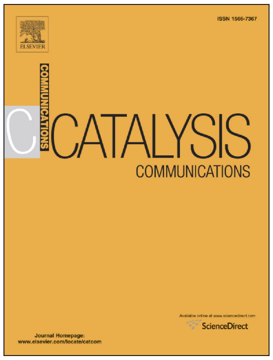

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A porphyrin-based microporous network polymer that acts as an efficient catalyst for cyclooctene and cyclohexane oxidation under mild conditions

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KEYWORDS: Porphyrins; Polymers of Intrinsic Microporosity (PIMs); Porous; Heterogeneous catalysis; Oxidation.

ABSTRACT: The highly efficient dibenzodioxin-forming reaction between the (pentafluorophenyl)porphyrin manganese(III) **(MnP)** and hexahydroxytriptycene **(HHT)** provide a new microporous network polymer **(P1)**, which demonstrated a large surface area (1080 m^2 g^{-1}) and proved to be an efficient solid for heterogeneous catalysis for cyclooctene and cyclohexane oxidation under mild conditions and with high capacity of recovery and reuse in many catalytic cycles.

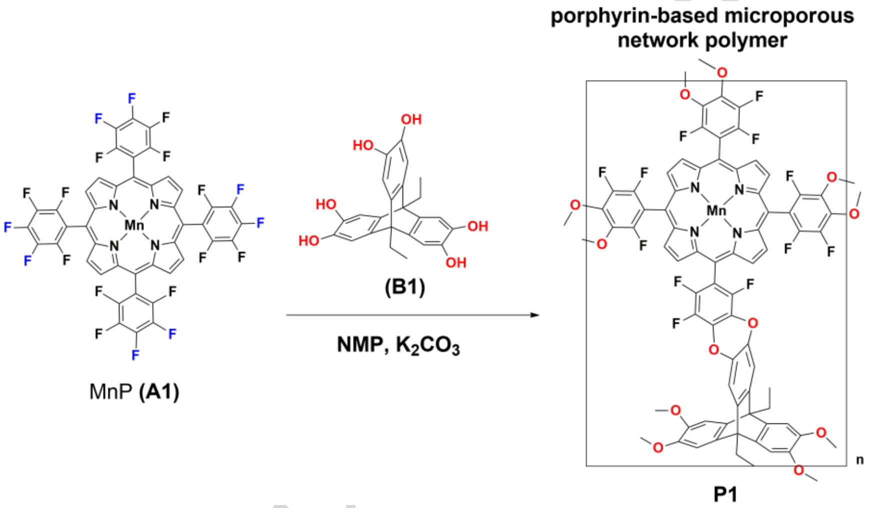
1. Introduction

Oxidation reactions of organic compounds, especially alkenes and alkanes, play an important role in the chemical industry, both in organic synthesis and in the production of bulk and fine chemicals. The development of efficient and selective methods that employ mild conditions and avoid toxic metal reagents is the major challenge in this area [1]. In this regard, significant progress has been achieved within the area of homogeneous molecular catalysis, especially using porphyrins. Synthetic metalloporphyrins, particularly those containing iron and manganese cations, have been widely studied as catalysts in many oxidation processes and as models for cytochrome P450 enzymes [2-6].

The synthetic development of novel catalysts is based upon a growing understanding of the mechanism of action and has led to improve catalytic results in homogeneous catalysis using porphyrins [,4-6]. Despite the efforts in the synthesis of more robust porphyrins, the catalytic process employing such compounds in homogeneous medium still have some drawbacks, such as difficulty or impossibility of the catalyst recovery, formation of μ-oxo dimmers or oxidative degradation of the porphyrin ring (even in a small extent) and contamination of the products formed at the end of the reaction [2-6]. In this regard, the search for more stable, efficient and selective catalysts, combined with the desire for recovery and reuse has also led to a growing interest in using porphyrin-based materials for heterogeneous catalysis [7-14].Hence, metalloporphyrins have been immobilized on many different supports [7-9], and also incorporated within porous materials, such as Metal Organic Frameworks (MOFs) [9,10] and porous network polymers [11-14]. These materials function as solid catalyst for heterogeneous process since the presence of porous enhances access of the substrate to the active metal catalytic centers of the solid catalyst. Moreover, the high density of active sites in these materials enhances catalytic performance. Although a number of research groups have explored the use of metalloporphyrins as building blocks for the design of porous polymers, catalytic studies using these materials are still rare [9-14].

