

A cross-linked manganese porphyrin as highly efficient heterogeneous catalyst for selective oxidation of cycloalkenes/alkanes

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Abstract. The monomeric *tetrakis* (5,10,15,20-*p*-bromophenyl) manganese porphyrin has been converted to a micro- and mesoporous material of surface area 1301 m²/g by carefully manipulating the reaction conditions of Suzuki coupling. This material has been tested for its oxidizing ability of cycloalkenes/alkane by *t*-BuOOH, H₂O₂, CumOOH and *m*-CPBA. The catalyst is found to oxidize the alkenes selectively and it is not destroyed even 5% in 10 cycles of successive oxidation processes in one pot. The parent monomer gets destroyed appreciably under similar oxidizing conditions.

Keywords. Metalloporphyrin; suzuki coupling; heterogeneous catalysts; oxidation.

1. Introduction

The cytochrome P450 and its model compound catalyzed oxidation reactions have been extensively explored over several decades.^{1–5} In model compound studies, tetraphenyl M(III) porphyrins (TPPM(III), where M = Fe, Mn) were found to mimic many reactions of the enzyme.^{6,7} These two metalloporphyrins, under different oxidizing conditions, have been very extensively investigated. In case of iron(III) and manganese(III) porphyrins, it has been well-established that the μ -oxo-dimers were formed from the starting catalysts during the oxidation reactions (scheme 1) causing major damage to the main catalytic cycle.^{8,9}

Many electronegatively substituted and sterically encumbered metalloporphyrins were employed to improve the survival of the catalyst.^{10–12} The stability of the catalyst was indeed improved. But in homogeneous catalytic systems, the separation of the catalysts from the reactants/products and also the higher cost of the halogenated catalysts were posing major problems for their industrial applications. It is to be noted that the native enzyme in biological systems is embedded in organs such as liver, etc.¹³ Thus the enzymatic destruction is minimal in the *in vivo* oxidation reactions. In order to avoid this, the encapsulation or attachment of functionalized metalloporphyrins on solid surfaces such as polyethylene glycol,¹⁴ double hydroxides,¹⁵ molecular squares¹⁶ and silica supports are done.^{17,18} The major

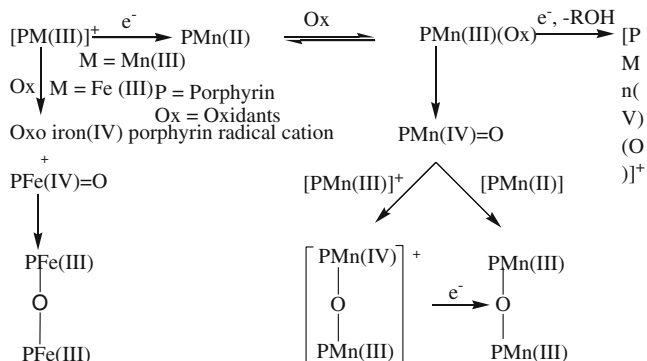
problem in such materials is their limited surface area of actual catalytic sites and this has limited their systematic study for further developments. Recently some of the catalysts have been prepared by covalent approach. These materials are amorphous in nature due to the conjugated structures. However, limited studies on oxidation of thio ether compounds and a few cycloalkenes have been reported with such catalysts.^{19,20} Herein we report our synthetic approach on evolving a material of high surface area from a very common, low-cost porphyrin complex: *p*-tetra bromophenyl manganese (III) porphyrin chloride. The amorphous material, prepared by Suzuki coupling, has a surface area of 1301 m²/g. Details of the method of the synthesis of this material and its catalytic property are reported here.

