Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 263 (2007) 200–205
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

# Synthesis and spectroscopic, electrochemical, and catalytic properties of a new manganese porphyrin bearing four positive charges close to the metal

Constance Bochot, Jean-François Bartoli, Yves Frapart, Patrick M. Dansette, Daniel Mansuy, Pierrette Battioni *

*Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, UMR 8601, Université René Descartes Paris 5, 45 Rue des Saints-Pères, 75270 Paris Cedex 06, France*

Received 6 July 2006; accepted 11 August 2006
Available online 22 August 2006

**Abstract**

A new Mn-porphyrin bearing four pyridinium substituents bound through their nitrogen atoms on the *meso*-positions of the tetrapyrrole ring was synthesized in three steps from Zn-β-octaethylporphyrin. It was characterized by elemental analysis, electrospray mass spectrometry, UV–vis and dual polarization mode EPR spectroscopy, and electrochemistry. Electrochemical and EPR studies showed that the Mn-porphyrin prepared by this method existed as a 80/20 Mn(II)/Mn(III) mixture, the redox potential of the Mn(III)/Mn(II) couple being +345 mV (versus SCE, in $CH_3CN$). It catalyzed alkene epoxidation and alkane hydroxylation by PhIO with characteristics comparable to those of Mn[TDCPP = *meso*-tetra-(2,6-dichlorophenyl)porphyrin]Cl. It also catalyzed the hydroxylation of anisole, naphthalene and ethylbenzene by $H_2O_2$ in $CH_2Cl_2/CH_3CN$, as well as the hydroxylation of the drug diclofenac by oxone in water. It is a new biomimetic catalyst exhibiting two distinctive characteristics: a good solubility in both hydrophobic aprotic solvents and water for pH > 5, and an unusual structure with four positive charges very close to the metallic centre.


*Keywords:* Biomimetic catalysts; Epoxidation; Hydroxylation; Oxone; Hydrogen peroxide

## 1. Introduction

Manganese porphyrins have been described as good catalysts for the monooxygenation of alkenes, alkanes and aromatic compounds by various oxygen atom donors, and several systems based on manganese and iron porphyrin catalysts have been reported to mimic the cytochrome P450 chemistry [1–6]. Many manganese porphyrins derived from Mn(III)(TPP = *meso*-tetraphenylporphyrin) have been synthesized in order to improve its efficiency as an oxidation catalyst. A first generation of better catalysts has been obtained after introduction of substituents, such as $CH_3$ or Cl, at positions 2 and 6 of each *meso*-phenyl ring, as in Mn(III)(TMP = *meso*-tetramesitylporphyrin) or Mn(III)[TDCPP = *meso*-tetra-(2,6-dichlorophenyl)porphyrin], or after replacement of the *meso*-phenyl rings by *N*-methyl-pyridinium substituents, as in Mn(III)[T4MPyP = *meso*-tetra-(4-N-methyl pyridiniumyl)porphyrin]. A second generation of even better catalysts has been obtained by introduction of electron-withdrawing substituents, such as Cl, Br, $SO_3H$ or $NO_2$, at the β-positions of the porphyrin ring of Mn(TMP), Mn(TDCPP) or Mn[$TF_5PP$ = *meso*-tetra-(pentafluorophenyl)porphyrin] for instance [1–6].

Very few catalysts have been described so far in the Mn(OEP = β-octaethylporphyrin) series and it has been reported, at the beginning of the development of metalloporphyrin oxidation catalysts, that metal complexes of OEP were less resistant towards oxidative degradation than the corresponding TPP complexes [7]. A recent article has shown that it was possible to synthesize a Zn(OEP) complex bearing four *meso*-pyridiniumyl substituents bound to the tetrapyrrole ring by their nitrogen atoms, by reaction of electrochemically oxidized Zn(OEP) with an excess of pyridine [8] (Fig. 1). This new

* Corresponding author. Tel.: +33 1 42 86 21 84; fax: +33 1 42 86 83 87.
*E-mail address:* pierrette.battioni@univ-paris5.fr (P. Battioni).

