

# A metal–organic framework material that functions as an enantioselective catalyst for olefin epoxidation†

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A new microporous metal–organic framework compound featuring chiral (salen)Mn struts is highly effective as an asymmetric catalyst for olefin epoxidation, yielding enantiomeric excesses that rival those of the free molecular analogue. Framework confinement of the manganese salen entity enhances catalyst stability, imparts substrate size selectivity, and permits catalyst separation and reuse.

Crystalline metal–organic framework (MOF) compounds, especially those exhibiting zeolite-like properties such as high internal surface area and microporosity, comprise a promising emerging class of functional materials.<sup>1</sup> Among the functions most often envisioned is chemical catalysis.<sup>2</sup> The notion is that MOF-based catalysts may be able to replicate some of the key features of zeolitic catalysts (*e.g.* single-site reactivity, pore-defined substrate size and shape selectivity, easy catalyst separation and recovery, and catalyst recyclability) while incorporating reactivity and properties unique to molecular catalysts. One important property of many molecular catalysts that has yet to be demonstrated with purely zeolitic catalysts is enantioselectivity. Herein, we report that a microporous MOF containing chiral (salen)Mn struts is highly effective as an asymmetric catalyst for olefin epoxidation. The observed enantiomeric excesses (*ee*) rival those of the free molecular catalyst. At the same time, framework confinement enhances catalyst stability, imparts substrate size selectivity, and permits catalyst separation and reuse.<sup>3–5</sup>

Employed as a catalytic strut was (*R,R*)-(–)-1,2-cyclohexanediamino-*N,N'*-bis(3-*tert*-butyl-5-(4-pyridyl)salicylidene)Mn<sup>III</sup>Cl, **L**.<sup>6</sup> Since MOFs based exclusively upon metal–pyridine bonding tend to collapse if evacuated, **L** was incorporated instead in a more robust pillared paddlewheel structure, **1**, containing pairs of zinc ions together with biphenyldicarboxylate (bpdc) as the second ligand.<sup>7</sup> Obtained by sealed-vial solvothermal synthesis in dimethylformamide (DMF), **1** has the formula Zn<sub>2</sub>(bpdc)<sub>2</sub>L·10DMF·8H<sub>2</sub>O and crystallizes in the triclinic *P1* space group (Fig. 1) as an interpenetrating pair of networks (Fig. 2†).

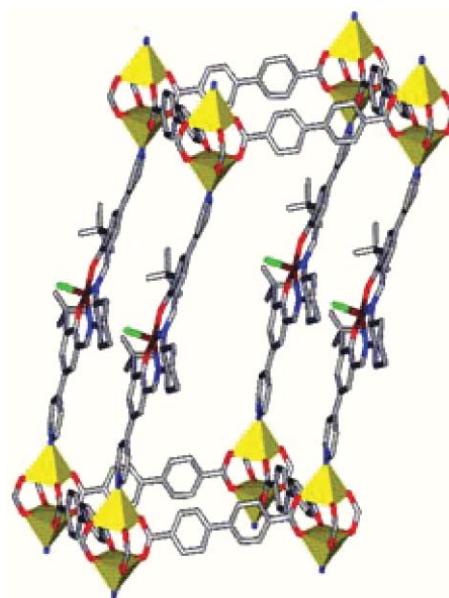
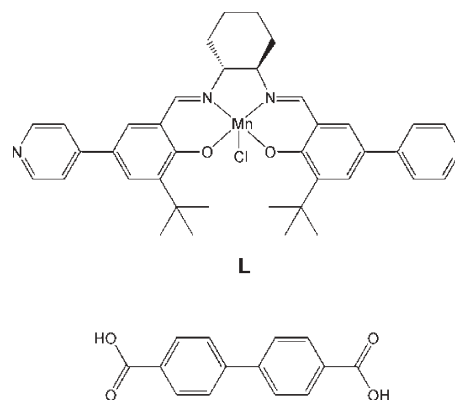


Fig. 1 A POVray view of a single network unit for **1**. Yellow polyhedra represent the zinc ions. Carbon: grey; oxygen: red; nitrogen: blue; chloride: green; manganese: brown.