2. Experimental

2.1 Materials

Organic solvents were distilled over appropriate drying reagents under argon or obtained as dehydrated reagent from Merck's chemical. Deuterated solvents for NMR measurement, benzene 1,4 diboronic acid and caesium carbonate were obtained from Sigma-Aldrich. Pyrrole, *p*-bromobenzaldehyde, propionic acid and manganese (II) acetate tetrahydrate were also obtained from Merck's chemical while *tetrakis* (triphenylphosphine) palladium(0) was obtained from spectrochemicals. Norbornene, cyclohexene, cyclohexane, cyclooctene and all the oxidation product standards, dodecane (internal

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Scheme 1. Possible pathways of the destruction of metal centres of metalloporphyrins during their reaction with various oxidants.

standards) were purchased from Aldrich and were used as received without further purification. *t*-BuOOH (~70%) and H₂O₂ (~30%) were purchased from Sigma-Aldrich as solution in water. CumOOH (Cumyl-OOH) was purchased from Fluka as ~80% solution in cumene and *m*-chloroperbenzoic acid was recrystallized up to 97% purity. The exact active oxygen content of these oxidants was determined iodometrically prior to use. All the monomeric non-metallated and metalloporphyrins were synthesized according to literature procedure.²¹

2.2 Catalyst preparation

The synthesis of the proposed cross-linked manganese catalyst was conducted first by reacting a mixture of *tetrakis* (5,10,15,20 bromophenyl) porphyrin Mn(III) chloride (400 mg, 0.39 mmol) and benzene 1,4 diboronic acid (112 mg, 0.67 mmol) in 1,4 dioxane (25 mL) under argon. To the mixture was added methanol (5 mL), Cs₂CO₃ (403 mg, 1.24 mmol) and Pd(PPh₃)₄ (50 mg, 43 μmol). The mixture was stirred at 110°C for 48 hrs. Finally, the mixture was allowed to cool at room temperature and was poured into water. The precipitate was collected by filtration and then thoroughly washed with water, THF, methanol and acetone after filtration. Then it was also rigorously washed by Soxhlet extraction for 24 hrs. with THF, methanol and acetone. It was dried in vacuum to give a material as dark green solid (300 mg) with 89% yield.

2.3 Catalyst characterization

Solid state ¹H-¹³C CP/MS NMR spectra were recorded by Bruker model 500MHz. Diffuse reflectance and UV-Visible spectra were recorded by PerkinElmer UV-Vis spectrometer Lambda Bio 20 model and Agilent Technologies 8453 model respectively. Fourier transformed

infrared spectra (FTIR) were recorded on KBr pellets using Agilent Technologies Cary 660 model. SEM images and EDX was recorded ZEISS EVO Series Microscope model EVO50. High-resolution electron microscopes (HR-TEM) images were recorded by PHILIPS Model CM 200. Metal concentration was measured by Inductively Coupled Plasma-Atomic Absorption Spectrometer (ICP-AAS) with Perkin Elmer instruments Analyst 100 model. Elemental analysis (C, H, N) was measured by Perkin Elmer instrument series II CHNS/O Analyser 2400 model. Powder X-ray data were collected on a Bruker D8 Advance diffractometer using Ni-filtered CuKα radiation. Data were collected with a step size of 0.02° and a count time of 2 s per step over the range 2° < 2θ < 70°. Nitrogen physisorption study was done with Quantachrome NovaWin-Data Acquisition and Reduction for NOVA instruments ©1994–2007, Quantachrome Instruments version 10.01 at 77K. The samples were degassed up to 150°C for 12 h.

2.4 Oxidation of cycloalkenes/alkane

The oxidations of cycloalkenes/alkane (425 mM) were carried out at room temperature in a 4 mL screw-capped vial fitted with PTFE septa. In all the experiments the cross-linked manganese porphyrin catalyst (2 mg) in 2.0 mL dichloromethane was used. The oxidation reactions were initiated by adding the oxidants (10 mM) at the end to the vial. This was followed by stirring the reaction mixture with a small magnetic bar and the reactions were carried out either under argon or under oxygen depending upon the objective of study. After the reaction was over, 2 μL dodecane was added to this reaction mixture as an internal standard and an aliquot (~1 μL) was withdrawn after regular intervals using a microlitre syringe from the reaction mixture for analysis. At the end of the reaction, the solid particles (catalyst) were separated by filtration and the product analysis for cycloalkenes/alkane oxidation was performed using Perkin-Elmer AutoSystemXL gas chromatography equipped with flame ionization detector (FID) and carbowax capillary column of 30 m length.

