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Highly Efficient C−H Oxidative Activation by a Porous Mn^{III}–Porphyrin Metal–Organic Framework under Mild Conditions

Ming-Hua Xie,[a] Xiu-Li Yang,[a] Yabing He,[b] Jian Zhang,[c] Banglin Chen,*[b] and Chuan-De Wu*[a]

Abstract: A simple strategy to rationally immobilize metalloporphyrin sites into porous mixed-metal–organic framework (M′MOF) materials by a metalloligand approach has been developed to mimic cytochrome P450 monooxygenases in a biological system. The synthesized porous M′MOF of $[Zn_2(MnOH–TCPP)(DPNI)]\cdot 0.5\,DMF\cdot EtOH\cdot 5.5\,H_2O$ (**CZJ-1**; CZJ = Chemistry Department of Zhejiang University; TCPP = tetrakis(4-carboxyphenyl)porphyrin); DPNI = *N*,*N*′-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide) has the type of doubly interpenetrated cubic α-Po topology in which the basic $Zn_2(COO)_4$ paddle-wheel clusters are bridged by metalloporphyrin to form two-dimensional sheets that are further bridged by the organic pillar linker DPNI to form a three-dimensional porous structure. The porosity of **CZJ-1** has been established by both crystallographic studies and gas-sorption isotherms. **CZJ-1** exhibits significantly high catalytic oxidation of cyclohexane with conversion of 94 % to the mixture of cyclohexanone (K) and cyclohexanol (A) (so-called K–A oil) at room temperature. We also provided solid experimental evidence to verify the catalytic reaction that occurred in the pores of the M′MOF catalyst.

Keywords: heterogeneous catalysis • metalloporphyrins • metal–organic frameworks • oxidation • porous materials

Introduction

C−H activation is a very important chemical process that could revolutionize the chemical industry.[1] Because this chemical process can readily transform a C−H bond into a C−X bond (X = C, O, N, and so forth), the realization of an efficient C−H activation process can allow us to fully utilize a variety of low-cost hydrocarbons such as methane, ethane, propane, hexane, and cyclohexane as raw materials for the production of useful synthetic organic chemicals. Furthermore, direct C−H activation can also shorten the multistep organic syntheses that have been widely implemented in the manufacture of organic pharmaceutical compounds. However, activation of C−H bonds, particularly those within saturated hydrocarbons, is very difficult given the fact that the single bonds in hydrocarbons are very stable. Extensive study on C−H activation did not start until the discovery of a few organometallic catalysts back in the 1960s and 1970s,[2] and now it is certainly one of the most active research areas in chemistry.[3] Controlled direct C−H oxidative activation of cyclohexane can produce a mixture of cyclohexanone (K) and cyclohexanol (A) (so-called K–A oil), which is a very important chemical for the industrial production of Nylon-6 and Nylon-6,6.[4] Although a tremendous amount of research endeavors have been pursued to target efficient catalysts for the oxidation of cyclohexane, no significant breakthrough has been made.[5,6]

The potential of metal–organic frameworks (MOFs) for this important C−H activation was pioneered by Suslick et al., who developed an Mn^{III}–porphyrin MOF catalyst.[7] It has been well known that synthetic metalloporphyrin molecular compounds can mimic catalytic properties of cytochrome P450;[8] this metalloporphyrinic MOF approach should be very promising to target efficient heterogeneous catalysts for hydrocarbon oxidation.[9] However, such a promise has not been fulfilled partly because of the difficulties a) to synthesize high-quality large crystals for single-crystal structure characterization, b) to stabilize the frameworks and sustain their pore structures, and c) to construct pores with suitable pore sizes, catalytic metal sites, and electronic environments to induce their high catalytic activities. This situation has been significantly improved recently,[10–12]

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[a] Dr. M.-H. Xie, X.-L. Yang, Prof. Dr. C.-D. Wu
Center for Chemistry of High-Performance
and Novel Materials, Department of Chemistry
Zhejiang University, Hangzhou, 310027 (P.R. China)
Fax: (+86) 571-87951895
E-mail: cdwu@zju.edu.cn