1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.08.032

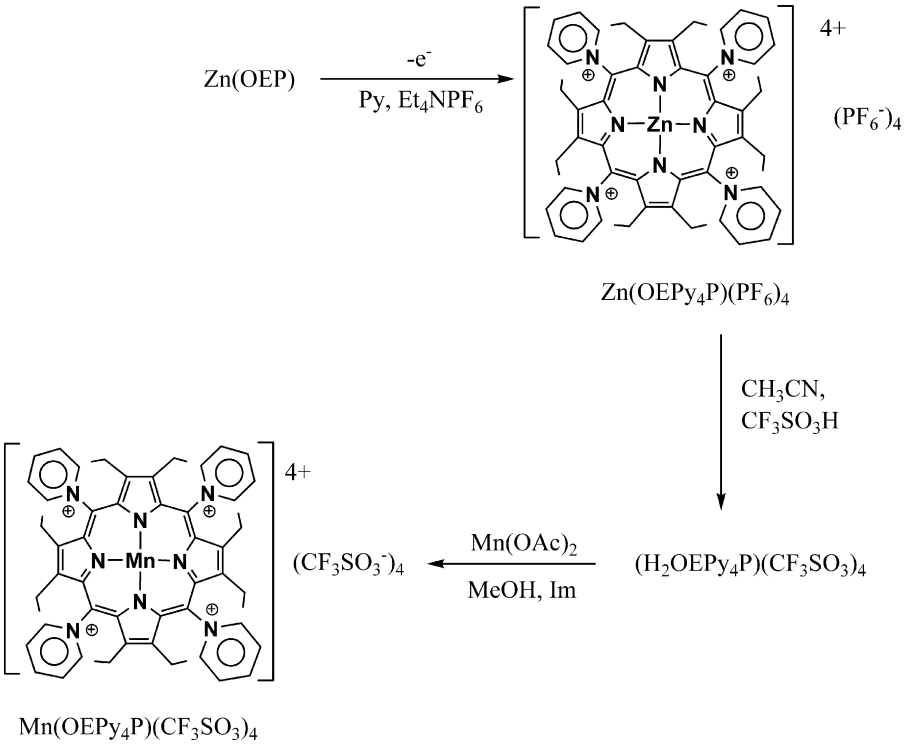



Fig. 1. Synthesis of $Mn(OEPy_4P)$ from Zn(OEP).

kind of dodeca-substituted porphyrin, $[H_2OEPy_4P]^{4+}$, appeared to be especially interesting because it incorporates four positive charges close to the porphyrin core. In order to study the influence of this particular structure on the catalytic properties of manganese porphyrins, we decided to synthesize the corresponding manganese porphyrin. This article describes the synthesis and the electrochemical, spectroscopic, and catalytic properties of this new manganese porphyrin.