3. Results and Discussion

3.1 Characterizations

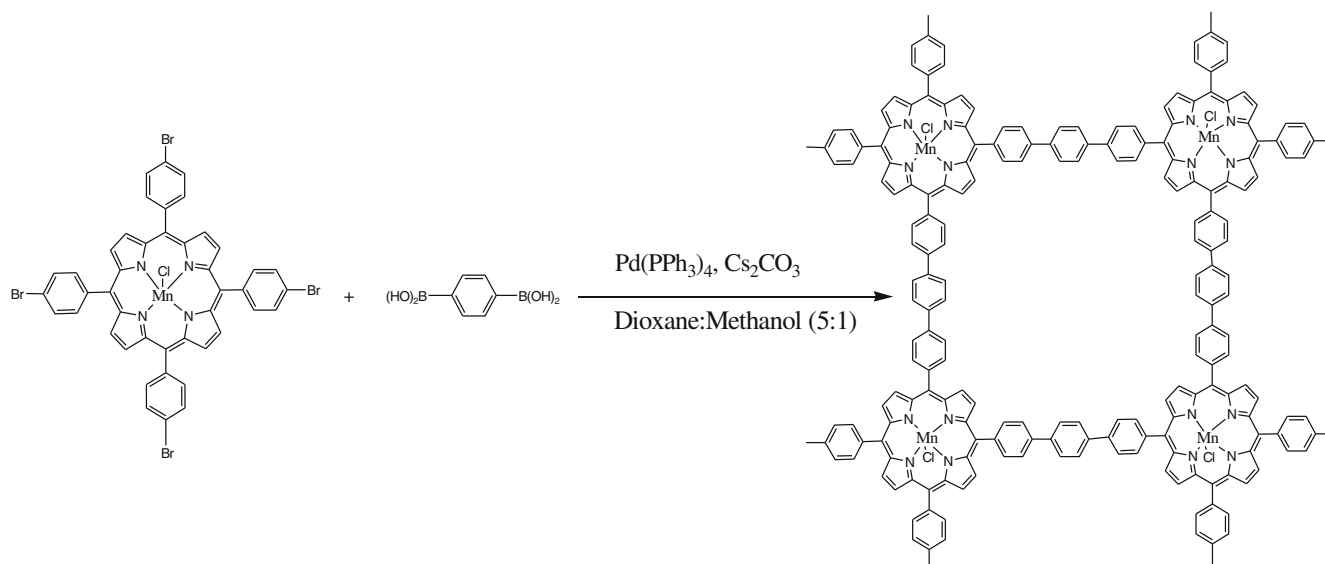
This polymeric catalyst was synthesized by Suzuki-Miyaura cross-coupling polycondensation of a manganese(III) *tetrakis*(4-bromophenyl) porphyrin ([*p*-Br]₄PMn) derivative and benzene 1,4 diboronic acid in the presence of Pd(0) as catalyst under alkaline

condition. Such polycondensation reaction leads to an inherent porous polymer with a built-in manganese(III) porphyrin framework. We examined the polycondensation reaction using solvent systems dioxane/methanol in alkaline Cs_2CO_3 , with the aim of achieving large surface areas for the resulting polymers. As an optimal condition, polycondensation in dioxane/methanol (5/1 in vol.) in the presence of Cs_2CO_3 as base and $\text{Pd}(\text{PPh}_3)_4$ as catalyst allows for the preparation of manganese cross-linked polymer with large surface areas. After repeated rinse with water, THF, methanol and acetone, manganese cross-linked porphyrin was rigorously washed by soxhlet extraction for 24 hrs. with THF, methanol and acetone as solvents respectively, to remove any entrapped molecules and impurities, and then dried under vacuum overnight. Nitrogen sorption isotherm measurements of manganese cross-linked porphyrins at 77 K displayed a typical type-III sorption isotherm curve along with large adsorption at low pressure ($P/P_0 < 0.1$), which is suggestive of the coexistence of micro- and mesopores in the framework. The Brunauer-Emmett-Teller (BET) surface areas were determined to be $1301 \text{ m}^2/\text{g}$ (figure S6). The average pore size were observed to be in the range of 2.2–2.4 nm (by non local-density functional theory) for catalyst which is very close to the size of a cube forming by four porphyrins unit ($\sim 2.4 \text{ nm}$).^{20b} On the basis of these data the most probable structure of catalysts could be as shown in scheme 2.

