in heterogeneous asymmetric catalysis or enantioselective separations (Newsam et al. 1988; Anderson et al. 1994; Sun et al. 2009). High temperatures used in the calcination processes during the zeolite synthesis inevitably destroy the chiral environments afforded by the chiral organic templates to result in achiral or racemic mixtures of zeolites. In contrast, MOFs have provided a fertile ground for the molecular engineering of solid asymmetric catalysts in the past decade, by employing a large inventory of homogeneous asymmetric catalysts (Trost & VanVranken 1996; Pu 1998; Boaz et al. 2002; Noyori 2002; Zhou et al. 2002) as the key building blocks. Because MOFs can be synthesized under mild conditions, racemization of chiral building blocks is avoided (Ma et al. 2009b; Yuan et al. 2009; Liu et al. 2010). Two different general strategies have been developed to prepare numerous MOF-based asymmetric catalysts in the past decade. Lin et al. first demonstrated the synthesis of highly active and enantioselective MOF catalysts via post-synthetic functionalization (Ngo et al. 2004; Ma et al. 2009a). Alternatively, catalytically competent bridging ligands can be directly incorporated into MOFs to afford solid asymmetric catalysts at remarkably high catalyst loadings (Hu et al. 2003a,b; Cho et al. 2006). Well-defined active sites in MOFs are accessible to bulky substrates and reagents via large open channels.

The modular nature of MOF synthesis also makes it possible to introduce two (or more) different catalytic sites into a single MOF material. For example, one active site can be incorporated into the MOF as part of the bridging ligand, whereas the other active site can be introduced in the metal-connecting points or the SBUs. In such MOFs, different chemical reactions can be catalysed by the different active catalytic centres in tandem to allow multiple-step transformations of organic compounds with a single solid. Chiral Mn-salen [salen is $(R, R)-N,N'$-
bis(5-tert-butylsalicylidene)-1,2-cyclohexanediamine] complexes are well-known homogeneous asymmetric catalysts for alkene epoxidation reactions (Zhang et al. 1990; Palucki et al. 1998; Canali & Sherrington 1999; Baleizão & García 2006), and it has been demonstrated that the Mn-salen can be immobilized in MOFs to serve as effective heterogeneous catalysts (Cho et al. 2006; Song et al. 2010). In particular, we recently reported an isoreticular MOF series built from chiral Mn-salen-derived dicarboxylate-bridging ligands, \( L_1-H_2 \) to \( L_3-H_2 \), and the \([Zn_4(\mu_1-O)(O_2CR)_6]\) SBUs (scheme 1). The MOF series adopts the predicted \textbf{pcu} topology with tunable pore/channel sizes, providing an ideal platform for studying catalytic alkene epoxidation reactions (Song et al. 2010). On the other hand, the \([Zn_4(\mu_4-O)(O_2CR)_6]\) SBUs are reported as effective catalytic sites by taking advantage of their Lewis acidity (Ravon et al. 2008; Phan et al. 2010). Hence, we propose that combining the two catalytic sites in a single MOF would result in a solid that can catalyse sequential alkene epoxidation and epoxide ring-opening reactions. Herein, we report the rational design and synthesis of two new chiral MOFs (1 and 2) built from Mn-salen-derived dicarboxylate-bridging ligands (\( L_1-H_2 \) and \( L_3-H_2 \)) and \([Zn_4(\mu_4-O)(O_2CR)_6]\) and \([Zn_5(H_2O)_2(\mu_3-OH)_2(O_2CR)_8]\) SBUs, respectively, and the application of 1 in sequential catalysis of stereoselective alkene epoxidation and regioselective epoxide ring-opening reactions.

2. Result and discussion

(a) Synthesis and structural characterization of chiral MOF 1 and 2

Mn-salen-derived dicarboxylic acids \( L_3-H_2 \) and \( L_4-H_2 \) were synthesized by the condensation of \((R,R)\)-cyclohexanediamine and corresponding salicylaldehyde derivatives followed by metalation with Mn(II) salts and air oxidation. CMOF-1 was synthesized by heating a mixture of \( L_4-H_2 \) and Zn(NO\(_3\))\(_2 \cdot 6\)H\(_2\)O in

\[ \text{Scheme 1. Chemical structures of Mn-salen-derived dicarboxylic acids } L_1-H_2 \text{ to } L_4-H_2. \]
diethylformamide (DEF)/ethanol at 60°C for two weeks. Dark crystals of CMOF-1 were obtained after filtration in 78 per cent yield (scheme 2). CMOF-2 was obtained in modest yields by heating a mixture of L₃-H₂ and Zn(NO₃)₂ · 6H₂O in dimethylformamide (DMF)/ethanol at 80°C for 4 days.

