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Metalloporphyrinic Framework Containing Multiple Pores for Highly Efficient and Selective Epoxidation

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Supporting Information

ABSTRACT: Metalloporphyrin Mn^{III}Cl-5,10,15,20-tetrakis(3,5-biscarboxylphenyl)porphyrin, having eight carboxylate groups in multiple coordination modes, connects with paddle-wheel $Zn_2(COO)_4$ units for the construction of an interesting porous porphyrinic framework that demonstrates high efficiency and stability upon epoxidation of olefins with excellent substrate size selectivity.

Metal–organic frameworks (MOFs), a class of emerging porous materials, are built from metal ions/clusters connecting with organic building blocks, in which the pore structures and functionalities are designable and predictable.[1] Because there are numerous organic and inorganic functional moieties that can be incorporated into the porous materials, MOFs demonstrate remarkable properties for applications in many fields of luminescence, gas storage, sensing, magnetics, and catalysis.[2,3]

Theoretically speaking, most homogeneous catalyst moieties can be incorporated into porous MOFs and thus realize heterogeneous catalytic application.[3] However, because the catalytic sites are easily blocked and sterically congested by the neighboring moieties upon in situ formation of MOFs, the active sites are therefore inaccessible to substrate molecules that could block heterogeneous catalysis. Metalloporphyrins are a class of functional molecules that have unique biological and chemical properties, which are highly active in biomimetic catalysis on the oxidation of a variety of organic molecules under mild conditions.[4] Because the bulky metalloporphyrins define the active metal sites in the rigid macrocycle centers, immobilization of metalloporphyrins onto the pore surfaces of MOFs with heme analogues in control over porous ambient represents an ideal chemical platform on heterogeneous biomimetic catalysis.[5−7] As shown in Scheme S1 in the Supporting Information (SI), the metal 5,10,15,20-tetrakis(3,5-biscarboxylphenyl)porphyrin (M-H_8OCPP) having four bulky *m*-benzenedicarboxylate moieties is a powerful ligand for the construction of highly porous porphyrinic MOFs.[7] Herein, we report a unique porphyrinic framework, $[Zn_{16}(H_2O)_8(Mn^{III}Cl\text{-}OCPP)_4]\cdot 19DMF\cdot 34CH_3COOH\cdot 45H_2O$ (CZJ-4; CZJ = Chemistry Department of Zhejiang University), that is built from the connection between Mn^{III}Cl-OCPP and Zn^{II} ions and demonstrates high dye sorption capability and remarkable catalytic efficiency upon epoxidation of olefin molecules at room temperature.

The porphyrinic framework CZJ-4 was synthesized by heating a mixture of Mn^{III}Cl-H_8OCPP and zinc nitrate in a mixed solvent of *N*,*N*-dimethylformamide (DMF) and acetic acid at 80 °C for 1 week. CZJ-4 crystallizes in the tetragonal *I*4/*mcm* space group, and the formula was established based on elemental analysis, thermogravimetric analysis, and single-crystal X-ray structure.[8] In the crystal structure shown in Figure 1, there are three kinds of secondary building units (SBUs) in CZJ-4: one binuclear $Zn_2(COO)_4(H_2O)$ ($\{Zn_2\}$) and two different OCPP moieties. The first OCPP(1) acts as a 16-dentate ligand to couple eight $\{Zn_2\}$ SBUs, whereas the eight carboxylate groups on the second OCPP(2) are monodentately occupying the apical sites of eight $\{Zn_2\}$ SBUs. The binuclear $\{Zn_2\}$ SBU, containing a pair of