The cross-linked manganese(III) porphyrin is stable and insoluble in most of the organic solvents as expected as a result of a cross-linked network. Owing to the high-spin paramagnetic effect, the solid state ^1H - ^{13}C CP/MS NMR spectrum of cross-linked manganese(III)

porphyrin gave only a weak and broad peak. The cross-linked manganese(III) porphyrin displayed a broad peak at 127 and 132 ppm assignable to the phenylene linkages and signals at 119 and 148 ppm owing to the porphyrin macrocycles (figure S1). Electronic absorption spectroscopy displayed absorption bands at 485 nm attributed to the Soret band at 580, 625 and 690 nm representing the Q bands of manganese(III) porphyrin units, respectively (figure S2). In relation to this, the IR spectrum of cross-linked manganese(III) porphyrin exhibited the characteristic N-Mn vibration band at 1005 cm^{-1} , which is close to that observed in the $[p\text{-Br}]_4\text{PMn}$. The characteristic new vibration band was observed at 3025 cm^{-1} for C-H stretching frequency of the phenylene linkages between manganese(III) porphyrin units (figure S3). Elemental analysis revealed that the C, H, N are 69.59%, 4.61%, 5.61% (theoretical formula for an infinite 2D polymer $\{\text{C}_{56}\text{H}_{32}\text{ClMnN}_4\}$ C 78.93%, H 3.78%, N 6.57%). The amount of manganese 4.0 wt% present in the catalyst was estimated by ICP-AAS. Electron dispersion X-ray (EDX) spectroscopy measurement also confirmed the existence of Mn, Cl, and Br (figure S5). These results indicate that manganese(III) porphyrin units were covalently integrated into porous framework of cross-linked manganese porphyrin.

The morphology and crystallinity of cross-linked manganese(III) porphyrin were investigated by scanning electron microscopy (SEM), transmittance electron microscopy (TEM) and powder X-ray diffraction (PXRD) measurements. SEM images displayed that cross-linked manganese(III) porphyrin adopts plate-shaped monoliths of several micrometers in size for cross-linked manganese porphyrin (figure S4a). A



Scheme 2. Schematic representation of the synthesis of cross-linked manganese porphyrin.

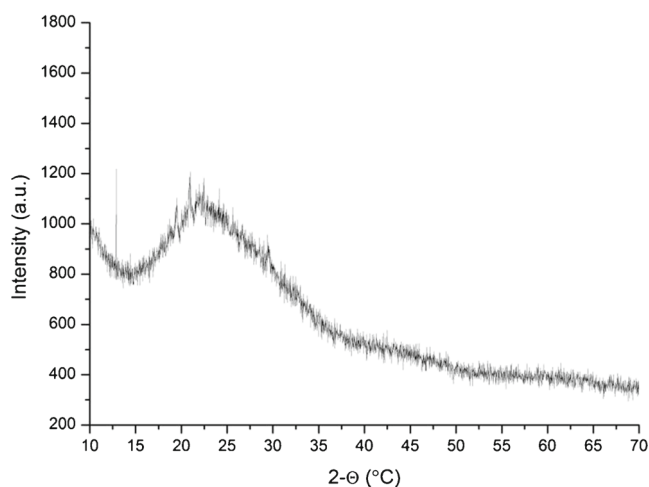


Figure 1. Powder X-ray diffraction pattern for cross-linked manganese(III) porphyrin.

closer look at high magnification SEM images showed that the monoliths consist of ~ 100 – 300 nm sized elementary platelets, while their surfaces are quite rough. High resolution TEM images revealed the presence of nanometer-scale cavities (figure S4b). The PXRD profile confirmed the amorphous character of cross-linked manganese porphyrin (figure 1). Therefore, cross-linked manganese(III) porphyrin is an amorphous, insoluble and nanoporous polymer bearing covalently linked manganese(III) porphyrin functionalities in the skeleton.