We hypothesized that linear Mn-salen-derived dicarboxylate ligands can link [Zn₄(μ₄-O)(O₂CR)₆] SBUsto form three-dimensional MOFs of the pcu topology, as reported previously (Song et al. 2010). Dark cuboid crystals of up to 0.4 mm in each dimension were obtained from the reactions between L₄-H₂ and Zn(NO₃)₂ · 6H₂O in DEF/ethanol at 60°C. However, the quality of single-crystal data for CMOF-1 was not high enough to allow for structural solution after collecting several datasets. The exceptionally large cell parameters were consistently determined from these datasets. The c/a ratio of this hexagonal unit cell (2.39) is very close to those of the previously reported CMOF-1′–CMOF-5′ series (2.40–2.45), indicating their structural similarity (table 1). We propose an isoreticular MOF (IRMOF)-like structure model based on the structures of the CMOF-1′–CMOF-5′ isoreticular series. The predicted powder X-ray diffraction (PXRD) pattern is consistent with the experimental one (figure 1), supporting the proposed structure model. We further assigned a fourfold interpenetrated structure based on solvent content determination by ¹H-NMR/thermogravimetric analysis (TGA) as well as porosity quantified by a dye uptake experiment (see below). Even after fourfold interpenetration, CMOF-1 still exhibits large triangular open channels with an edge size of 1.5 nm (figure 2) along the ⟨001⟩ directions as well as square open channels of the dimension of 1.0 nm along the ⟨10−2⟩ directions.

It is now well established that MOF frameworks are prone to adopting interpenetrating structures when the bridging ligands become highly elongated (Evans et al. 1999; Evans & Lin 2001, 2002). To date, single-crystal X-ray crystallography is still the only direct method for determining the number of interpenetrating networks in a MOF. PXRD patterns often do not differ much between interpenetrated and non-interpenetrated structures, except in special cases when additional symmetry/pseudo-symmetry is present in the interpenetrated structure that can lead to new systematic absences. The different density of interpenetrated versus non-interpenetrated structures of the same chemical composition was also used to differentiate or even separate the two different crystals (Farha et al. 2008; Song et al. 2010). Unfortunately, density measurement is not suitable for MOFs with very large open channels (such as the CMOF-1′–CMOF-5′ and CMOF-1 series) owing to the fast exchange of solvent molecules which, in many cases, account for the majority of the crystal weight. We have resorted to solvent weight losses determined by TGA as a simple but reliable way to identify the number of interpenetrating networks in
Table 1. Comparison of isoreticular structures of CMOF-1’–CMOF-5’ (Song et al. 2010) and CMOF-1.

<table>
<thead>
<tr>
<th>Framework formula</th>
<th>CMOF-1’</th>
<th>CMOF-2’</th>
<th>CMOF-3’</th>
<th>CMOF-4’</th>
<th>CMOF-5’</th>
<th>CMOF-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>R32</td>
<td>R3</td>
<td>R32</td>
<td>R3</td>
<td>R3</td>
<td>N/A</td>
</tr>
<tr>
<td>Cell dimension (Å)</td>
<td>29.7 × 29.7 × 72.7</td>
<td>29.6 × 29.6 × 72.5</td>
<td>35.9 × 35.9 × 87.8</td>
<td>35.9 × 35.9 × 87.9</td>
<td>41.9 × 41.9 × 100.3</td>
<td>48.3 × 48.3 × 115.9</td>
</tr>
<tr>
<td>Void space (%)</td>
<td>61.1</td>
<td>80.2</td>
<td>76.8</td>
<td>88.4</td>
<td>75.9</td>
<td>75.2</td>
</tr>
<tr>
<td>Interpenetration (fold)</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Solvent content</td>
<td>20DMF·2H2O</td>
<td>22DEF·4H2O</td>
<td>42DMF</td>
<td>37DEF·23EtOH·4H2O</td>
<td>38DMF·11EtOH·11H2O</td>
<td>19DEF·13EtOH·11H2O</td>
</tr>
<tr>
<td>Solvent weight loss (%)</td>
<td>41.3</td>
<td>53.2</td>
<td>55.5</td>
<td>68.1</td>
<td>53.0</td>
<td>50.0</td>
</tr>
<tr>
<td>BBR-250 uptake weight (%)</td>
<td>2.1</td>
<td>15.4</td>
<td>6.3</td>
<td>37.7</td>
<td>16.3</td>
<td>14.5</td>
</tr>
</tbody>
</table>
MOFs. We have established an empirical linear relationship between the void space% of a MOF calculated by PLATON and the solvent weight loss of an MOF determined by TGA, based on crystal structures published by our group during the past decade (figure 3). CMOF-1 possesses 75.2 per cent of void space as calculated by PLATON based on the fourfold interpenetrated structural model. The TGA analysis gives a solvent weight loss of 50.0 per cent. These two pieces of information lead to a point close to the linear line on the void space versus solvent weight loss plot, supporting the assignment of fourfold interpenetrating structure of CMOF-1. With a combination of $^1$H-NMR/TGA, the complete formula of CMOF-1 is determined to be $\text{Zn}_4\text{O}(\text{L}_4)(\text{DEF})_{19}(\text{EtOH})_{13}(\text{H}_2\text{O})_{11}$. Dye uptake measurements also give indirect evidence of channel sizes. A 14.5 wt% uptake of Brilliant Blue R-250 inside the channels of CMOF-1 verifies the existence of large channels in the structure to transport molecules as large as the dye compound.