## 2. Experimental

### 2.1. Synthesis of $Mn(OEPy_4P)$

It was done in three steps. The first one, the preparation of $Zn(OEPy_4P)(PF_6)_4$ from Zn(OEP) was performed as described previously [8], with a slightly modified workup procedure. After the electrolysis, a precipitate was formed on the working electrode. This precipitate was dissolved in $CH_3CN$. Then, after evaporation of the solvents of the crude reaction mixture, the residue was dissolved in $CH_3CN$. Both $CH_3CN$ fractions were put together, evaporated, and the resulting residue was dissolved in a large volume of $CH_2Cl_2$/ether (4/1). The precipitate obtained upon cooling of the solution at 0 °C was filtered on a sintered glass no. 4 and thoroughly washed with a $CH_2Cl_2$/ether (4/1) mixture (80% yield of $Zn(OEPy_4P)(PF_6)_4$). In the second step, $Zn(OEPy_4P)(PF_6)_4$ (136 mg, 0.091 mmol) in 1 ml $CH_3CN$ was demetallated by treatment with 2 ml $CF_3SO_3H$ (22.6 mmol, 248 equiv.). After 1 h at 20 °C, the solution was carefully poured on ice. The free base porphyrin slowly precipitated. After filtration the solid was treated by water and $CH_2Cl_2$. The aqueous phase was evaporated, and the resulting residue was dissolved in the minimum quantity of $CH_3OH$ and filtered on a LH20 column to eliminate Zn salts. After evaporation of the solvent, the solid was washed two times with ether and filtered. After drying, the protonated free base $(H_2OEPy_4P)(CF_3SO_3)_4$, $CF_3SO_3H$, was obtained in a 80% yield (106 mg, 0.073 mmol). El. anal. for $C_{60}H_{63}F_{12}N_8O_{12}S_4, CF_3SO_3, 4H_2O$—found: C, 43.85; H, 3.85; N, 6.69; calc.: C, 44.02; H, 4.24; N, 6.73. UV–vis ($CH_3CN$): $\lambda_m$ ($\varepsilon$ in $cm^{-1}\,M^{-1}$) = 368 (50,700) (sh), 423 (73,800) (sh), 459 (93,400), 552 (15,100) and 611 nm (10,300) (sh). $^1H$ NMR (250 MHz, $CD_3CN$): $\delta$ (ppm relative to $Me_4Si$) = 10.52 (d, 8H), 9.42 (t, 4H), 8.8 (dd, 8H), 2.74 (broad s, 8H), 1.63 (broad s, 8H), 0.59 (t, 24H); −0.98 (broad s, 2H, NH). Mass spectrum (electrospray): $m/z$ = 1443.4 $[H_2OEPy_4P(CF_3SO_3)_4 + H]^+$, 1293.4 $[H_2OEPy_4P(CF_3SO_3)_3]^+$, 572.3 $[H_2OEPy_4P(CF_3SO_3)_2]^{2+}$ and 332.3 $[H_2OEPy_4P(CF_3SO_3)]^{3+}$.

The third step was the insertion of manganese into the free base porphyrin. $Mn(OAc)_2$, $4H_2O$ (79 mg, 0.33 mmol) was added to $(H_2OEPy_4P)(CF_3SO_3)_4$, $CF_3SO_3H$ (100 mg, 0.066 mmol) dissolved in 1 ml methanol containing imidazole (8 mg, 0.132 mmol). After 30 min at 30 °C, the solution was evaporated and the residue dissolved in methanol and filtered three times on a LH20 resin column. After evaporation and drying, $Mn(OEPy_4P)$ was obtained in a 75% yield. El. anal. for $Mn(OEPy_4P)(CF_3SO_3)_4$, $8H_2O$, $C_{60}H_{60}F_{12}MnN_8O_{12}S_4$, $8H_2O$—found: C, 43.68; H, 4.02; Mn, 3.33; calc.: C, 43.93; H, 4.67; Mn, 3.35. UV–vis ($H_2O$) $\lambda_m$ = 381, 466 and 580 nm. Mass spectrum (electrospray): $m/z$ = 1346.4 $[Mn(OEPy_4P)(CF_3SO_3)_3]^+$, 598.2 $[Mn(OEPy_4P)(CF_3SO_3)_2]^{2+}$ and 349.6 $[Mn(OEPy_4P)(CF_3SO_3)]^{3+}$.

Table 1
Comparison of the catalytic properties of Mn(OEPy$_4$P)[a] and Mn(T4MPyP)[b] in the oxidation of various compounds by PhIO

| Substrate | Products | Yields (%)[c] | |
|---|---|---|---|
| | | Mn(OEPy$_4$P) | Mn(T4MPyP) |
| Cyclooctene | Epoxide | 90 | 40 |
| Cyclohexene | Epoxide | 66 | – |
| | ene-2-ol | 9 | |
| | ene-2-one | 9 | |
| | Total yield | 93 | |
| *Cis*-stilbene | *Cis*-epoxide | 60 | 55 |
| | *Trans*-epoxide | 5 | 9 |
| | Total yield | 65 | 64 |
| Cyclohexane | ol | 25 | 5 |
| | one | 17 | 1 |
| | Total yield | 59 | 7 |
| Anisole | *o*-Phenol | <1 | <1 |
| | *p*-Phenol | <1 | <1 |
| Naphthalene | α-OH | 23 | <1 |
| | β-OH | 3 | <1 |
| | Total yield | 26 | |
| Ethylbenzene | $PhCHOHCH_3$ | 32 | 11 |
| | $PhCOCH_3$ | 68 | 44 |
| | Phenols | <1 | <1 |

