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A chiral metal–organic framework for sequential asymmetric catalysis†

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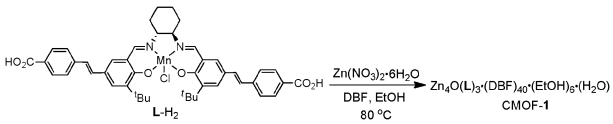
A chiral metal–organic framework (MOF) of the lcy topology was constructed from the Mn–Salen derived dicarboxylic acid and the $[Zn_4(\mu_4\text{-}O)(O_2CR)_6]$ secondary building unit, and used in highly regio- and stereo-selective sequential alkene epoxidation/epoxide ring-opening reactions.

Metal–organic frameworks (MOFs) have emerged as an ideal platform for engineering functional materials.[1] The ability to incorporate functional building blocks has allowed the design and synthesis of MOFs for a number of applications, including gas storage,[2] chemical sensing,[3] nonlinear optics,[4] biomedical imaging,[5] and drug delivery.[6] In particular, MOFs have recently provided a tunable platform for designing solid catalysts for a number of organic transformations.[7] MOF catalysts can be easily recovered and reused, which is highly desirable for cost and sustainability considerations.

Although a large number of MOFs have been examined as heterogeneous catalysts, most of these studies focus on simple organic transformations that can be efficiently catalyzed by known microporous solids such as zeolites.[8] Direct incorporation of a well-defined homogeneous catalyst (or precatalyst) into the framework of a MOF has recently been shown to be an excellent strategy toward generating a new generation of solid catalysts with uniform active sites and open channel structures for shape-, size-, chemo-, and enantio-selective reactions.[9] In this approach, it is common to introduce different metal centers into the MOFs both as the primary catalytic sites and as the metal connecting points. We hypothesize that the disparate metal centers in such MOFs can be used to catalyze different chemical reactions to allow multiple-step manipulations of organic substrates with a single solid.

Chiral MOFs based on Mn–Salen derived bridging ligands have been previously demonstrated as effective heterogeneous asymmetric catalysts for alkene epoxidation reactions.[10] On the other hand, $[Zn_4(\mu_4\text{-}O)(O_2CR)_6]$ secondary building units (SBUs) were reported to be responsible for several cases of MOF catalysis by taking advantage of their Lewis acidity.[11] We proposed that the Mn–Salen based dicarboxylate ligands and $[Zn_4(\mu_4\text{-}O)(O_2CR)_6]$ SBUs in a chiral MOF can catalyze stereoselective alkene epoxidation and epoxide ring-opening reactions, respectively, without deleterious interference from each other, as a result of catalytic site isolation in a solid. Herein we report the rational design of a chiral MOF built from $[Zn_4(\mu_4\text{-}O)(O_2CR)_6]$ SBUs and a Mn–Salen derived dicarboxylate bridging ligand and its application in sequential stereoselective alkene epoxidation and epoxide ring-opening reactions.



Scheme 1 Synthesis of CMOF-**1**.