[b] Dr. Y. He, Prof. Dr. B. Chen
Department of Chemistry
University of Texas at San Antonio
One UTSA Circle, San Antonio
TX 78249-0698 (USA)
Fax: (+1) 210-458-7428
E-mail: Banglin.Chen@utsa.edu

[c] Prof. Dr. J. Zhang
Fujian Institute of Research on the Structure of Matter
Chinese Academy of Sciences
Fuzhou, 350002 (P.R. China)

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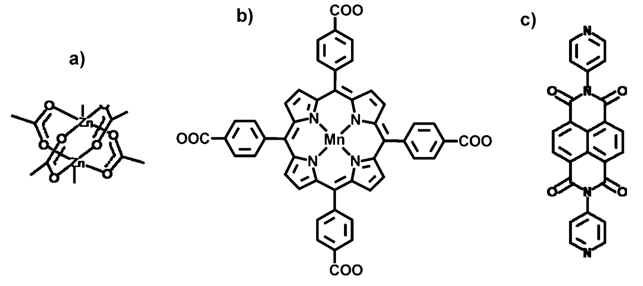
which is attributed to scientific advances in structural characterization and our capability to master the synthesis of such framework materials with predictable structures.[13] To immobilize metalloporphyrin sites into the porous mixed-metal–organic frameworks (M′MOFs) by making use of two types of linkers,[14] we target a highly efficient heterogeneous M′MOF catalyst for direct C−H oxidative activation. Herein we report the structure, porosity, and catalytic oxidation property of $[Zn_2(MnOH\text{–}TCPP)(DPNI)]\cdot 0.5\,DMF\cdot EtOH\cdot 5.5\,H_2O$ (**CZJ-1**; CZJ = Chemistry Department of Zhejiang University; TCPP = tetrakis(4-carboxyphenyl)porphyrin); DPNI = *N*,*N′*-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide; Scheme 1), which exhibits significantly high efficiency in the catalytic oxidation of cyclohexane with conversion of 94 % to a mixture of cyclohexanone and cyclohexanol at room temperature.



Scheme 1. a) $Zn_2(COO)_4$ SBU, b) Mn–TCPP metalloligand, and c) DPNI organic pillar linker.

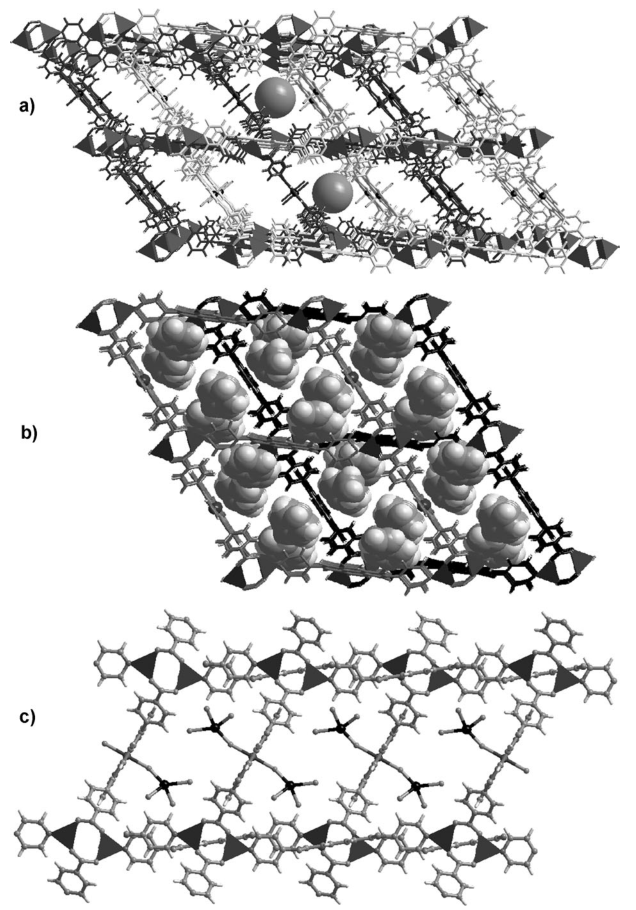


Figure 1. X-ray crystal structures of a) **CZJ-1**, b) **CZJ-1**⊃2 styrene, and c) **CZJ-1-Ti** viewed along the channels, respectively.