[a] Conditions: Mn-porphyrin:PhIO molar ratio = 20:1 in $CH_2Cl_2/CH_3CN$ (1/1), 2 h at 20 °C; [Mn-porphyrin] = 1 mM in the presence of substrate in excess; substrate/catalyst = 800 for cyclooctene, cyclohexene, and cyclohexane, 1000 for anisole and ethylbenzene, 500 for naphthalene and 200 for *cis*-stilbene.
[b] Identical conditions except that the solvent mixture was $CH_3CN/CH_2Cl_2/CH_3OH$ = 6/3/1.
[c] Yields (%) based on starting PhIO. Yields of cyclohexenone, cyclohexanone, and acetophenone were calculated on the basis that 2 mol of PhIO were consumed for their formation.

### 2.2. Typical procedure for catalytic oxidations

PhIO or $H_2O_2$ (10 μmol) was added to a $CH_2Cl_2/CH_3CN$ (1/1) solution of the manganese catalyst (0.5 μmol) and the substrate in excess (see Tables 1 and 2 for the molar ratio used). The total volume was adjusted to obtain a final 1 mM concentration of the catalyst. After 2 h at room temperature, an internal standard was added and the reaction mixture was analyzed by gas chromatography. Experiments using Mn(T4MPyP) as catalyst were done in $CH_3CN/CH_2Cl_2/CH_3OH$ (6/3/1) in order to completely solubilize the Mn-porphyrin.

### 2.3. Product analysis and identification

UV–vis spectra were recorded on a SAFAS mc2 spectrometer operating at room temperature. $^1$H NMR spectra were recorded on a Bruker WR250 spectrometer, and EPR spectra on a X-band Bruker ESP Elexsys 500 spectrometer equipped with a dual mode cavity fitted with a liquid helium cryostat, at 5 K.

Electrochemical experiments were carried out with an EGG-PAR model 173 potentiostat, controlled by an Apple II computer *via* an EGG-PAR model 276 interface, or with a Tacussel PJT 120-1 potentiostat controlled by a PC computer *via* a Tacussel IMT-1 interface.

Analysis of the reaction mixtures was done by gas chromatography using an Intersmat IGC120 apparatus equipped with a packed 5% FFAP column with FID detection. In the particular case of the catalytic oxidations of *cis*-stilbene, the reaction mixtures were analyzed by $^1$H NMR spectroscopy. Mass spectra were recorded on a Bruker ES/MS Microtof apparatus.

## 3. Results and discussion

### 3.1. Synthesis of Mn(OEPy$_4$P)

It was performed in three steps starting from Zn(OEP) (Fig. 1). The first step that led to $[Zn(OEPy_4P)]^{4+}(PF_6)_4$ was done according to the aforementioned published reaction [8] (Fig. 1). Proper conditions for the demetallation of this Zn complex were found by analogy to those reported for metalloporphyrins bearing electron-withdrawing substituents, that exhibit relatively high redox potentials and whose demetallation is difficult [9]. In the case of $[Zn(OEPy_4P)]^{4+}(PF_6)_4$ the best conditions found involved a treatment by $CF_3SO_3H$ in excess which led to the $CF_3SO_3^-$ salt of $[H_2OEPy_4P]^{4+}$. The last step, metallation by $Mn(OAc)_2$, was easy (30 min at 30 °C), as usually found for porphyrins bearing electron-withdrawing substituents [10]. It led to the triflate salt of the expected manganese porphyrin, $Mn(OEPy_4P)^{4+}(CF_3SO_3)_4$ (Fig. 1), with an overall yield of 50% based on starting Zn(OEP). Actually, as one will see in the following, the Mn-porphyrin prepared from this procedure existed as a Mn(II)/Mn(III) mixture. It will be called Mn(OEPy$_4$P) in