The four networks in CMOF-1 randomly occupy six possible positions. Such a partial filling (i.e. disorder) of multiple network positions was also observed in CMOF-5'. There is, however, a significant difference between the partial-filling
patterns of CMOF-1 and CMOF-5'. In CMOF-5', single-crystal X-ray diffraction data were successfully modelled with two of the three networks fully occupying two positions and the third network randomly occupying three possible positions at one-third occupancy (Song et al. 2010). In CMOF-1, we believe all of the four networks are disordered and randomly occupy six possible positions, which essentially reduce the crystallinity of CMOF-1 and weaken its X-ray diffraction intensity, making the single-crystal structure unsolvable.

We have shown that the interpenetration of MOFs can be controlled by using different solvents, taking advantage of the size difference of solvents as space-filling templates (Song et al. 2010). For example, treating Zn(NO$_3$)$_2$·6H$_2$O with L$_1$-H$_2$ ligand in DMF/EtOH gave the twofold interpenetrated CMOF-1', whereas in (DEF)/EtOH afforded the non-interpenetrated CMOF-2' (Song et al. 2010). Similar reactions of Zn(NO$_3$)$_2$·6H$_2$O and L$_2$-H$_2$ also resulted in interpenetrated framework CMOF-3' and the non-interpenetrated CMOF-4'. The interpenetration patterns of these CMOFs are highly depending on the steric effects of the solvents but not on the reaction temperatures. However, as ligands became even longer, the reaction between L$_3$-H$_2$ or L$_4$-H$_2$ and Zn(NO$_3$)$_2$·6H$_2$O only resulted in threefold interpenetrated CMOF-5' (Song et al. 2010) and fourfold interpenetrated CMOF-1 in either DMF/EtOH or DEF/EtOH solution, implying a fine balance between solvent template effects and network catenation. In these cases, intrinsic disorders of relative positions of the different folds of frameworks bring additional challenges in single-crystal X-ray determination of the structures (see above).
As reported previously, cubooctahedral single crystals of CMOF-6′ were obtained from the reaction of $\text{L}_4\text{H}_2$ and $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ in the dibutylformamide/EtOH solution at 80°C (Song et al. 2011). As determined
by single-crystal X-ray crystallography, CMOF-6' crystallizes in the trigonal $R_3$ space group with the asymmetric unit of four $L_4$ ligands and four-third of the $Zn_4(\mu_4-O)$ clusters. However, unlike in the cases of IRMOF series, the $Zn_4(\mu_4-O)$ clusters in CMOF-6' are highly distorted. Instead of forming regular four-member rings and three-dimensional network of pcu topology, CMOF-6' adopts the unusual lcy ($3^5 \cdot 5^6 \cdot 6^3$) topology with the presence of three- and five-member rings. The whole structure can be described as a close packing of seven-node cages constructed from three pentagonal faces and a triangular face (figure 4). Adopting a twofold interpenetrated structure, CMOF-6' exhibits triangular open channels with the edge length of 2.9 nm and a void space of 87.8 per cent (Song et al. 2011). Compared with the IRMOF framework CMOF-1, CMOF-6' exhibits higher solvent weight loss (70.5% versus 50.0%) and dye uptake (70.5 versus 14.5 wt% for Brilliant Blue R-250), verifying the larger open channel sizes and higher porosity of CMOF-6' than CMOF-1 as shown in the structural models.