**H<sub>2</sub>bpdc**

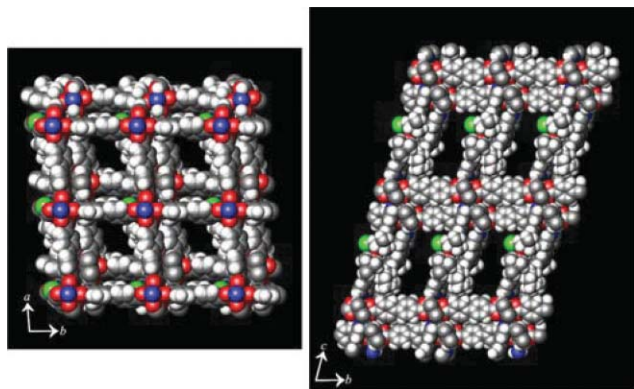
Notwithstanding the interpenetration, solvent occupies 57% of the volume of **1** as determined by PLATON. Notably, the ligands **L** of the paired networks are parallel to each other with cyclohexyl and *tert*-butyl groups protruding along the [100] direction. As such, the channel in the crystallographic *b* direction is essentially blocked, leaving distorted-rectangular and rhombic channels in the *c* and *a* directions with dimensions of 6.2 × 15.7 Å and

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**Fig. 2** Space-filling diagram of **1** showing network interpenetration and framework openings. Channels are viewed down crystallographic *c* (left) and *a* (right).

$6.2 \times 6.2 \text{ \AA}$ , respectively. Importantly, diagonal displacement of the networks leaves all  $\text{Mn}^{\text{III}}$  sites accessible to the channels. The shortest distance between Mn ions on different networks is  $7.2 \text{ \AA}$ .

Thermogravimetric analyses (TGA) of **1** showed that 40% of its mass is lost in the temperature range  $25\text{--}200 \text{ }^\circ\text{C}$ , consistent with solvent loss as calculated from structural data (40.2%); little additional loss occurs until *T* exceeds  $360 \text{ }^\circ\text{C}$ . Powder X-ray diffraction (PXRD) measurements showed that the evacuated compound retains crystallinity. However, diffraction peaks are shifted, implying structural distortions. Notably, resolution by DMF reverses the shifts. TGA measurements with resolvated material confirmed that porosity is retained. In contrast, we have previously observed that when shifts in diffraction peaks for a pillared paddlewheel compound are *irreversible*, resolution (as measured by TGA) does not occur.<sup>7</sup>

The catalytic activity of **1** toward asymmetric epoxidation was examined with 2,2-dimethyl-2*H*-chromene as substrate and 2-(*tert*-butylsulfonyl)iodosylbenzene (a soluble compound) as oxidant||:

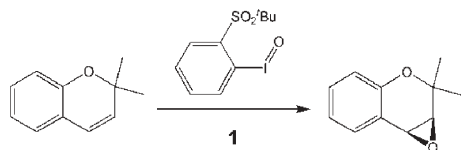
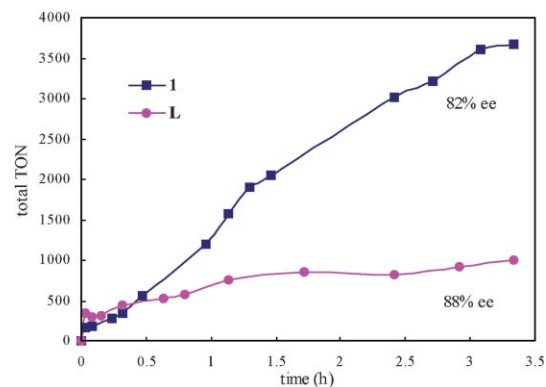


Fig. 3 compares the framework's reactivity with that of free **L**. As is often seen for homogeneous epoxidation catalysts, **L** is initially highly effective, but loses much of its activity after the first few minutes. After a few hours, essentially all activity is lost. In contrast, the framework-immobilized catalyst exhibited close to constant reactivity, culminating in nearly four times the number of turnovers seen for **L** by the time the experiment was terminated at 3.4 h. For (salen)Mn complexes, loss of catalytic activity typically is associated with oxidation of the salen ligand. If salen oxidation is facilitated by reactive encounters with other catalyst molecules, immobilization should prevent encounters and extend the catalyst lifetime. TGA evaluation of MOF particles after catalysis, followed by evacuation and re-immersion in DMF for two days, established that the material remained porous (see ESI,† Fig. S3).

For Jacobsen-type catalysts like **L**, the flexibility of the salen complex is believed to be important in achieving enantioselectivity.<sup>8</sup> We were concerned, therefore, that framework immobilization might strongly attenuate the selectivity of **L**. Remarkably,



**Fig. 3** Plots of total turnover number versus time for epoxidation of 2,2-dimethyl-2*H*-chromene catalyzed by **1** (blue squares) and **L** (magenta circles).

however, only minor selectivity degradation was observed (82% ee for **1** vs. 88% ee for free **L**). Enantioselectivity is known to decrease when electron-withdrawing substituents are introduced.<sup>9</sup> Thus, a potential alternative explanation for the modest decrease in enantioselectivity is the electronic effect arising from binding pyridyl groups to zinc cations.