Results and Discussion

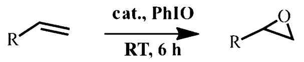
Compound **CZJ-1** was synthesized by heating a mixture of $MnOH\text{−}H_4TCPP$, DPNI, and zinc nitrate in a mixed solvent of DMF, EtOH, and nitric acid at 80 °C for two days. The structure, composition, and phase purity were characterized by single-crystal and powder X-ray diffraction (PXRD), as well as elemental and thermogravimetric analysis (TGA).

The single-crystal X-ray diffraction study revealed that **CZJ-1** has the doubly interpenetrated cubic α-Po topology, which has been well established in traditional porous MOFs.[13i,14,15] The basic $Zn_2(COO)_4$ paddlewheel clusters as the secondary building units (SBUs) are bridged by Mn–TCPP to form two-dimensional sheets, which are further bridged by the organic pillar linker DPNI to form a three-dimensional porous structure. As shown in Figure 1a, **CZJ-1** has pores of about 6.1×7.8 Å^2, taking into account the van der Waals radii, viewed along the channels in which the metal sites have been uniformly immobilized on the pore surfaces. PLATON calculations indicate that **CZJ-1** has an accessible pore volume of 51.9 %.[16]

TGA shows that **CZJ-1** loses solvent molecules between 25 and 150 °C (11.5 %), and the desolvated framework can be thermally stable up to 360 °C. After the as-synthesized **CZJ-1** was heated at 90 °C under vacuum for 6 h, the PXRD of the activated sample was different from the freshly as-synthesized sample, thus indicating that some structural phase transformations might occur during the desolvation process. We have successfully characterized the structure of the desolvated framework **CZJ-1-a** by single-crystal X-ray diffraction analysis. As expected, **CZJ-1-a** retains the identical framework connectivity to the as-synthesized **CZJ-1** and thus the same doubly interpenetrated cubic α-Po topology, and the framework shrinks by 18 % in terms of unit-cell volume. It is interesting that the original PXRD pattern of **CZJ-1** can be regenerated when a desolvated sample of **CZJ-1-a** was exposed to DMF vapor at 80 °C for 24 h (see Figure S7 in the Supporting information). These results suggest that **CZJ-1** is flexible.[13j,k] The porous nature of **CZJ-1** was further confirmed by the CO_2 sorption isotherm. The evacuated **CZJ-1** at 90 °C for 6 h under high vacuum takes up 47 $cm^3\,g^{-1}$ of CO_2 at 273 K and 1 atm, which is about half that of the reported M′MOF **ZnMn-RPM** activated by supercritical CO_2 activation of a surface area of 1000 $m^2\,g^{-1}$.[11]

We examined **CZJ-1** as a potential catalyst for the catalytic epoxidation of styrene. The catalytic epoxidation was carried out using iodosylbenzene (PhIO) as the oxidant at room temperature. As shown in Table 1, **CZJ-1** exhibits high catalytic activity in which styrene can be almost fully

Table 1. Selective oxidation of olefins catalyzed by **CZJ-1**.[a]



Entry	Substrate	Catalyst	Conv. [%][b]	Select. [%][b]
1	styrene	**CZJ-1**	>99	98
2	styrene	**CZJ-1**	98	98[c]
3	styrene	**CZJ-1**	94	95[d]
4	cyclohexene	**CZJ-1**	99	>99
5	styrene	$MnCl_2$	27	80
6	styrene	DPNI	5	97
7	styrene	$MnOH-H_4TCPP$	64	94
8	styrene	$MnOH-H_4TCPP$ and DPNI	80	94
9	styrene	$MnOH-H_4TCPP$, DPNI, and $Zn(NO_3)_2$	78	67

[a] Olefin (0.1 mmol), PhIO (0.15 mmol for styrene, 0.20 mmol for cyclohexene), catalyst (0.005 mmol; 5 mol %), and acetonitrile (1.5 mL) sealed in a Teflon-lined screw-cap vial were stirred at room temperature for 6 h. [b] Conversion [%] and selectivity [%] were determined by GC-MS using an SE-54 column. [c] The second cycle. [d] The sixth cycle.