Table 2
Comparison of the catalytic properties of Mn(OEPy$_4$P), Mn(TDCPP)Cl and Mn(TDCPN$_6$P) in the oxidation of aromatic compounds by $H_2O_2$

| Products | Substrate | | | | | | |
|---|---|---|---|---|---|---|---|
| | Anisole | | Naphthalene | | Ethylbenzene | | |
| | *p*-OH | *o*-OH | α-OH | β-OH | $PhCHOHCH_3$ | $PhCOCH_3$ | Phenols |
| Mn(OEPy$_4$P)[a] | 23 | 3 | 18 | 3 | 7 | 47 | <1 |
| Mn(TDCPN$_6$P)[b] | 7 | 1 | 20 | 3 | 7 | 12 | <1 |
| Mn(TDCPP)Cl[b] | 67 | 7 | 62 | 5 | 20 | 22 | <1 |

[a] Conditions: Mn-porphyrin:$H_2O_2$:ammonium acetate ratio = 1:40:20; [Mn-porphyrin] = 1 mM in $CH_2Cl_2/CH_3CN$ (1/1), 2 h at 20 °C in the presence of substrate in excess; substrate/catalyst = 3000, 1500 and 500 for anisole, ethylbenzene and naphthalene, respectively. Yields (%) are based on starting $H_2O_2$. *p*-OH and *o*-OH represent *para*- and *ortho*-hydroxylated products.
[b] Results from Ref. [10] for reactions performed under very similar conditions.

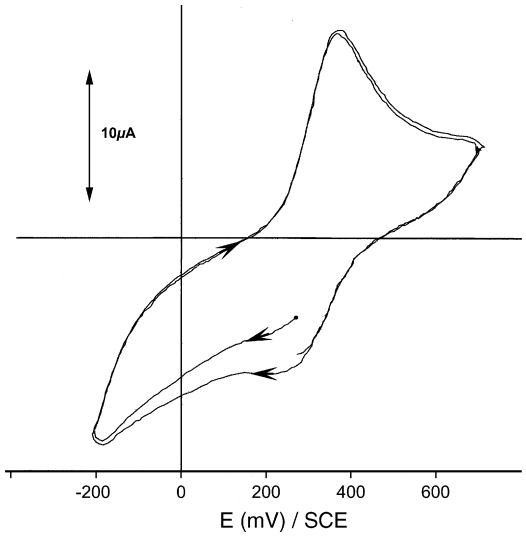



Fig. 2. Cyclic voltammogram of Mn(OEPy$_4$P) obtained by a three-step synthesis from Zn(OEP). [Mn-porphyrin] = 1 mM in $CH_3CN$ containing 0.1 M $Et_4NPF_6$; potentials relative to SCE.

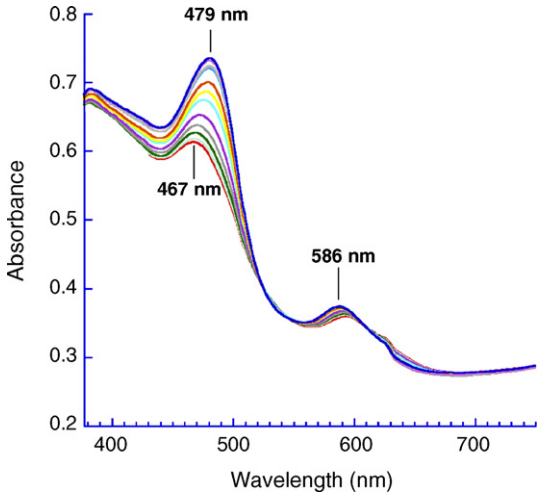



Fig. 3. UV–vis spectroscopy study of the electrochemical oxidation of Mn(II)(OEPy$_4$P) at +550 mV (vs. SCE) in deaerated $CH_3CN$ containing 0.1 M $Et_4NPF_6$ at 20 °C. Mn(II)(OEPy$_4$P) ($10^{-5}$ M) was obtained upon electrochemical reduction of the starting Mn complex at +100 mV; it was the species absorbing at 467 nm. Then, the potential was raised to +550 mV and spectra were recorded every 2 min, leading to the Mn(III) species absorbing at 479 nm.

the following, without mention of the counterions and possible Mn ligands that depend on the medium, except when they are clearly known.