Single crystals of CMOF-2 possess a different structure than the IRMOF series. In CMOF-2, Mn-salen centres dimerize in a cross-linking way to form dimers with each manganese coordinates to two halves of each $L_3$ ligand, and each $L_3$ ligand is connected to two manganese centres, resulting in a MOF that is not suitable for epoxidation catalysis. Instead of the well-known $[Zn_4(\mu_4-O)(O_2CR)_6]$ SBUs, a trinuclear zinc node $[Zn_5(H_2O)_2(\mu_3-OH)_2(O_2CR)_8]$ is observed in CMOF-2. The $[Zn_5(H_2O)_2(\mu_3-OH)_2(O_2CR)_8]$ SBUs are linked by the $(L_3)_2$ dimers to form a diamondoid network. CMOF-2 crystallizes in the $C_2$ space group with the asymmetric unit of two $(L_3)_2$ dimers and one Zn$_5$(H$_2$O)$_2$(L$_3$)$_4$ clusters, leading to a framework formula of $[Zn_5(H_2O)_2(\mu_3-OH)_2(L_3)_4]$. The MOF exhibits a threefold interpenetration, leading to a void space of 65.8 per cent and channel size of $1.1 \times 0.7$ nm$^2$ (figures 5 and 6).

(b) *Asymmetric epoxidation catalysis*

Catalytic activities of CMOF-1 and CMOF-6' towards asymmetric epoxidation were evaluated with 2-(t-butylsulphonyl)iodosylbenzene as the oxidant and aromatic substituted olefins as the substrates (Song et al. 2010, 2011). As shown in table 1, the MOF-catalysed reaction gave good to excellent yields and moderate to good ees which are comparable with the homogeneous controls. These catalytic experiments showed the MOF catalysts gave similar activity and selectivity as the homogeneous control (Song et al. 2010). On the basis of TGA solvent weight loss, dye uptake experiments as well as proposed structures of the polymorphs, CMOF-1 is less porous and of smaller open channel sizes than CMOF-6'. However, CMOF-1 exhibits slightly higher catalytic activities towards asymmetric epoxidation, which is different from the open channel--catalytic activity relationships we observed previously for the CMOF-1'–CMOF-5' series, where time-dependent conversion measurements showed that the yields and reaction rates followed the same trend as the increasing channel sizes (Song et al. 2010). This interesting difference can be rationalized from their subtle structure differences. In CMOF-6', the catalytic active Mn-salen sites are less accessible to the substrates owing to the nearby $[Zn_4(\mu_4-O)(O_2CR)_6]$ nodes from the other network, which are rather sterically bulky. The hindrance thus lowers the catalytic activities of Mn-salen sites in CMOF-6' (table 2).
(c) Sequential catalysis of alkene epoxidation and epoxide ring-opening reactions

We proposed that the $[\text{Zn}_4(\mu_3-O)(\text{O}_2\text{C}R)_6]$ nodes can catalyse epoxide ring-opening reactions without significant interference with the Mn-salen centres. Thus, the CMOF series can serve as catalysts for sequential reactions of alkene epoxidation and epoxide ring-opening. As shown in Table 3, both CMOF-1 and CMOF-6' showed sequential catalytic activities to give the desired ring-opening product with considerable yields and ee values. Only one pair of enantiomers out of all possible four pairs was observed, and the ees of the ring-opening products were almost identical to the corresponding epoxides, showing that the ring-opening reaction is of high regio- and stereo-selectivity. To rule out the possibility that the epoxide ring-opening reaction is catalysed by the Mn-salen centre, we carried out a control experiment using homogeneous Mn(salen)Cl...
Table 2. Asymmetric catalytic epoxidation by CMOF-1 and CMOF-6<sup>a</sup>.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>alkene</th>
<th>conv. (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>ee (%)&lt;sup&gt;c&lt;/sup&gt;</th>
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<td></td>
<td>&gt;99</td>
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<td>CMOF-6'</td>
<td></td>
<td>96</td>
<td>22</td>
</tr>
<tr>
<td>3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>L&lt;sub&gt;3&lt;/sub&gt;-Me&lt;sub&gt;2&lt;/sub&gt;</td>
<td>la</td>
<td>60</td>
<td>64</td>
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<td>CMOF-1</td>
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<td>5</td>
<td>CMOF-6'</td>
<td></td>
<td>83</td>
<td>82</td>
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<tr>
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<tr>
<td>18&lt;sup&gt;d&lt;/sup&gt;</td>
<td>L&lt;sub&gt;3&lt;/sub&gt;-Me&lt;sub&gt;2&lt;/sub&gt;</td>
<td>lf</td>
<td>97</td>
<td>88</td>
</tr>
<tr>
<td>19</td>
<td>CMOF-1</td>
<td></td>
<td>&gt;99</td>
<td>31</td>
</tr>
<tr>
<td>20</td>
<td>CMOF-6'</td>
<td></td>
<td>&gt;99</td>
<td>31</td>
</tr>
<tr>
<td>21&lt;sup&gt;d&lt;/sup&gt;</td>
<td>L&lt;sub&gt;3&lt;/sub&gt;-Me&lt;sub&gt;2&lt;/sub&gt;</td>
<td>lg</td>
<td>&gt;99</td>
<td>45</td>
</tr>
</tbody>
</table>