oxidized into the epoxide product with 98 % selectivity after 6 h (Table 1, entry 1). These excellent heterogeneous catalysts should not only have high catalytic activity and selectivity, but should also be highly stable and thus be easily recycled for long-term usage. Compound **CZJ-1** can be simply recovered by filtration, which was subsequently reused in successive runs. Even after the sixth recycle, the recovered **CZJ-1** (Table 1, entry 3) still exhibits a very high conversion of 94 % and selectivity of 95 %, thus indicating that **CZJ-1** is indeed a superior heterogeneous catalyst for styrene epoxidation at room temperature. A study of the turnover numbers (TONs) indicated that the catalyst **CZJ-1** can be utilized in much lower amounts and still be highly stable after 14068 turnovers without affecting its high catalytic activity. We further examined the catalytic activity for the epoxidation of cyclohexene at room temperature. Again, **CZJ-1** (Table 1, entry 4) exhibits much higher catalytic activity (99 %) and selectivity (99 %).

The recycle usage of **CZJ-1** basically establishes its heterogeneous nature, and the active catalytic sites should be the Mn^{III}–porphyrin moieties within the pores in **CZJ-1**. To further confirm this claim, we compared the catalytic activities of **CZJ-1** with their molecular components of $MnCl_2$, DPNI, and $MnOH-H_4TCPP$, and their mechanically combined mixtures under identical reaction conditions. $MnCl_2$ and DPNI show very low catalytic activity with conversions of 27 (Table 1, entry 5) and 5 % (Table 1, entry 6), respectively. $MnOH-H_4TCPP$ and its mechanical mixtures with DPNI and/or $Zn(NO_3)_2$ do show quite moderate catalytic activity that can transform 64–80 % of the styrene into the styrene epoxide (Table 1, entries 7–9) but still are not as efficient as heterogeneous **CZJ-1** (>99 % conversion).

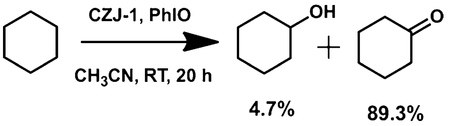
No trace product was detected when the filtrate from a mixture of PhIO and solid **CZJ-1** in acetonitrile was used instead of **CZJ-1** as the catalyst, which proved that the present catalyst platform is heterogeneous in nature. The PXRD pattern of the recovered solid after catalysis is identical to the as-synthesized sample, thus indicating that **CZJ-1** is stable during the catalytic reaction. The catalytic property of **CZJ-1** was further compared with the analogous homogeneous catalyst Mn–tetraphenylporphyrin (Mn–TPP) under identical conditions. As shown in Figure S26 of the Supporting Information, heterogeneous **CZJ-1** is apparently superior to homogeneous Mn–TPP: **CZJ-1** not only exhibits systematically high catalytic activity but also significantly high catalytic stability. Compound **CZJ-1** basically keeps the similar catalytic activities even after the sixth run, whereas Mn–TPP loses its catalytic activities after the second run.

We are aware that an ideal heterogeneous catalyst should have accessible catalytic sites and pores by substrate molecules to facilitate substrate transformation. We therefore examined the accessibility of the open channels to substrate molecules of styrene, cyclohexene, and cyclohexane by ^{1}H NMR spectroscopy. Compound **CZJ-1** takes up 2.5 molecules of styrene, 4.0 molecules of cyclohexene, and 2.0 molecules of cyclohexane per formula unit, respectively. Such different sorption capacities of **CZJ-1** for these substrates might be attributed to their different molecular geometries and sizes (Figure S9 in the Supporting Information). Styrene is longer than cyclohexene and cyclohexane, but is a flatter molecule with a thickness of about 3.4 Å. The double bond within cyclohexene makes it thinner (3.4–3.8 Å) than cyclohexane (3.8 Å), so the packing of cyclohexene can be more efficiently realized than that of cyclohexane within **CZJ-1**, which enables **CZJ-1** to take up more cyclohexene molecules than cyclohexane.