### 3.2. Electrochemical properties of Mn(OEPy$_4$P)

The cyclic voltammogram of Mn(OEPy$_4$P) in $CH_3CN$ is shown in Fig. 2. It indicates a half-wave redox potential for the Mn(III)/Mn(II) couple of +345 mV (versus the saturated calomel electrode = SCE). It also suggests that the Mn-porphyrin complex synthesized by the above-mentioned procedure exists as a 80/20 Mn(II) Mn(III) mixture. The existence of these electron-poor Mn-porphyrins as stable Mn(II) complexes in the presence of $O_2$ is not surprising. A similar behavior has been reported for β-polyhalogenated [11] and β-polynitrated [10] Mn-porphyrins. Moreover, in the Mn[*meso*-tetra-(2,6-dichlorophenyl)-β-polynitroporphyrin] series, the compounds bearing between 1 and 4 β-nitro substituents existed as Mn(III) complexes, whereas those bearing between 6 and 8 β-nitro groups existed as Mn(II) complexes [10]. The Mn-porphyrin bearing 5 β-nitro substituents existed as a Mn(II)/Mn(III) mixture [10], as Mn(OEPy$_4$P).

### 3.3. Spectroscopic properties of Mn(OEPy$_4$P)

The UV–vis spectrum of Mn(II)(OEPy$_4$P) was obtained by spectroelectrochemistry, at +100 mV (versus SCE) under argon, on a $CH_3CN$ solution of the crude Mn(II)/Mn(III) mixture resulting from the three-step synthesis described above. It was characterized by a Soret peak at 467 nm and a band at 586 nm. Upon rising the potential to +550 mV, one observed the one-electron oxidation of Mn(II)(OEPy$_4$P) to Mn(III)(OEPy$_4$P), with isosbestic points at 524 and 608 nm. The Mn(III) complex was characterized by a red-shifted Soret peak at 479 nm (Fig. 3). Lowering the potential to +100 mV resulted in the appearance of the visible spectrum of starting Mn(II)(OEPy$_4$P), which showed that the electrochemical one-electron oxidation of Mn(II)(OEPy$_4$P) and reduction of Mn(III)(OEPy$_4$P) were completely reversible, without irreversible changes of the starting complex.

The mass spectrum (electrospray) of Mn(OEPy$_4$P)$(CF_3SO_3)_4$ showed a peak at $m/z = 1346.4$ for the molecular ion corresponding to $[Mn(OEPy_4P)(CF_3SO_3)_3]^+$ of the starting complex having lost one $CF_3SO_3^-$ counterion. It also showed peaks at $m/z = 598.2$ and 349.6 corresponding to $[Mn(OEPy_4P)(CF_3SO_3)_2]^{2+}$ and $[Mn(OEPy_4P)(CF_3SO_3)]^{3+}$, respectively.