Polymers of Intrinsic Microporosity (PIMs) are highly rigid amorphous materials, easily prepared using dibenzodioxin forming reactions, for which microporosity is generated from their rigid and contorted structures [15]. Insoluble networks PIMs with high surface area (up to 1000 m^2g^{-1}) and potential use in heterogeneous catalysis have been prepared previously using planar functional units such as phthalocyanines and porphyrins [12,13,16]. These materials are assembled via covalent bond formation rather than by formation of usually weaker coordination or hydrogen bonds and display high chemical and thermal stability which encourage the synthesis of new network PIMs and their assessment for heterogeneous oxidation catalysis.

For the present study, the dibenzodioxin-forming reaction [16] between (pentafluorophenyl)porphyrin manganese(III) **(MnP)** and 9,10-diethyl-2,3,6,7,12,13-hexahydroxytriptycene **(HHT)** was used to prepare a new network PIM porphyrin-based **(P1)** (Scheme 1). The new polymer exhibits remarkable activity and stability on catalytic oxidation of cyclooctene and cyclohexane under heterogeneous conditions with high capacity of recovery.



Scheme 1. Schematic representation of **P1** preparation.

2. Experimental

2.1 General information

The free-base porphyrin (**H_2P**) [17], the metalloporphyrin (**MnP**) [18], the compounds 9,10-diethyl-2,3,6,7,12,13-hexahydroxytriptycene (**HHT**) [19] and the 2,3-dihydroxy-9,10-dimethyltriptycene (**DHT**) [20] were synthesized as reported previously (see Supporting Information SI). Iodosylbezene (PhIO) was prepared according to a literature procedure [21], assayed by iodometric titrations and stored in a freezer.

2.2 Synthesis and characterization of the network PIM porphyrin **P1**

The polymer **P1** was prepared by reacting the metalloporphyrin **MnP** (monomer **A1**) and 9,10-diethyl-2,3,6,7,12,13-hexahydroxytriptycene **HHT** (monomer **B1**) (Scheme 1) according to the reported procedure [16]. The metalloporphyrin **MnP** (0.17 g, 0.156 mmol), 9,10-diethyl-2,3,6,7,12,13-hexahydroxytriptycene **HHT** (0.1 g, 0.208 mmol) and anhydrous K_2CO_3 (0.32 g, 2.34 mmol) were stirred in anhydrous NMP (5 mL) at 170 °C under nitrogen atmosphere. After about 24 h the system was allowed to reach room temperature, methanol (30 mL) was added and the mixture was stirred for 30 min, from which a black solid (**P1**) was filtered off. The solid was purified by Soxhlet extraction and reflux in various solvents (in the order THF, $CHCl_3$, $CHCl_2$, acetone and methanol). The solid was dried in vacuum oven for 6 h at 110 °C (yield 90%). **Elemental analysis** (%) for $C_{78}H_{32}O_{10}F_{12}N_4Mn$: **calcd** C 63.82, H 2.20, N 3.82; **found:** C 55.40, H 1.80, N 4.20 **ICP OES** (Mn, %) **calcd.**: 3.74, **found:** 3.24. **BET surface area** =1080 m^2 g^{-1}. **IR** (cm^{-1}):1651, 1455, 1419, 1334, 1300, 1254, 1157, 1064, 1006, 947, 797, 759, 705. **UV-VIS** λ_{max}(mineral oil, nm): 475, 376.**TGA** (nitrogen):~ 3.5% loss of mass < 200 °C. Initial weight loss due to thermal degradation commences at ~400 ºC (Figure S17, SI). Note that the mass loss < 200 °C is ascribed to the removal of adsorbed gas (O_2, N_2, CO_2) and solvent or water molecules, which we account for the lower than expected carbon content from elemental analysis. Moreover, thermal degradation results in a loss of mass of only ~50% of original weight up to 1000 °C, indicating that carbonization is occurring, which is consistent with the low values for carbon obtained during elemental analysis.