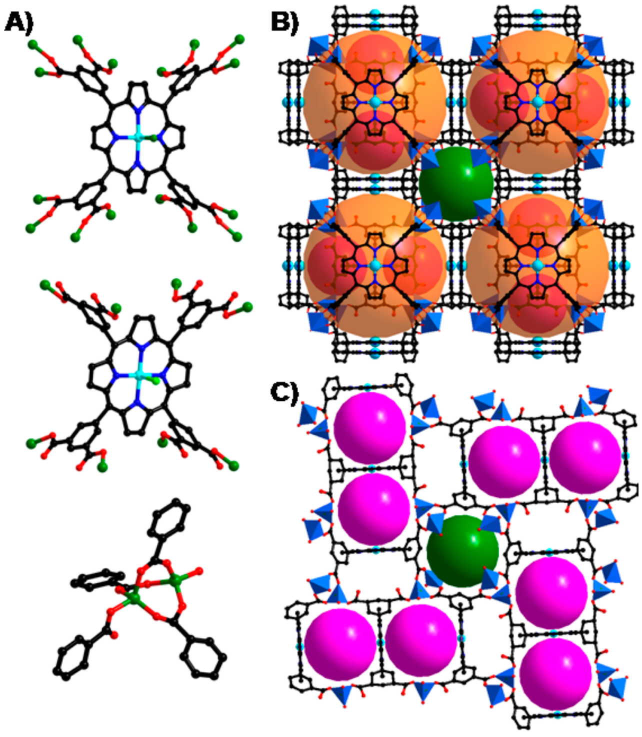

Figure 1. (A) Three kinds of building units in CZJ-4. (B) Crystal structure of CZJ-4, as viewed along the *c* axis. (C) Fragment structure in CZJ-4, as viewed along the *c* axis, showing the substrate-accessible Mn^{III} sites inside the cages (the different colored balls indicate different cavities). Color scheme: Zn, green balls and blue tetrahedra; Mn, cyan; O, red; N, blue; C, deep gray.

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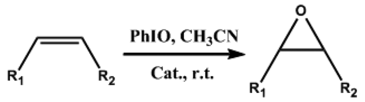
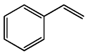
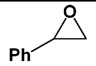
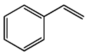
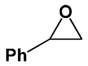
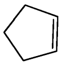
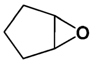
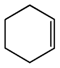
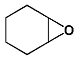
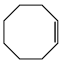
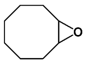
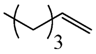
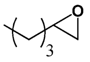
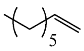
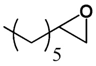
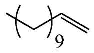
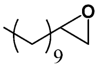
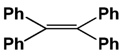
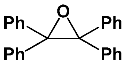
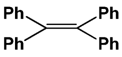
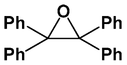
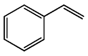
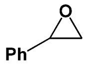
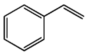
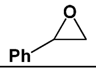
tetrahedrally coordinated zinc ions, is coupled by three carboxylate groups on three OCPPs(1) and coordinating to a monodentate OCPP(2) carboxylate and a water ligand. It is interesting that the connection between six OCPP(1) and eight {Zn_2} SBUs results in a very large cage (large transparent orange balls in Figure 1b) that has pseudo-O_h symmetry. Because the cage is very large (about 2.3 nm diameter), the second OCPP(2) is encapsulated into the cage and splits the cage into two smaller cages (approximate diameters of 1.0 nm) by coordinating with the apical sites of eight {Zn_2} SBUs. As a result, there are two kinds of cages in CZJ-4 (about 1.0 nm diameter), and the corresponding pore windows are of about 1.0 nm diameter. *PLATON* calculations indicate that CZJ-4 has an accessible pore volume of 61.4%.[9]

Table 1. Selective Epoxidation of Olefins Catalyzed by CZJ-4[a]



Entry	Substrate	Product	Conv. (%)[b]	Select. (%)[b]
1			>99	94
2			98	88[c]
3			>99	86
4			96	90
5			91	85
6			85	94
7			46	88
8			37	79
9			0	-
10			40	>99[c]
11			98	93[d]
12			trace	-[e]

[a] Catalyst (0.005 mmol), substrate (0.1 mmol), and PhIO (0.3 mmol) in 1 mL of CH_3CN were stirred at room temperature for 24 h. [b] Conversion % and selectivity % were determined by GC−MS on a SE-54 column. [c] Catalyzed by MnCl−Me_8OCPP. [d] The sixth cycle. [e] The second cycle catalyzed by MnCl−Me_8OCPP.

To quantify the access of the active sites inside the pores of CZJ-4, a dye-uptake assay was therefore employed by taking advantage of the intrinsic high porosity of CZJ-4. By soaking a sample of CZJ-4 in an ethanol solution of melanin dye with the cross dimensions of 5.03 × 9.08 Å^2 for 24 h at room temperature, the dye was almost fully adsorbed by CZJ-4. Monitored by UV−vis absorption spectroscopy, the dye uptake of CZJ-4 is 56 mol %. However, the adsorption of Sudan black B with the cross dimensions of 10.31 × 30.32 Å^2 is negligible. These results demonstrate that CZJ-4 has a size-selective property in sorption of different reagents that are typically required in heterogeneous catalysis.