The X-band perpendicular mode EPR spectrum of the Mn-porphyrin resulting from the three-step synthesis from Zn(OEP), either in $CH_3CN$ or in 0.1 M HCl, at 5 K, showed a signal at $g = 1.996$ consisting of six $^{55}Mn$ hyperfine lines ($A = 81.8$ G) (Fig. 4), as expected for a Mn(II) complex. However, such conventional, perpendicular mode EPR studies, that are well-adapted for the observation of half-integer spin systems (e.g. Mn(II)), are less useful for the study of integer spin Mn(III) complexes [12,13]. Therefore, parallel polarization EPR studies were done in the objective to detect the minor Mn(III) component that was present in the Mn-porphyrin resulting from the three-step synthesis from Zn(OEP), as suggested by our electrochemical studies (Fig. 2). The parallel polarization EPR spectrum of this Mn-porphyrin at 5 K showed a six-lines signal at $g = 7.91$ ($A = 45$ G) as expected for a Mn(III) complex [13] (Fig. 4). After treatment of the Mn-porphyrin by Zn amalgam, this signal of the parallel polarization EPR spectrum disappeared, whereas the intensity of the signal at $g = 1.996$ of the perpendicular polarization EPR spectrum, that was assigned to Mn(II)(OEPy$_4$P), slightly increased. Inversely, a treatment of the Mn-porphyrin by strong oxidants, such as PhIO or $PhI(OCOCH_3)_2$, at room temperature, led to the disappearance of the perpendicular polarization EPR signal at $g = 1.996$, and to an increase of the intensity of the parallel polarization EPR signal at $g = 7.91$. These

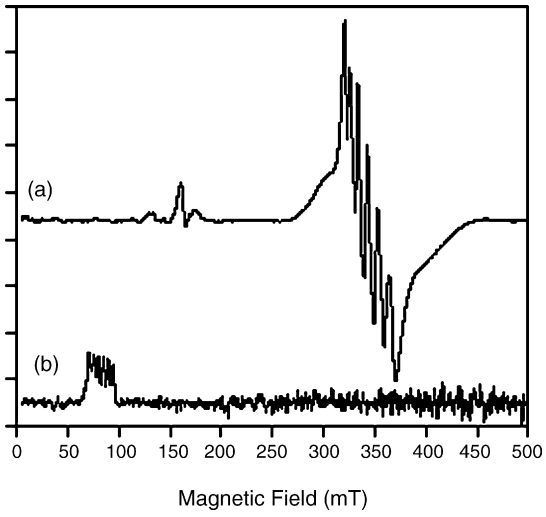



Fig. 4. Perpendicular and parallel polarization EPR spectra of Mn(OEPy$_4$P). 1.1 mM Mn(OEPy$_4$P) in 0.1 M HCl at 5 K. (a) Perpendicular polarization spectrum at 9.628995 GHz; (b) parallel polarization spectrum at 9.279611 GHz (amplitude of spectrum (b) has been multiplied by 10 when compared to that of spectrum (a)). All the EPR parameters were identical: microwave power 20.12 mW, modulation amplitude 6.28 G, and modulation frequency 50 kHz.

EPR data are in complete agreement with the electrochemical data (Fig. 2) suggesting that the Mn-porphyrin prepared from Zn(OEP) exists as a Mn(II)/Mn(III) mixture.