2.3 Catalytic reactions

The efficiency of the network PIM porphyrin (**P1**) as catalyst for oxidation reactions was tested using (Z)-cyclooctene (previously purified on neutral alumina column) and cyclohexane as substrates using iodosylbenzene as oxygen donor. The reactions were performed in a 1.5 mL glass flask equipped with a magnetic stirrer, in a dark chamber. The solvent mixture (acetonitrile/dichloromethane,ACN:DCM 1:1, v/v) and the substrates were purged with argon for 15 min. The catalyst **P1** (0.001 g, 0.00059 mmol) and the oxidant iodosylbenzene (0.0013 g, 0.0059 mmol) (**P1**/PhIO at a molar ratio of 1:10) were added in the reaction flask and they were also purged with argon for 15 min. Then, the mixture of solvents (ACN:DCM, 1:1) was added to the reactions flasks, followed by addition of the substrates (**P1**/PhIO/substrate molar ratio of 1:10:1000). The molar ratio was based on the amount of metal of the polymer **P1** measures by ICP (heterogeneous catalysis) or based on the molecular mass of the metalloporphyrin **MnP** (homogeneous catalysis). The oxidation reactions were performed under magnetic stirring, for 1 hour, at room temperature, in the absence of light. At the end of the reaction, the excess of iodosylbenzene was eliminated by adding a solution of sodium sulfite in acetonitrile. The catalyst **P1** remained insoluble during the reaction, so the process was heterogeneous in all cases. At the end of the heterogeneous reaction, the reaction mixture was separated from the insoluble catalysts by centrifugation and the supernatant was transferred to a volumetric flask (2 mL). The solid catalyst was washed three times with the mixture of solvents (ACN:DCM) to extract any reaction products that might have adsorbed onto the solids catalysts. The washing solutions were added to the previously separated reaction supernatant in a volumetric flask (2 mL). In case of the homogeneous catalysis (**MnP**), the reaction mixture was transferred directly to a volumetric flask (2 mL) by the end of the reaction.

To study the recyclability of **P1**, the solid catalyst was recovered after each use by centrifugation, washed with different solvents (water, acetonitrile, dichloromethane and methanol) and dried at 100 °C on a vacuum oven for about 12h. The dried solid was then reused in a new catalytic reaction in the same conditions as the ones described above.

The products were analyzed by gas chromatography using bromobenzene as internal standard. Product yields were based on the quantity of PhIO added to each reaction.

3. Results and discussion

3.1 Synthesis and characterization of the network PIM porphyrin **P1**

Significant nitrogen (N_2) adsorption at 77 K for **P1** at low values of relative pressure (P/P^0) and the isotherm shape (Type I) [22] are both consistent with a predominantly microporous structure (Fig. 1a). The isotherm permitted an apparent BET surface area of 1080 m^2/g to be calculated. The hysteresis observed for **P1** extends down to low relative pressures and this characteristic may be attributed to swelling of the polymer rather than to the presence of mesopores [12,15,23].

The UV-VIS spectrum in mineral oil (Fig. 1b) of the metalloporphyrin **MnP** showed the Soret band at 475 nm and the charge transfer band at 365 nm, both consistent with Mn(III) porphyrins [24]. The same bands were observed in the spectrum of the polymer **P1** which suggest the presence of the Mn(III)porphyrin in its structure.

(a) (b)