<sup>a</sup>0.5 equivalent of oxidants 2 were added in 10 portions at 15 min intervals, and the reaction continued for another 0.5 h after the oxidant addition. For detailed experimental procedure, see electronic supplementary material.

<sup>b</sup>Determined by gas chromatography (GC).

<sup>c</sup>Determined by chiral GC with the supelco β-DEX 120 capillary column or by chiral high performance liquid chromatography (HPLC) with Chiralcel AD and OJ columns.

<sup>d</sup>These values are cited from the study of Song <i>et al.</i> (2010) for comparison.

catalyst for ring-opening reaction of indene epoxide with TMSN<sub>3</sub>. After 2.5 days, only less than 5 per cent of the ring-opening product was obtained. The control experiment thus confirms that the zinc centres are mainly responsible for the ring-opening reactions.
Sequential asymmetric catalysis

Table 3. Results for the sequential epoxidation/ring-opening reactions catalysed by CMOF-1 and CMOF-6’ (Song et al. 2011)\textsuperscript{c}.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>alkene</th>
<th>product</th>
<th>conv. (%)\textsuperscript{a}</th>
<th>ee (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CMOF-1</td>
<td>1a</td>
<td>(\text{N}_3\text{OTMS}) (3a)</td>
<td>40</td>
<td>39 (39)</td>
</tr>
<tr>
<td>2</td>
<td>CMOF-6’</td>
<td></td>
<td></td>
<td>60</td>
<td>50 (48)</td>
</tr>
<tr>
<td>3</td>
<td>CMOF-1</td>
<td>(\text{MeO})</td>
<td>(\text{MeO}) (3b)</td>
<td>41</td>
<td>86 (84)</td>
</tr>
<tr>
<td>4</td>
<td>CMOF-6’</td>
<td></td>
<td></td>
<td>57</td>
<td>81 (82)</td>
</tr>
</tbody>
</table>

\(\text{a}\)Isolated yields.
\(\text{b}\)Determined by chiral GC with the supelco \(\beta\)-DEX 120 capillary column or by chiral HPLC with Chiracel AD, OJ column. ee in the parenthesis is the ee of the corresponding epoxide.
\(\text{c}\)For detailed experimental procedures, see electronic supplementary material.

Interestingly, CMOF-1 showed slightly higher conversions than CMOF-6’ in the epoxidation reactions, but CMOF-1 afforded lower yields than CMOF-6’ in the epoxidation/epoxide ring-opening sequential reactions. This result indicates that the CMOF-1 is less active than CMOF-6’ in the epoxide ring-opening step. The larger channel sizes in CMOF-6’ thus led to higher sequential catalytic activities owing to enhanced transport of reagents and substrates through the open channels.

3. Conclusions

This study reports the synthesis and catalytic applications of new Mn-salen-based chiral MOFs. The CMOF series is shown to exhibit similar catalytic activities to their homogeneous counterparts. We have demonstrated the ability to rationally design and fine-tune MOF structures to obtain optimal heterogeneous asymmetric catalysts. By incorporating two different catalytic sites in the same framework, we succeeded in carrying out sequential catalysis of alkene asymmetric epoxidation and epoxide ring-opening reaction with one single solid. The two active sites do not interfere with each other, owing to the isolation of the active sites in the framework. With further study of chiral MOFs, practically useful heterogeneous
asymmetric catalysts could arise from this molecular building block approach, paving the way of synthesizing complex molecules with excellent regio- and stereo-controls using solid catalysts.

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References