In light of the persistence of the framework compound's catalytic activity, its recyclability was examined. Remarkably, after three cycles no loss of enantioselectivity and only a small loss of activity were observed (Table 1). Recycling was accompanied by MOF particle fragmentation and a decrease, therefore, in average particle size. Evaluation of the product solution by inductively coupled plasma (ICP) spectroscopy after removal of MOF particles showed that between 4 and 7% of the manganese initially present in the framework material was lost per cycle – either as molecular species or as particles too small to be removed by filtration through Celite. Measurements of reaction progress after removal of MOF particles by filtration established that the remaining small quantity of dissolved manganese did not catalyze the reaction.

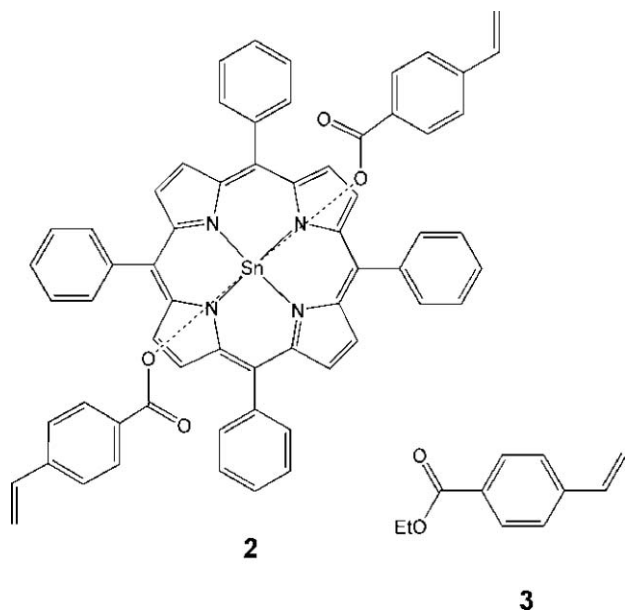
To determine whether catalysis by **1** occurs predominantly within the channel-containing material or instead on the external surface, competitive size selectivity studies were performed (see ESI†). A large porphyrinic substrate, **2** (too large to enter the channels of **1**), and a small substrate, ethyl 4-vinyl benzoate, **3**, were mixed in 1 : 1 olefinic unit ratio and reacted with 2-(*tert*-butylsulfonyl)iodosylbenzene in the presence of **1**. Initially, the ratio of small to large substrate reactivity was 2, but at 45% conversion the reactivity ratio had increased to  $\sim 18$ . Control experiments with free **L** as a homogeneous catalyst gave a time-independent 1 : 1 reactivity ratio. Evidently, at the beginning a

**Table 1** Recyclability of **1** in the asymmetric epoxidation of 2,2-dimethyl-2*H*-chromene<sup>a</sup>

Entry	Cycle <sup>b</sup>	Yield [%] <sup>c</sup>	TON	ee [%] <sup>d</sup>
1	1st	71	1430	82
2	2nd	71	1420	82
3	3rd	66	1320	82

<sup>a</sup> Reaction performed in a conical vial under ambient conditions using magnetic stirring. Molar ratio olefin/oxidant/catalyst = 4000/2000/1. <sup>b</sup> After each cycle, **1** was separated by centrifugation, thoroughly washed and reused in a freshly made reaction mixture. <sup>c</sup> GC yield after 2 h using undecane as an internal standard. <sup>d</sup> Determined using a Supelco  $\beta$ -DEX 120 chiral GC column.

significant fraction of the framework-based catalysis occurs on the MOF surface, but at later stages catalysis occurs chiefly in the MOF interior – perhaps because of surface catalyst over-oxidation and inactivation. If so, then intentionally poisoning or destroying the outermost catalytic sites, as is sometimes done with zeolites, could be a useful strategy for eliciting selectivity. Indeed, pre-treatment of **1** by exposure to solution containing oxidant, but lacking substrate, led to a three-fold increase in the substrate size selectivity measured at 10% conversion.



In summary, asymmetric catalytic oxidation behavior has been demonstrated with a paddlewheel-stabilized MOF material. In comparison to the free catalyst, framework-immobilization confers multiple advantages: higher stability, easier separation, recyclability, and substrate size selectivity. By varying the metal center and ligand structure of the catalytic strut, a spectrum of usefully heterogenized molecular catalysts should be obtainable. Of particular interest may be multi-site catalysts that exploit crystalline channel geometries to enhance chemical selectivity.