The single-crystal X-ray structure study on the styrene-included crystal **CZJ-1**$\supset$2 styrene clearly indicated that styrene molecules do locate inside the pore channels of the **CZJ-1** framework (Figure 1b), which provided the fundamental basis for the examined heterogeneous catalytic reaction to take place inside the pores.[17] The unit-cell parameters of **CZJ-1**$\supset$2 styrene can be transferred to $a=22.041$, $b=16.530$, $c=16.713$ Å; $\alpha=89.947$, $\beta=116.282$, and $\gamma=93.331°$. Compared with the unit-cell parameters of **CZJ-1**, the unit-cell lengths were not significantly affected during the single-crystal-to-single-crystal transformation. However, large variations were observed in the α, β, and γ angles. Due to the fact that the α and γ angles are significantly deviated from 90°, the space group of **CZJ-1**$\supset$2 styrene is triclinic $P\bar{1}$ as opposed to monoclinic $C2/m$ for **CZJ-1**, and the unit-cell parameters were correspondingly reduced to the reported ones. When a sample of **CZJ-1**$\supset$2 styrene was exposed to the DMF vapor at 80 °C for 24 h, the sharp PXRD peaks of **CZJ-1**$\supset$2 styrene were almost identical to that of **CZJ-1**, which once again confirmed the flexible and reversible framework of **CZJ-1** (see Figure S8 in the Supporting Information). We also intentionally interrupted the catalytic oxidation of styrene after 2 h and collected the solid **CZJ-1** catalyst to study the chemical species inside the pores. GC-MS analysis of the desorbed species from this solid catalyst indicates that the collected solid catalyst **CZJ-1** does encapsulate both reactant styrene and product 1,2-epoxyethylbenzene molecules of about 1.6 and 0.9 moles per **CZJ-1**. Moreover, we further designed an experiment to evaluate the accessibility of the porphyrinic metal sites inside the pores of **CZJ-1**. The crystals of **CZJ-1** were suspended in toluene with $Ti(OEt)_4$ for three days. Structural analysis on a newly formed crystal of **CZJ-1-Ti** showed that the Ti species are combined with the hydroxyl group on porphyrin Mn^{III} cations (Figure 1c). These solid experimental results suggest that **CZJ-1** firstly adsorbed styrene molecules inside the pore space to react with the catalytic metal sites, and further transformed into the product 1,2-epoxyethylbenzene molecules, which are then released from the pores of the catalyst solid into the reaction solution during the catalytic oxidation of styrene by the microporous **CZJ-1** catalyst.

As demonstrated above, the catalytic reactions take place inside the pore space; the inclusion of the substrate reactants is essential for the catalytic chemical transformations. It is thus expected that such microporous M′MOF heterogeneous catalyst will exhibit size-selective catalytic activities. Indeed, **CZJ-1** does not exhibit any catalytic activity toward the oxidation of 1,1,2,2-tetraphenylethene, because 1,1,2,2-tetraphenylethene is too bulky (about 8.2 × 12.7 $Å^2$) to have access into the pores of **CZJ-1**. On the contrary, the homogeneous molecular catalyst Mn–TPP can catalyze oxidation of 1,1,2,2-tetraphenylethene in 18.1 % conversion.

The success of **CZJ-1** as a stable heterogeneous catalyst for the highly efficient and selective oxidation of styrene and cyclohexene motivated us to examine this powerful M′MOF catalyst on a much more challenging oxidation reaction: oxidation of cyclohexane. Strikingly, **CZJ-1** exhibits extremely high catalytic activity for the oxidation of cyclohexane even at room temperature with the conversion up to 94 % and about 100 % selectivity toward K–A oil (Scheme 2). Even after recycling six times, the recovered **CZJ-1** can still display quite high catalytic activity with a conversion of 79 %. The turnover number can reach up to 2668 without any deactivated signal. The molecular components MnOH−H_4TCPP and Mn–TPP, however, can only lead to much lower conversions of 40 and 47 %, respectively. Moreover, the conversion of cyclohexane cannot be significantly improved when additional DPNI and/or $Zn(NO_3)_2$ were added to the reaction mixture (48 % for MnOH−H_4TCPP and DPNI; and 52 % for MnOH−H_4TCPP, DPNI, and $Zn(NO_3)_2$). Furthermore, these molecular homogeneous catalysts immediately lose catalytic activity after the first run.