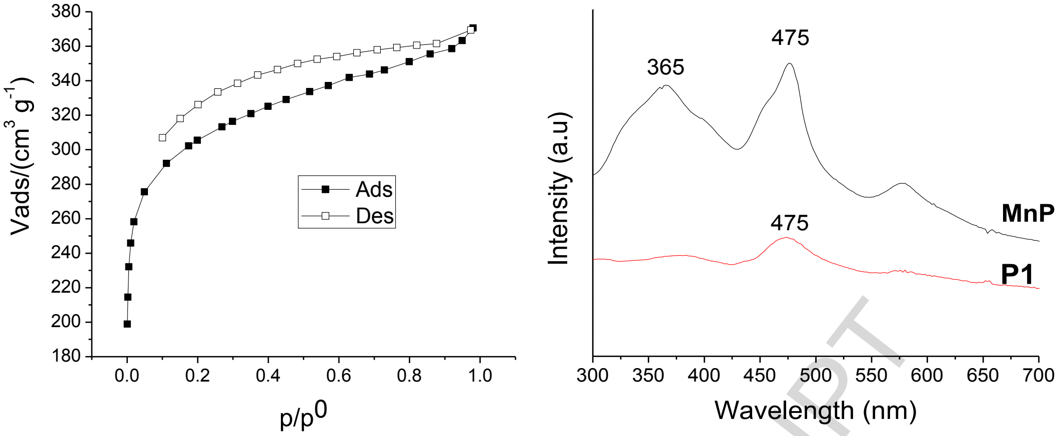
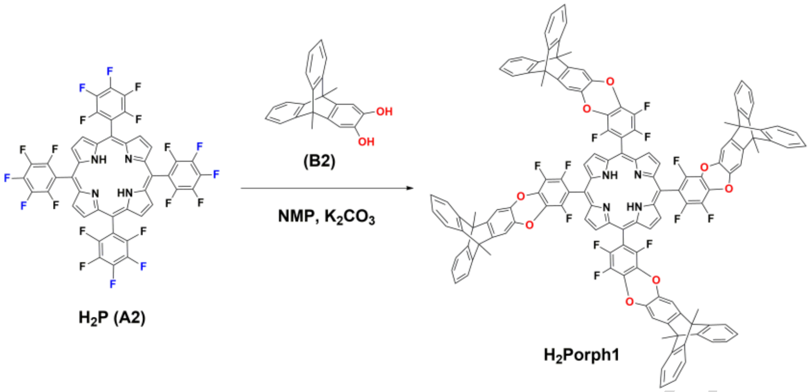


Figure 1. (a) Nitrogen adsorption/desorption isotherm for **P1** (BET surface area = 1080 m^2 g^{-1}), **(b)** UV-VIS spectra of the **MnP** (monomer **A1**) and network PIM porphyrin **P1** (both samples in mineral oil).

Thermogravimetric analysis (TGA) (SI, Fig. S17) indicated that the polymer **P1** has excellent thermal stability with decomposition starting as high as 350 °C, which can be important for some catalytic processes.

The synthesis of the polymer **P1** involves an aromatic nucleophilic substitution (S$_N$Ar) mechanism. As reported previously, the fluorine atoms in the *para* position of the porphyrin core are readily substituted by nucleophiles [25,26]. This is followed by a second rapid intramolecular substitution on the neighboring fluorine atoms when catechols are used as nucleophiles [16]. Therefore, in order to confirm the reaction between the monomers **MnP** and **HHT** (Scheme 1), a model S$_N$Ar reaction using the free-base tetrakis(pentafluorophenyl)porphyrin **(H$_2$P)** and four molar equivalents of the 2,3-dihydroxy-9,10-dimethyltriptycene **(DHT)** was performed (Scheme 2), according to the reported procedure [16]. The novel triptycene-substituted porphyrin **(H$_2$Porph1)** was characterized by MALDI-MS and ^{1}H and ^{19}F NMR spectroscopy, all of which confirmed its structure (see S I).



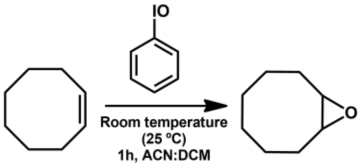
Scheme 2. Schematic representation of the **H_2Porph1** preparation.

3.2 Catalytic reactions

(Z)-cyclooctene is a useful diagnostic substrate as it is easily oxidized in the presence of metalloporphyrins as catalysts and (Z)-cyclooocteneoxide is usually the sole product [27,28]. For comparison, the performance of **MnP** as catalyst was also determined (Table 1)) as it had shown previously high catalytic activity in homogeneous oxidation reactions [27]. This enhanced performance of the porphyrin MnP can be attributed mainly to its greater stability under oxidation conditions, resulting from the electron withdrawing nature of the pentafluorophenyl substituents.