The Mn–Salen ligand **L**-H_2 was synthesized by a Schiff base condensation reaction between (*R*,*R*)-cyclohexanediamine and (*E*)-4-(3-*tert*-butyl-5-formyl-4-hydroxystyryl)benzoic acid, and then metalated with $Mn(OAc)_2{\cdot}4H_2O$ followed by *in situ* oxidation in air. Reactions of $Zn(NO_3)_2{\cdot}6H_2O$ with **L**-H_2 in dibutylformamide (DBF)/EtOH at 80 °C for 96 h afforded dark brown cuboctahedral single crystals of $[Zn_4(\mu_4\text{-}O)(\mathbf{L})_3]{\cdot}40DBF{\cdot}6EtOH{\cdot}H_2O$ (CMOF-**1**, Scheme 1). **1** crystallizes in the trigonal *R*3 space group as determined by single crystal X-ray crystallography.‡ The asymmetric unit of **1** contains four **L** ligands and 4/3 of $Zn_4(\mu_4\text{-}O)$ clusters which are composed of five Zn atoms of full occupancy, one Zn atom of 1/3 occupancy, one O atom of full occupancy, and one O atom of 1/3 occupancy. The carboxylate groups from six adjacent **L** ligands coordinate to four Zn centers to form $[Zn_4(\mu_4\text{-}O)(\text{carboxylate})_6]$ SBUs of highly distorted octahedral geometry which are linked by ditopic **L** ligands to form a 3D network of the unusual **lcy** topology (Fig. 1).[12] The most striking feature of **lcy** ($3^35^96^3$) topology when compared to other 6-connected uninodal nets such as **pcu** ($4^{12}6^3$), **roa** ($4^46^{10}8$) and **rob** (4^86^68) is the presence of 3-membered and 5-membered rings. The structure of **1** can be represented by close packing of 7-node cages constructed from one triangular face and three pentagonal faces (Fig. 1a). Because of the elongated **L** ligands, **1** adopts a 2-fold interpenetrated structure with 87.8% of accessible void space as calculated by PLATON. Open channels of triangular shapes with the edge length of 2.9 nm run along the ⟨001⟩ and ⟨1−1−1⟩ directions in the crystal structure of **1** (Fig. 1c). The solvent content in **1** was established by a combination of thermogravimetric analysis and ^1H NMR studies.

High porosity is needed for asymmetric MOF catalysts in order to efficiently transport large reagent and product molecules through the MOF open channels. Removal of solvent molecules from MOF channels can however result in significant framework

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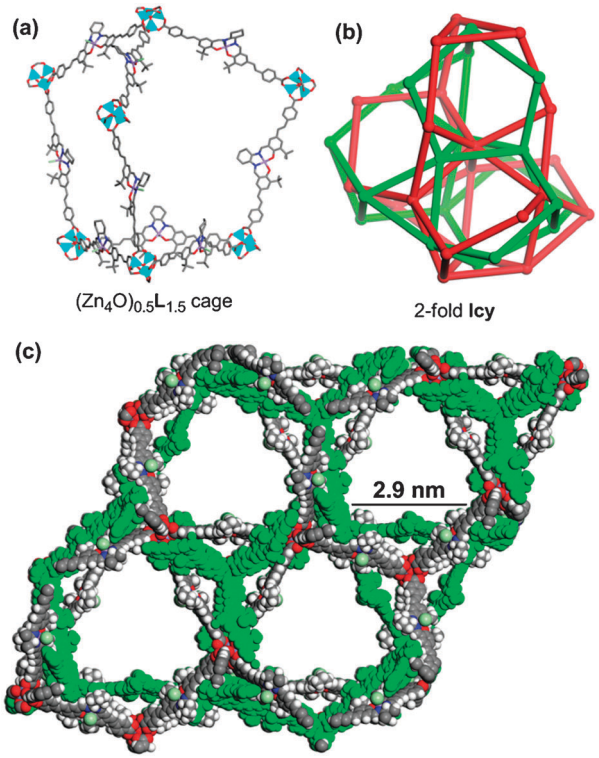


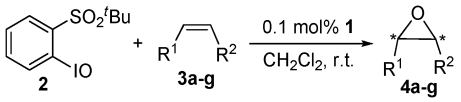
Fig. 1 (a) Stick/polyhedra model of CMOF-**1** showing the $(Zn_4O)_{0.5}L_{1.5}$ cage built from distorted octahedral SBUs and dicarboxylate bridging ligands. (b) Schematic showing 2-fold interpenetrating networks of the **lcy** topology. (c) Space-filling model of **1** as viewed perpendicular to the (001) plane.

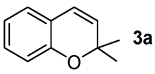
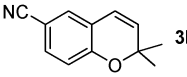
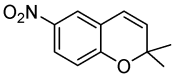
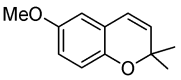
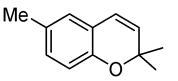
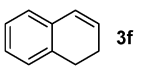
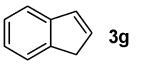
distortion,[13] preventing the accurate determination of their intrinsic porosity. We recently demonstrated that a simple dye uptake assay can be used to reliably quantify the intrinsic porosity of CMOFs as well as to probe the capability of the open channels in transporting large molecules.[7c,14] **1** uptakes 34.0 wt% of Brilliant Blue R-250, proving the accessibility of their open channels to large molecules.