Scheme 2. Selective oxidation of cyclohexane catalyzed by **CZJ-1**.

These results show that **CZJ-1** is a superior heterogeneous catalyst for the oxidation of cyclohexane under mild conditions. As shown in molecular homogeneous catalysts $\{[Fe^{IV}(O)(N_4Py)](ClO_4)\}^+$ and $\{[Fe^{IV}(O)(Bn\text{-}tpen)](O_3SCF_3)\}^+$ (Py = pyridine; tpen = tetrakis(2-pyridylmethyl)ethylenediamine) for the catalytic oxidation of hydrocarbons, oxidation of cyclohexane is the most difficult among the different substrates Ph_3CH, cumene, PhEt, PhMe, 2,3-dimethylbutane (2,3-DMB), and cyclohexane because of the much stronger C−H bond dissociation energy (D_{C-H}) of about 99.3 kcal mol^{-1} in cyclohexane.[18] Previous efforts directed at metalloporphyrin-containing mixed-metal–organic frameworks for C−H oxidation activation have been mainly focused on those unsaturated hydrocarbons such as styrene and ethylbenzene. Oxidative activation of the C−H in unsaturated hydrocarbons is much easier than the one in saturated hydrocarbons.[10] Hence, the highly efficient and selective oxidation of cyclohexane catalyzed by **CZJ-1** is remarkable.

It is speculated that the catalytically active species are those in situ formed porphyrin–Mn^V = O, as is well established in their homogeneous Mn–porphyrin catalysts. The confined Mn–porphyrin sites within the **CZJ-1** framework not only prevent μ-oxo dimerization, which is commonly observed in homogeneous molecular catalysts, but might also collaboratively work together to enhance their catalytic activity, given the fact that the neighboring Mn–porphyrin sites are quite close and flexible with Mn•••Mn distances of about 13.9 Å. The pores of 6.1 × 7.8 $Å^2$ in this flexible M′MOF **CZJ-1** can readily encapsulate the substrate cyclohexane while possibly excluding the larger molecules of cyclohexanone and cyclohexanol, thus facilitating the product release and their chemical transformations. The specific electronic environments around the catalytic Mn^{III} catalytic sites that have been tuned by both porphyrin moieties and the secondary organic linker DPNI might play important roles as well.

Conclusion

The power to rationally immobilize different metal sites, to tune the pore structures by different combinations of metalloligands and organic linkers, and to subtly change the steric and electronic environments around the metal catalytic sites by systematically modifying the metalloligands, has highlighted the M′MOF approach to be a very promising strategy to develop porous heterogeneous C−H oxidative activation catalysts. This work is expected to initiate more extensive research endeavors on this very important topic in the near future.

Experimental Section

Materials and methods: All of the chemicals were obtained from commercial sources and were used without further purification. MnOH–TCPP and DPNI were synthesized according to the literature.[19,20] Elemental analysis was performed using a ThermoFinnigan Flash EA 1112 element analyzer. IR spectrum (KBr pellet) was taken using an AVATAR-370 Nicolet spectrometer in the 4000–400 cm^{-1} region. TGA was carried out using an SDT Q600 compositional analysis instrument from 30 to 800 °C under N_2 atmosphere at a heating rate of 10 °C min^{-1}. PXRD was recorded using a Rigaku D/MAX 2550/PC for $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å). ^1H NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$, and the chemical shifts were reported relative to the internal standard TMS ($\delta = 0$ ppm).