The polymer **P1** showed excellent activity for the oxidation of (Z)-cyclooctene (80% yield) (Table 1), similar to the activity of the **MnP** in homogeneous medium (86% yield) suggesting that the catalytic centers of **MnP** in the **P1** structure are readily accessible to both cyclooctene and PhIO reactants. The control reaction using PhIO in the absence of any catalyst showed low epoxide yield (7%), proving that catalytic activity is due to the presence of **MnP** or **P1**.

Table 1 Oxidation of (Z)-Cyclooctene using PhIO as oxidant and the porphyrin PIM network **P1** as solid catalyst for heterogeneous process or the precursor **MnP** as homogeneous one.



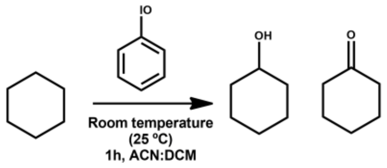
Catalyst	(Z)-Cyclooctene[a]
	Epoxide (%)[b]
MnP[c]	86.1 ± 0.4
P1	80.0 ± 3.0
PhIO[d]	7.20 ± 0.2

[a]Reactions conditions: reaction time= 1 h, solvent mixture of acetonitrile/dichlorometane (ACN:DCM, 1:1 v/v), room temperature (25 °C), Catalyst (**P1**)/PhIO/substrate molar ratio= 1:10:1000. [b]The product yields were calculated based on the amount of iodosylbenzene used in the reactions.[c]Homogeneous catalysis with the metalloporphyrin **MnP** (monomer **A1**). [d]Control reaction using only substrate + PhIO.

Cyclohexane is less reactive than cyclooctene and its oxidation can produce a mixture of cyclohexanone (K) and cyclohexanol (A) (so-called K–A oil), which is of considerable importance in the industrial production of nylon [1].

The catalytic oxidation using metalloporphyrins usually affords both cyclohexanone (K) and cyclohexanol (A) (as major products [27,28]. Both **MnP** and **P1** showed selectivity for the alcohol in the cyclohexane oxidation (Table 2), which is also in agreement with homogeneous catalysis using other metalloporphyrins [27-30]. The polymer **P1** showed catalytic activity similar to that achieved with the **MnP** in homogeneous medium (~50% yield) and a higher alcohol selectivity (98% for **P1** and 83% for **MnP**) as shown in Table 2. Although much effort has been made in the development of catalysts for oxidation of cyclohexane [27,29-31], few catalysts with efficient catalytic activity under mild conditions have been reported in heterogeneous catalysis [9-11,28,32]. Furthermore, in some cases the catalyst showed selectivity for ketone rather than alcohol [7,10,33]. Nevertheless, few studies have shown recyclability tests using cyclohexane as substrate [10].

Table 2 Oxidation of cyclohexane using PhIO as oxidant and the porphyrin PIM network **P1** as heterogeneous catalyst or the precursor porphyrin **MnP** as homogeneous catalysts.



Catalyst	Cyclohexane[a]		
	Alcohol[b] (%)	Ketone[b] (%)	Alcohol Selectivity (%)
MnP[c]	54.0 ± 3.0	10.7 ± 0.5	83.6
P1	53.1 ± 1.3	1.0 ± 0.4	98.2
PhIO[d]	Not detected	Not detected	-

[a]Solvent mixture of acetonitrile/dichlorometane (ACN:DCM, 1:1 v/v), room temperature (25 °C), Catalyst (**P1**)/PhIO/substrate molar ratio = 1:10:1000.[b]The products yields were calculated based on the amount of iodosylbenzene used in the reactions. [c]Homogeneous catalysis with the metalloporphyrin **MnP** (monomer **A1**). [d]Control reaction using only substrate and PhIO.

The catalytic activity and the alcohol selectivity of **P1** for cyclohexane oxidation is impressive in comparison to some previously catalytic results using other materials in heterogeneous medium [8,27,29-31]. In general, for cyclohexane oxidation, metalloporphyrins show lower catalytic activity in heterogeneous medium than in solution (homogeneous catalysis) [27-30]. These impressive results suggest the stability of the active sites within the **P1** structure and also the easy accessibility of the catalytic centers to the cyclohexane substrate in the polymer structure.