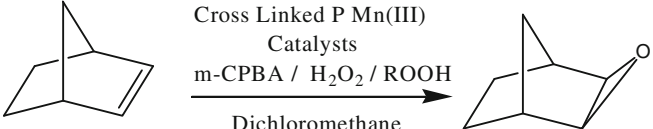
3.2 Norbornene oxidation

The catalytic behaviour of this catalyst was studied next. In this study we have judiciously chosen *cis*-2,3 norbornene as the alkene to be oxidized first because it is more difficult to oxidize with respect to other alkenes such as cyclohexene, etc., and secondly it gives many oxidation products. So, whether the catalyst has the property of selective oxidation is also answerable with this substrate. The oxidation of *cis*-2,3 norbornene in the presence of this catalyst was thus conducted in dichloromethane by hydroperoxides and *m*-chloroperbenzoic acid under argon atmosphere.

It was observed that with monomeric manganese(III) porphyrin as catalysts; the *t*-BuOOH, H_2O_2 , CumOOH and *m*-CPBA oxidizes *cis*-2,3 norbornene to *exo*-2,3 epoxy norbornane with only 10%, 5%, 22% and 8% yields respectively with substantial destruction of catalysts. On the other hand, the corresponding yields were improved to 98%, 32%, 94% and 78% respectively using the cross-linked manganese(III) porphyrin as the catalyst. In the reactions it has been noted that the CumOOH reacts faster with respect to *t*-BuOOH, and the conversion reached a maximum of 32% and 78% in case of H_2O_2 and *m*-CPBA (table 1).

Thus the selective oxidation of *cis*-2,3 norbornene to *exo*-2,3 epoxy norbornane by *t*-BuOOH in 99%

Table 1. Selective oxidation of norbornene by different oxidants.

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Catalysts	Oxidants	atm	Optimal reaction time (hrs)	Yield (%)
Br ₄ TPPMn(III)Cl	<i>t</i> -BuOOH	Ar	24	10
		O ₂	24	23
	H_2O_2	Ar	6	5
		O ₂	6	5
	CumOOH	Ar	24	22
		O ₂	24	48
	<i>m</i> -CPBA	Ar	1	8
		O ₂	1	9
Cross-linked manganese(III) porphyrin (1301 m ² /g)	<i>t</i> -BuOOH	Ar	15	98
		O ₂	8	99
	H_2O_2	Ar	6	32
		O ₂	6	39
	CumOOH	Ar	10	94
		O ₂	4	95
	<i>m</i> -CPBA	Ar	1	78
		O ₂	1	82

Norbornene (425 mM), Oxidants (10 mM), Catalysts (2 mg), Dichloromethane (2 mL), stirred at room temperature under argon and oxygen atmosphere, conversion (%) by GC. The yields are w.r.t. oxidants.