Synthesis of [Zn_2(Mn–TCPP)(DPNI)]·0.5 DMF·EtOH·5.5 H_2O (CZJ-1): A mixture of MnOH–H_4TCPP (44 mg, 0.05 mmol), $Zn(NO_3)_2·6H_2O$ (44.5 mg, 0.15 mmol), DPNI (42 mg, 0.1 mmol), and 1.0 M nitric acid (150 µL, 0.15 mmol) in a mixed solvent of DMF (3 mL) and EtOH (7 mL) was sealed in a screw-cap vial and heated at 80 °C for two days. Brownish crystals of **CZJ-1** were filtered, washed with DMF, EtOH, and diethyl ether, and dried in the air. Yield: 75 %. IR (KBr pellet): $\tilde{\nu} = 1719$ (s), 1677 (s), 1654 (w), 1607 (m), 1560 (m), 1514 (w), 1483 (w), 1384 (s), 1345 (s), 1249 (s), 1205(s), 1147 (w), 1011 (s), 870 (w), 805 (m), 779 (m), 716 (m), 669 (m), 643 (w), 532 (w), 493 cm^{-1} (w); elemental analysis calcd (%) for **CZJ-1**: H 3.62, C 57.67, N 7.57; found: H 3.56, C 58.02, N 7.63. Crystals of **CZJ-1** were easily broken into fragments during solvent evaporation. We thus carefully activated the ethanol-exchanged crystals of **CZJ-1** under vacuum at −20 °C for 24 h to prevent crystal cracking and to generate the solvent-free **CZJ-1-a**. Compound **CZJ-1**⊃2 styrene was accordingly prepared by immersing the solvent-free **CZJ-1-a** crystals in styrene at −20 °C for 12 h. Compound **CZJ-1-Ti** was prepared by suspending the crystals of **CZJ-1** in a solution of $Ti(OEt)_4$ in toluene at −20 °C for 3 d.

Single-crystal X-ray data collections and structure determinations: The determinations of the unit cells and data collections for the crystals of compounds **CZJ-1**, **CZJ-1-a**, **CZJ-1**⊃2 styrene, and **CZJ-1-Ti** in sealed capillaries were performed using an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector. The data were collected using graphite-monochromated-enhanced ultra Cu radiation ($\lambda = 1.54178$ Å) at 293 K. The data sets were corrected by empirical absorption correction by using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[21] The structures of all compounds were solved by direct methods and refined by full-matrix least-squares methods with the SHELX-97 program package.[22] The solvent molecules in compounds **CZJ-1** and **CZJ-1-Ti** are highly disordered; the SQUEEZE subroutine of the PLATON software suite was used to remove the scattering from the highly disordered guest molecules.[16] The resulting new files were used to further refine the structures. The H atoms on C atoms were generated geometrically.

Substrate absorption experiments: The sample of **CZJ-1** was treated under vacuum at 90 °C for 6 h. After the solvent-free samples of **CZJ-1** were respectively exposed to the vapors of styrene, cyclohexene, and cyclohexane for 12 h at room temperature, the solids were thoroughly washed with diethyl ether to remove surface-adsorbed molecules. The solids were subsequently submersed in $CDCl_3$ for 12 h. The supernatant liquids were used for ^1H NMR spectroscopic study. With an acetone or benzene internal standard and $CDCl_3$ as the solvent, ^1H NMR spectroscopic integrations suggest that 2.5 styrene, 4 cyclohexene, or 2 cyclohexane molecules were embedded in **CZJ-1** per formula unit.

A typical procedure for epoxidation of olefin: A mixture of catalyst **CZJ-1** (0.005 mmol), styrene (0.1 mmol), and PhIO (0.15 mmol) in CH_3CN (1.5 mL) was sealed in a small Teflon-lined screw-cap vial and stirred at room temperature for 6 h. The identity of the product was determined by analyzing aliquots of the bulk solution using GC-MS, and compared with the authentic samples analyzed under the same conditions, whereas the conversion and selectivity were obtained by GC analysis with a flame-ionization detector (FID) using a capillary SE-54 column.

A typical procedure to study the chemical species adsorbed inside the pores of CZJ-1 during oxidation of styrene: Compound **CZJ-1** (0.015 mmol), styrene (0.6 mmol), and PhIO (0.3 mmol) in CH_3CN (1.5 mL) reacted at room temperature for 2 h. The solid was recovered by filtration, quickly washed with acetonitrile three times, digested by dilute aqueous ammonia solution, and then extracted by diethyl ether. The aliquots of the bulk solution was subjected to GC-MS analysis, and compared with the authentic samples analyzed under the same conditions.

A typical procedure for oxidation of cyclohexane: A mixture of catalyst **CZJ-1** (0.005 mmol), cyclohexane (0.1 mmol), and PhIO (0.2 mmol) in CH_3CN (1.0 mL) was sealed in a small Teflon-lined screw-cap vial and stirred at room temperature for 20 h. The identities of the products were determined by analyzing aliquots of the bulk solution using GC-MS and compared with the authentic samples analyzed under the same conditions, whereas the conversion and selectivity were obtained by GC analysis with an FID using a capillary SE-54 column.