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## Notes and references

§ *Preparation of*  $Zn_2(\text{bpdc})_2(\text{L})\cdot 10\text{DMF}\cdot 8\text{H}_2\text{O}$  (**1**): in a small vial were mixed  $Zn(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (12 mg, 0.04 mmol),  $\text{H}_2\text{bpdc}$  (7.2 mg, 0.03 mmol) and **L** (34 mg, 0.05 mmol) with dimethylformamide (DMF, 6 mL). The vial was capped and heated at 80 °C in an oil-bath for one week, over which time brown block-shaped crystals slowly formed. The crystals were collected by filtration and washed with DMF several times. The crystals, which were insoluble in water and common organic solvents (ethanol, acetonitrile, acetone, chloroform and DMF), were left to air-dry for 0.5 h before being analyzed by XRPD and TGA. Elemental analysis for freshly synthesized **1** gave a formula of  $Zn_2(\text{bpdc})_2(\text{L})\cdot 10\text{DMF}\cdot 8\text{H}_2\text{O}$ , which is consistent with TGA data and powder X-ray diffraction analysis; calc. (%): C 53.24, H 6.66, N 9.06; found (%): C 52.97, H 6.36, N 9.07. Elemental analysis for evacuated samples at 100 °C overnight gave a formula of

$Zn_2(\text{bpdc})_2(\text{L})\cdot 3\text{H}_2\text{O}$ ; calc. (%): C 58.95, H 4.76, N 4.17; found (%): C 58.33, H 4.39, N 4.85. Note that the synthesis employs an excess of **L**. Initially, stoichiometric amounts of **L** were used. While the desired compound (**1**) was obtained, samples invariably were contaminated with white microcrystals of the cubic MOF,  $(Zn_4\text{O})(\text{bpdc})_3$ .

¶ *Crystal data*: compound **1**,  $\text{C}_{96}\text{H}_{144}\text{Zn}_2\text{MnClN}_{14}\text{O}_{28}$ ,  $M = 2163.38$ , triclinic,  $P1$ ,  $a = 15.1376(18)$ ,  $b = 15.2092(18)$ ,  $c = 26.300(3)$  Å,  $\alpha = 73.271(2)$ ,  $\beta = 77.508(2)$ ,  $\gamma = 82.596(2)^\circ$ ,  $U = 5647.2(12)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.272$  Mg m<sup>-3</sup>,  $\mu = 0.630$  mm<sup>-1</sup>,  $F(000) = 2288$ ,  $\text{GoF} = 0.797$ .  $R1$  and  $wR2$  are 0.0638 and 0.1396, respectively, for 1477 parameters and 20334 reflections [ $I > 2\sigma(I)$ ]. The data were collected on a Bruker SMART1000 CCD with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 120(1) K. The structures were solved by direct methods and refined by a full matrix least squares technique based on  $F^2$  using the SHELXL97 program. CCDC 284675. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600408c.

|| *General procedure* for the asymmetric epoxidation catalyzed by **1** and **L**: to a 3.7-mL screw-thread vial (15 × 45 mm) were added a dichloromethane solution (2 mL of a 2.5 mM solution of substrate) of 2,2-dimethyl-2H-chromene ( $5.0 \times 10^{-3}$  mol) and undecane (35.7 mg) as an internal standard. Crystals of **1** (1.1 mg, containing  $5.0 \times 10^{-7}$  mol of **L**) were placed in the vial along with a micro stir bar. The oxidant, 2-(*tert*-butylsulfonyl)iodosylbenzene (85 mg,  $2.5 \times 10^{-4}$  mmol), was added to the solution to start the reaction. The same quantity of oxidant was added 15 more times at 10 min intervals (total amount added =  $4.0 \times 10^{-3}$  mmol). Aliquots (20  $\mu\text{L}$ ) of the reaction mixture were taken periodically over 3.4 h, filtered through a silica plug (60 mg) and washed with dichloromethane (5 mL). The filtrate was analyzed by GC and chiral GC for yield and enantioselectivity, respectively.

For the comparison study with **L**, the same [chromene + undecane] solution was mixed with **L** (0.32 mg,  $5.0 \times 10^{-7}$  mol) providing a brown homogeneous solution. 2-(*tert*-Butylsulfonyl)iodosylbenzene (85 mg,  $2.5 \times 10^{-4}$  mmol), was added in the same manner as mentioned above. Aliquots (40  $\mu\text{L}$ ) of the reaction mixture were removed *via* syringe and passed through a plug of silica (120 mg), washed with dichloromethane (8.0 mL) and the combined filtrate was analyzed *via* GC and chiral GC.

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