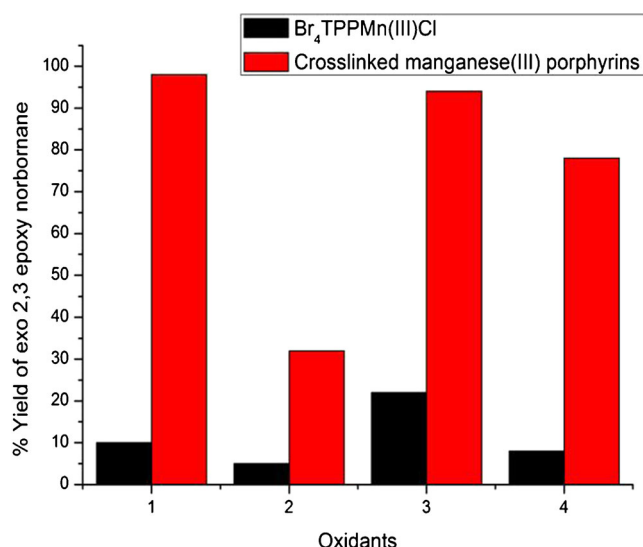


Figure 2. Norbornene was oxidized by various oxidants (1) *t*-BuOOH (2) H₂O₂ (3) CumOOH (4) m-CPBA with catalysts Br₄TPPMn(III)Cl and cross-linked manganese(III) porphyrin under argon atmosphere.

yields by using this cross-linked manganese(III) porphyrin has indeed been achieved. Notable was that the reaction time was much less in this case. It has also been observed that it behaves as a robust catalyst with no sign of any destruction for 10 such catalytic cycles studied by adding oxidants in aliquots after completion of each cycles. It was also observed that the conversion of cis-2,3 norbornene to exo-2,3 epoxy norbornene by H₂O₂ and m-CPBA were substantially increased from 10–32% and 35–78% respectively by changing the catalyst from monomer to cross-linked manganese(III) porphyrin (figure 2).

In these reactions it has been observed that the epoxidation of cis 2,3-norbornene was very high under oxygen atmosphere as compared to that in argon atmosphere for *t*-BuOOH and CumOOH. While in case of H₂O₂ and m-CPBA there was not much significant change under oxygen w.r.t. argon atmosphere (table 1, figure S7). The most rational way to understand the product profile under dioxygen would be through a radical path for hydroperoxides where the evolved RO• further reacts with dioxygen and generates ROO• radical and the increased yield of the product could be accountable due to this.^{14,22} Thus we believe the selective epoxidation of cis 2,3 norbornene by hydroperoxides proceeds through radical path and the oxidation by m-CPBA through non-radical path.

3.3 Oxidation of cyclohexene

Next the catalytic oxidation reaction of cyclohexene by these hydroperoxides, hydrogen peroxide and m-CPBA were conducted. In these reactions it has been observed that cyclohexane epoxide, cyclohexenone and cyclohexenol were formed but cyclohexenone was stereoselectively found with 52–76% by various oxidants with monomer and cross-linked manganese(III) porphyrin. The catalytic behaviours of these catalysts are shown in table 2.

3.4 Oxidation of cyclooctene

In the oxidation of this substrate it was observed that cyclooctane epoxide was formed selectively from cyclooctene oxidation by various oxidants with cross-

Table 2. The oxidation of cyclohexene.

Catalysts	Oxidants	atm	Time (hrs.)	Yield (%)	Selectivity (%)
Br ₄ TPPMn(III)Cl	<i>t</i> -BuOOH	Ar	12	60	70
	H ₂ O ₂	Ar	4	18	52
	CumOOH	Ar	12	85	74
	m-CPBA	Ar	1	52	65
Cross-linked Manganese(III) Porphyrin (1301 m ² /g)	<i>t</i> -BuOOH	Ar	1.5	99	72
	H ₂ O ₂	Ar	1	54	70
	CumOOH	Ar	1.5	99	70
	m-CPBA	Ar	0.5	99	75

Cyclohexene (425 mM), Oxidants (10 mM), Catalyst (2 mg), Dichloromethane (2 mL), stirred at room temperature under argon and oxygen atmosphere, conversion (%) by GC. The yields are w.r.t. oxidants.

linked manganese(III) porphyrin. The comparative oxidation of cyclooctene with the monomeric catalyst is shown in table 3. In case of all the oxidants it has been noted that the cross-linked manganese polymeric catalyst is superior to the monomer.