In general, microporous materials usually show better catalytic activity for substrates of smaller size [33-35].The excellent catalytic activity of polymer **P1** after only one hour of reaction and under mild conditions for both substrates investigated, suggests that they can readily access the catalytic sites inside the porous structure of the material. Further investigations using substrates of different steric bulk are being planned.

As mentioned before, one of the main advantages of heterogeneous catalysis in relation to homogeneous one is the recyclability of the catalyst. Therefore, the polymer **P1** was easily recovered from the reaction medium and reused without loss of the catalytic activity during at least four catalytic cycles (Fig 2). Moreover, the catalyst **P1** maintained the high alcohol selectivity in all cycles studied.

We ascribe this remarkable retention of catalytic activity to the highly robust nature of the polymer and its rigidity, which maintains site-isolation of the metal centres and stops self-oxidation of the porphyrin ligands.

In addition, heterogeneous catalysis using P1 provides greater purity of the products compared to homogeneous using MnP since they are separated by simple centrifugation and washing of the solid catalyst.

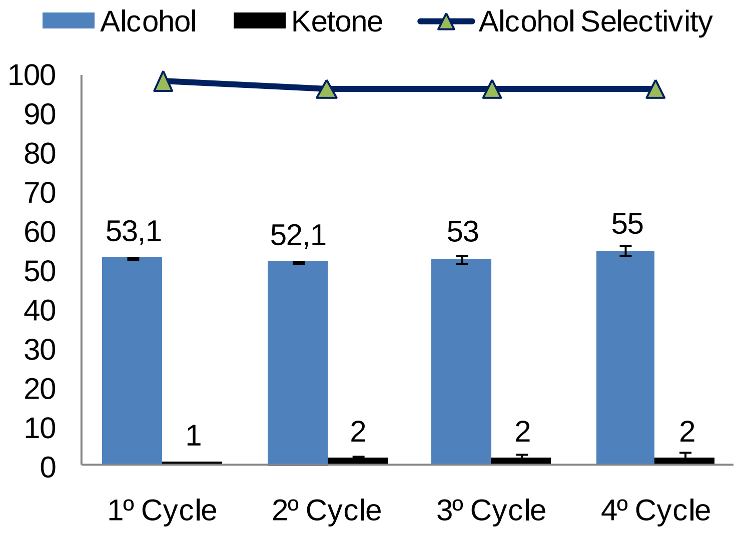


Figure 2. Study of the recyclability of the catalyst solid **P1** for cyclohexane oxidation reaction under the same conditions mentioned in the Table 2.

4. Conclusions

To conclude, a microporous network polymer **P1** was easily prepared by an efficient dibenzodioxin-forming reaction from a simple manganese(III)porphyrin precursor (**MnP**) which has recognized catalytic activity in homogenous oxidation catalysis. The polymer **P1** proved to be a highly active catalyst for (Z)-cyclooctene and cyclohexane oxidation, showing catalytic activity comparable to the **MnP** precursor in solution (homogeneous catalysis). In addition, the P1 polymer showed excellent catalytic activity in the oxidation of cyclohexane with high alcohol selectivity under mild conditions and was also easily recovered by centrifugation and reused without loss of catalytic activity, maintaining a high alcohol selectivity in all cycles studied.

We expected that this work will contribute scientifically to research on porous porphyrinic materials for heterogeneous catalysis under mild conditions, mainly for the oxidation of inert substrates like cyclohexane, and thus leads to the development of some industrially useful materials in the future.

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Appendix A. Supporting Information.

Supporting data to this article can be found online at

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Highlights

- Efficient dibenzodioxin-forming reaction with Mnporphyrin and hexahydroxytriptycene.
- A new microporous network polymer which large surface area (1080 m^2 g^{-1}).
- An efficient solid for heterogeneous catalysis of oxidation reactions.
- Solid catalyst with high capacity of recovery and reuse in many catalytic cycles.