The catalytic activity of **1** in enantioselective epoxidation of unactivated alkenes with 2-(*tert*-butylsulfonyl)iodosylbenzene (**2**) as oxidant was first evaluated.[10] As shown in Table 1, **1** is highly effective in asymmetric epoxidation of unfunctionalized alkenes to afford chiral epoxides in good to excellent yields and moderate to good ee's.[15] When 2,2-dimethyl-2*H*-chromene and its derivatives (**3a–3e**) were used as substrates, the corresponding epoxides **4a–4e** were obtained in good yields and ee's in the presence of 0.1 mol% CMOF-**1** (Table 1, entries 1–5). The ee's of these reactions are comparable to those of the homogeneous Mn–Salen catalytic struts.[10a] Epoxidation of 1,2-dihydronaphthalene (**3f**) or 1*H*-indene (**3g**) in the presence of 0.1 mol% MOF catalysts led to the corresponding epoxide in excellent yields but modest ee's of $<31\%$ (Table 1, entries 6 and 7). The ee of indene oxide improved from 22% to 48% when the loading of **1** was increased to 1 mol% (Table 1, entry 8).

We also examined the reuse of CMOF-**1**. When 2,2-dimethyl-2*H*-chromene-6-carbonitrile (**3b**) was used as the substrate, **1** was readily recovered from the reaction mixture *via* centrifugation and the recovered catalyst only showed slight deterioration in

Table 1 **1**-catalyzed enantioselective epoxidation of alkenes[a]



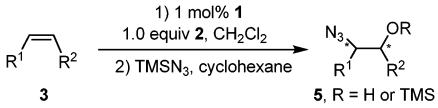
Entry	Alkene	Conv.[b] (%)	ee[c] (%)
1	 **3a**	71	84
2	 **3b**	60	78
3	 **3c**	76	77
4	 **3d**	83	82
5	 **3e**	64	72
6	 **3f**	>99	31
7	 **3g**	96	22
8[d]		82	48

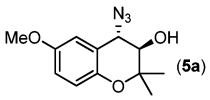
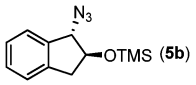
[a] 0.5 equiv. of oxidant **2** were added in 10 portions at 15 min intervals, and the reaction continued for another 0.5 h after the oxidant addition. [b] Determined by GC. [c] Determined by chiral GC with the supelco β-DEX 120 capillary column or by chiral HPLC with Chiralcel AD and OJ columns. [d] The reaction was carried out with 1.0 equiv. of **2** in the presence of 1 mol% of **1**.

conversion and ee after each use. The conversions were 78%, 75%, 68%, and 58% in four consecutive runs, whereas the corresponding ee values were 77%, 75%, 70%, and 64% in these runs.

To test the viability of the $[Zn_4(\mu_4\text{-}O)(O_2CR)_6]$ SBUs in **1** for ring-opening reactions of epoxides generated from the alkene epoxidation reactions, we examined the ability of MOF-5 $[Zn_4(\mu_4\text{-}O)(\text{benzenedicarboxylate})_3]$ in mediating epoxide ring-opening reactions.[11] When indene oxide was used as substrate and $TMSN_3$ was used as nucleophile, 30% GC yield of (*trans*-1-azido-2,3-dihydro-1*H*-inden-2-yloxy)trimethylsilane was obtained after 24 h in the presence of 1 mol% MOF-5. This result indicates that the $[Zn_4(\mu_4\text{-}O)(O_2CR)_6]$ SBUs can catalyze the ring-opening reaction of epoxides. Next, we attempted sequential epoxidation reaction of alkenes with oxidant **2** and ring-opening reaction of the generated epoxide with $TMSN_3$ using 1 mol% CMOF-**1**. The epoxidation step was carried out in CH_2Cl_2 over a period of 3 h. The solvent was changed to cyclohexane followed by the addition of $TMSN_3$. The resulting solution was stirred at rt for 2–3 days to afford the epoxide ring-opening products. **1** catalyzed the sequential reactions to afford the ring-opening product in good yields (Table 2). The epoxide ring-opening products showed high regio- and stereo-selectivities as indicated by GC analyses. Only one pair of enantiomers (out of a possibility of four pairs) was obtained from the sequential catalytic