3.5 Oxidation of cyclohexane

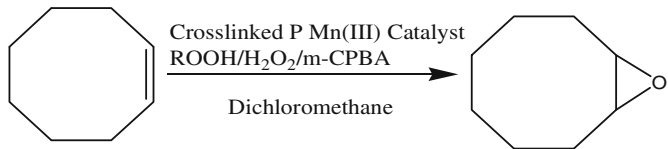
As usual it has been observed that it is very difficult to oxidize this alkane. Cyclohexane was oxidized by these hydroperoxides, H_2O_2 and *m*-CPBA into cyclohexanone (55–60% stereoselectively) and cyclohexanol. The catalytic activity of these cross-linked manganese porphyrin was shown in table 4 by various oxidants. It

was noted that cyclohexane was oxidized to cyclohexanone and cyclohexanol up to 29%, with this polymeric catalyst by CumOOH.

3.6 Recyclability

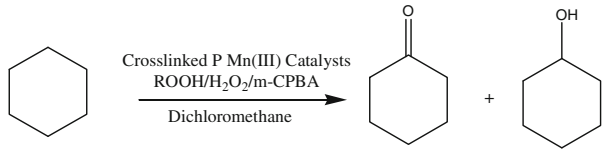
In these oxidizing systems it has been noted that the cross-linked manganese porphyrin was not destroyed after 10 cycles of the oxidation cycles. After completion of the first cycle to the same pot, another aliquate of oxidants were added and the yields of products in the mixture were measured in these processes and continuous oxidation has been noted till 10 cycles measured. This shows that this catalyst was more recyclable, robust and

Table 3. Selective oxidation of cyclooctene.

				
Catalysts	Oxidants	atm	Time (hrs.)	Yield (%)
$\text{Br}_4\text{TPPMn(III)Cl}$	<i>t</i> -BuOOH	Ar	24	10
	H_2O_2	Ar	6	5
	CumOOH	Ar	24	21
	<i>m</i> -CPBA	Ar	1	10
Cross-linked Manganese(III) porphyrin ($1301 \text{ m}^2/\text{g}$)	<i>t</i> -BuOOH	Ar	18	91
	H_2O_2	Ar	1.5	16
	CumOOH	Ar	8	99
	<i>m</i> -CPBA	Ar	0.5	38

Cyclooctene (425 mM), Oxidants (10 mM), Catalyst (2 mg), Dichloromethane (2 mL), stirred at room temperature under argon and oxygen atmosphere, conversion (%) by GC. The yields are w.r.t. oxidants.

Table 4. Selective oxidation of cyclohexane.

				
Catalysts	Oxidants	atm	Time (hrs.)	Yield (%)
$\text{Br}_4\text{TPPMn(III)Cl}$	<i>t</i> -BuOOH	Ar	24	8
	H_2O_2	Ar	6	2
	CumOOH	Ar	24	9
	<i>m</i> -CPBA	Ar	1	4
Crosslinked Manganese(III) porphyrin ($1301 \text{ m}^2/\text{g}$)	<i>t</i> -BuOOH	Ar	24	26
	H_2O_2	Ar	6	7
	CumOOH	Ar	24	29
	<i>m</i> -CPBA	Ar	1	11

Cyclohexane (425 mM), Oxidants (10 mM), Catalyst (2 mg), Dichloromethane (2 mL), stirred at room temperature under argon and oxygen atmosphere, conversion (%) by GC. The yields are w.r.t. oxidants.

enantioselective as compared to monomeric manganese porphyrin. The recyclability of cross-linked manganese porphyrin was shown in table S1 under argon and oxygen both.

4. Conclusions

The most easily degradable catalyst known, TPPMnCl has now been made to be a non-degradable catalyst, so that the representative catalyst does not require any electronegative substituent on porphyrin backbone. The catalyst with surface area of 1301 m²/g in particular was thus found to oxidize at least 1/4th of the alkene present in the reaction flask selectively to the epoxide in one pot without much catalyst destruction. This result is very promising for the possible industrial application of the catalyst. The work on application of the catalytic oxidation of several other alkenes with this catalyst and the development of other similar catalysts are in progress.

Supplementary Information

Solid state ¹H-¹³C CP/MS NMR, electronic absorption spectroscopy, FTIR, SEM, HRTEM, EDX, N₂ physisorption isotherm, recyclability table, catalytic graph data.

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