Study of the TONs for epoxidation of styrene by CZJ-1: Styrene (100 mmol), PhIO (150 mmol), and **CZJ-1** (0.005 mmol) in acetonitrile (50 mL) were reacted at room temperature. The aliquots were regularly taken out for GC analysis to determine the conversion of styrene and TONs (TON is defined as the mole ratio of the substrate converted to the catalyst).

Study of the TONs for oxidation of cyclohexane by CZJ-1: Cyclohexane (50 mmol), PhIO (100 mmol), and **CZJ-1** (0.0025 mmol) in acetonitrile (50 mL) were sealed in a Teflon-lined screw-cap vial and reacted at room temperature. The aliquots were regularly taken out for GC analysis to determine the conversion of cyclohexane and TONs.

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[15] **CZJ-1**: $C_{72}H_{37}MnN_8O_{13}Zn_2$; $M_r=1407.78$; monoclinic, space group $C2/m$, $a=22.058(7)$, $b=16.907(2)$, $c=16.240(4)$ Å; $\beta=121.36(4)°$; $V=5172(2)$ Å^3; $Z=2$; $\mu=1.895$ mm^{-1}; $R1=0.0882$, $wR(F^2)=0.1757$, and $S=0.891$. **CZJ-1-a**: $C_{72}H_{36}MnN_8O_{12}Zn_2$; $M_r=1390.77$; monoclinic, space group $C2/m$; $a=21.453(5)$, $b=16.258(5)$, $c=15.921(5)$ Å; $\beta=130.17(4)°$; $V=4243(2)$ Å^3; $Z=2$; $\mu=2.296$ mm^{-1}; $R1=0.1279$, $wR(F^2)=0.2546$, and $S=1.072$. **CZJ-1⊃2** styrene: $C_{88}H_{52}MnN_8O_{12}Zn_2$; $M_r=1599.06$; triclinic, space group $P\bar{1}$; $a=13.372(3)$, $b=14.164(3)$, $c=16.713(3)$ Å; $\alpha=69.626(16)°$, $\beta=68.786(17)°$, $\gamma=73.544(17)°$; $V=2721.1(9)$ Å^3; $Z=1$; $\mu=1.843$ mm^{-1}; $R1=0.1339$, $wR(F^2)=0.2799$, and $S=1.013$. **CZJ-1-Ti**: $C_{72}H_{37.5}MnN_8O_{14.5}Ti_{0.5}Zn_2$; $M_r=1456.23$; monoclinic, space group $C2/m$; $a=22.136(4)$, $b=16.647(4)$, $c=16.551(3)$ Å; $\beta=114.63(2)°$; $V=5543.9(19)$ Å^3; $Z=2$; $\mu=2.071$ mm^{-1}; $R1=0.0997$, $wR(F^2)=0.2220$, and $S=1.060$. CCDC-923792 (**CZJ-1**), -882569 (**CZJ-1-a**), -882227 (**CZJ-1⊃2** styrene), and -923793 (**CZJ-1-Ti**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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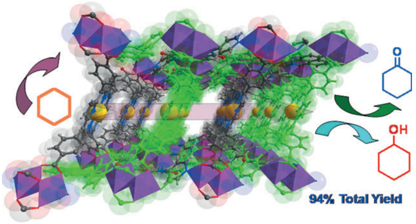
Copycatalyst: To mimic the cytochrome P450 oxidation catalyst, a manganese–porphyrin metalloligand has been incorporated into a 3D porous mixed-metal–organic framework as the highly efficient heterogeneous catalyst for alkene epoxidation and cyclohexane oxidation at room temperature (see figure).



Metalloporphyrins

M.-H. Xie, X.-L. Yang, Y. He, J. Zhang, B. Chen, C.-D. Wu** .... ■■■■–■■■■

Highly Efficient C–H Oxidative Activation by a Porous Mn^{III}–Porphyrin Metal–Organic Framework under Mild Conditions