Because the Mn^{III} sites in metalloporphyrins are toward the pores in CZJ-4, which are accessible to the included substrate molecules, we were encouraged to evaluate the catalytic epoxidation property. When a mixture of the styrene substrate, iodosylbenzene (PhIO) oxidant, and CZJ-4 catalyst in CH_3CN was stirred at room temperature for 24 h, gas chromatography−mass spectrometry (GC−MS) analysis indicates that styrene was fully oxidized, in which the selectivity for the epoxide product is 94% (Table 1, entry 1). The catalytic property of heterogeneous CZJ-4 is superior to that of the homogeneous molecular counterpart Mn^{III}Cl−Me_8OCPP in terms of substrate conversion and product selectivity (entry 2). Under identical conditions, CZJ-4 also epoxidizes a series of olefins (entries 3−8). Accompanying the substrate size increases, the substrate conversion decreases gradually. This is because the large substrates have difficulty accessing the interior pores of CZJ-4. The hypothesis was supported by epoxidation of tetraphenylethene under otherwise identical conditions. As shown in Table 1, because the cross dimensions of tetraphenylethene are 7.05 × 11.55 Å^2, which are too bulky to access the active sites inside the pores of CZJ-4, the tetraphenylethene substrate cannot be epoxidized under those conditions (entry 9). However, because the homogeneous molecular catalyst Mn^{III}Cl−Me_8OCPP does not have such a property, the epoxidation reaction proceeds smoothly (entry 10).

Catalyst CZJ-4 can simply be recovered by centrifugation, which was subsequently used in the successive run without loss of the catalytic efficiency (entry 11). No trace product was detected when the filtrate from a mixture of PhIO and CZJ-4 in acetonitrile was used in the epoxidation reaction, which proved that the present catalyst platform is heterogeneous in nature. However, the recovered homogeneous catalyst MnCl−Me_8OCPP loses its catalytic activity after the first cycle (entry 12). The different stabilities of CZJ-4 and MnCl−Me_8OCPP in the catalytic epoxidation of olefins can be attributed to the homogeneous metalloporphyrin catalyst having very high suicidal inactivation by formation of the catalytically inactive μ-oxometalloporphyrin dimers, whereas immobilization of metalloporphyrins on the pore surfaces of CZJ-4 can significantly enhance and sustain the catalytic activities by blocking formation of the inactive species.[10]

To prove that the catalytic reaction mainly occurs inside the interior pore space of CZJ-4, we studied the substrate and product inclusion property. The activated CZJ-4 takes up 23 styrene or 21 styrene oxide molecules per formula unit. We have also intentionally interrupted the catalytic reaction after 6 h and collected the catalyst CZJ-4 solid to study the chemical species absorbed inside the pores. GC−MS analysis of the desorbed species from this reacted CZJ-4 reveals that about six styrene and four styrene oxide molecules are incorporated into the pores per formula unit. This study demonstrates that the catalytic epoxidation of styrene does mainly occur inside the pores of CZJ-4. However, when the same procedure is applied for the absorption of bulky tetraphenylethene substrate, GC−MS analysis cannot detect a trace of the substrate. These results unambiguously proved that the heterogeneous catalysis reaction mainly occurs inside the pores of CZJ-4 on the epoxidation of small olefins.

In summary, to make use of the metalloporphyrin MnCl−H_8OCPP ligand to connect with paddle-wheel {Zn_2} SBUs, we have successfully constructed a novel porous porphyrinic framework material, whose structure consists of two kinds of cages and open windows of about 1.0 nm diameter. Upon immobilization of manganese(III) porphyrin sites onto the pore surfaces of MOF, CZJ-4 exhibits high catalytic efficiency, selectivity, and stability upon epoxidation of olefins, in which high conversions and selectivities have been achieved for the oxidation of small olefins. CZJ-4 also demonstrates excellent substrate size selectivity in heterogeneous epoxidation catalysis. We envision that further use of the bulky metalloporphyrin ligands may lead to some highly porous porphyrinic MOFs with unusual structural topologies and properties for applications in a number of fields.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystal data, scheme, additional figures, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(8) Crystal data for CZJ-4: $C_{208}H_{96}Cl_4Mn_4N_{16}O_{72}Zn_{16}$, $M = 5378.49$, tetragonal, space group $I4/mcm$, $a = 30.4589(8)$ Å, $c = 44.287(4)$ Å, $V = 41087(4)$ Å^3, $T = 135(2)$ K, $Z = 4$, $\mu(\mathrm{Cu}\ K\alpha) = 2.603\ \mathrm{mm}^{-1}$, $\rho = 0.869$ g/cm^3, R1 = 0.1304 $[I > 2\sigma(I)]$, wR2(F^2) = 0.2537 $[I > 2\sigma(I)]$, $S = 1.116$.

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