Table 2 Sequential asymmetric epoxidation/ring-opening reactions of alkenes catalyzed by **1**



Entry	Substrate	Product	Yield[a] (%)	ee[b] (%)
1	**3d**	 (**5a**)	57	81 (82)
2	**3g**	 (**5b**)	60	50 (48)

[a] Isolated yields. [b] Determined by chiral GC with the supelco β-DEX 120 capillary column or by chiral HPLC with Chiralcel AD, OJ column. ee in the parenthesis is the ee of the corresponding epoxide.

reactions. The ee's of the ring-opening products are essentially identical to those of the epoxides generated from the epoxidation step. For the reaction of **3d**, only product **5a** was obtained, presumably as a result of the sequential epoxidation/ring-opening reactions followed by the TMS deprotection during the work-up. **5a** and **5b** were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and mass spectrometry. The structure of **5a** was further determined by a single crystal analysis (Fig. 2),§ confirming the assignments of the regio- and stereo-isomers. The deprotection of the TMS group from **5b** with K_2CO_3/MeOH led to the known *trans*-1-azido-2,3-dihydro-1*H*-inden-2-ol, proving the structural assignment for **5b**.

Finally, ring-opening reaction of indene with $TMSN_3$ in the presence of 1 mol% of a homogeneous (Salen)MnCl complex in cyclohexane for 2.5 days afforded **5b** in <5% GC yield. This result further supports that the $[Zn_4(\mu_4\text{-}O)(O_2CR)_6]$ SBUs in **1** are primarily responsible for the ring-opening reactions.

In summary, we have designed and synthesized a chiral MOF by direct incorporation of a Mn–Salen complex into the framework. The chiral MOF was used in highly enantioselective alkene epoxidation reactions. We have also demonstrated the first MOF-catalyzed sequential asymmetric alkene epoxidation/epoxide ring-opening reactions. MOF-mediated sequential reactions should prove highly valuable for the efficient synthesis of complex molecules with excellent regio- and stereo-controls.

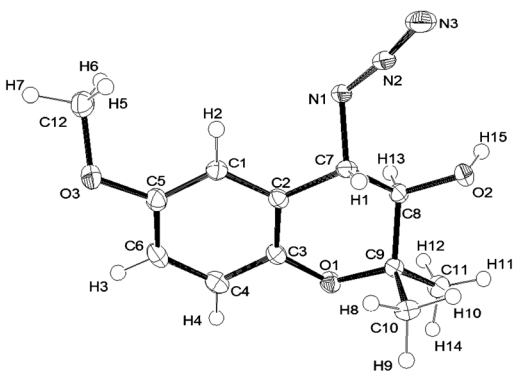


Fig. 2 Single crystal X-ray structure of (3*R*,4*S*)-**5a**.

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Notes and references

‡ Crystal data for **1**: trigonal, *R*3, a = 77.9421(3) Å, c = 47.734(2) Å, V = 251 133(11) Å^3, ρ_{calc} = 0.205 g cm^{-3}. R_1 = 0.098, wR_2 = 0.265.
§ Crystal data for **5a**: orthorhombic, $P2_12_12_1$, a = 8.9026(2) Å, b = 9.2288(2) Å, c = 14.7549(4) Å, V = 1212.27(5) Å^3, ρ_{calc} = 1.366 g cm^{-3}. R_1 = 0.032, wR_2 = 0.096.

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