### 3.4. Properties of Mn(OEPy$_4$P) as an oxidation catalyst

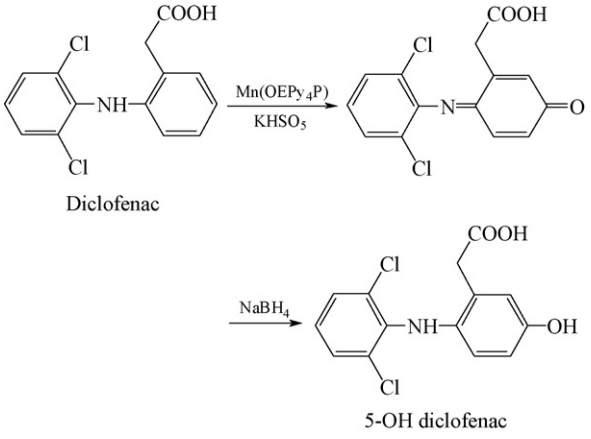
Table 1 compares the properties of Mn(OEPy$_4$P) and Mn(T4MPyP), a similar tetracationic Mn-porphyrin, even though its four positive charges are farther from the porphyrin core, as catalysts for the oxidation of hydrocarbons by PhIO. The former Mn-porphyrin was a relatively good catalyst for the epoxidation of alkenes, with yields, based on starting PhIO, of 90% in the case of cyclooctene, and of 65–66% for *cis*-stilbene and cyclohexene. Yields of cyclooctene epoxidation were much higher than those found with Mn(T4MPyP) (40%), and similar to those previously reported for the usual good epoxidation catalyst Mn(TDCPP)Cl [14]. Oxidation of cyclohexene also led to the products of allylic oxidation, cyclohexen-2-ol and cyclohexen-2-one (9% yield), and the total yield of cyclohexene oxidation was 93%, if one assumes that two moles of PhIO are necessary for cyclohexenone formation. It is noteworthy that the epoxidation of *cis*-stilbene mainly led to the *cis*-epoxide, with a 93/7 *cis*/*trans*-epoxide ratio. The stereoselectivity of the metalloporphyrin-catalyzed epoxidation of *cis*-stilbene has been used as an index of the capacity of the high-valent metal-containing active oxygen species to more or less efficiently control the free radical intermediate derived from addition of the metal-oxo species on the alkene double bond [15,5]. The *cis*/*trans*-epoxide ratio observed for epoxidation of *cis*-stilbene by PhIO catalyzed by Mn(TPP)Cl, Mn(T4MPyP), Mn(TDCPP)Cl and Mn(OEPy$_4$P) were 39/61 [14,16], 85/15 (Table 1), 96/4 [14] and 93/7 (Table 1), respectively. In that regard, Mn(OEPy$_4$P) more resembles Mn(TDCPP)Cl than the Mn-porphyrins that do not bear bulky substituents at the *ortho* and *ortho*′ positions of the *meso*-aryl rings, such as Mn(TPP)Cl and Mn(T4MPyP).

Mn(OEPy$_4$P) also was a much better catalyst than Mn (T4MPyP) for the hydroxylation of alkanes by PhIO. Thus, cyclohexane was oxidized to cyclohexanol and cyclohexanone with a total yield of 59% based on PhIO in the presence of the former catalyst, as compared to 7% in the presence of the latter. Hydroxylation of naphthalene by the Mn(OEPy$_4$P)/PhIO system led to α- and β-naphthols with moderate yields (23 and 3%, respectively). However, Mn(OEPy$_4$P) was also a much better catalyst than Mn(T4MPyP) for the oxidation of this aromatic substrate (Table 1). Finally, oxidation of ethylbenzene by PhIO in the presence of both tetracationic Mn-porphyrin catalysts exclusively led to benzylic oxidation products, 1-phenylethanol and acetophenone, with good yields. The lack of formation of products deriving from an hydroxylation of the aromatic ring of ethylbenzene is not surprising for Mn-porphyrin/PhIO systems, presumably because of the great reactivity of the phenolic metabolites towards PhIO [17–21]. Actually, the best biomimetic catalytic systems for the oxidation of aromatic compounds to phenols are those using $H_2O_2$ as oxygen atom donor and Mn-porphyrins as catalysts in the presence of ammonium acetate as a cocatalyst [10]. Very good results have been reported in that context by using Mn(TDCPP)Cl and some of its β-polynitro derivatives as catalysts [10]. It is why we have compared the hydroxylation of anisole, naphthalene and ethylbenzene by $H_2O_2$ catalyzed either by Mn(OEPy$_4$P) or by the previously described Mn(TDCPP)Cl and Mn[TDCP(NO$_2$)$_6$P] catalysts.

Table 2 shows that Mn(OEPy$_4$P) catalyzed the hydroxylation of the aromatic ring of anisole by $H_2O_2$ with preferential formation of *para*-hydroxy anisole (23% yield based on starting $H_2O_2$), and the hydroxylation of naphthalene with major formation of α-naphthol. The Mn(OEPy$_4$P)-catalyzed hydroxylation of ethylbenzene only occurred at its benzylic position with the major formation of acetophenone. These regioselectivities were very similar to those observed for the corresponding reactions catalyzed by Mn(TDCPP)Cl and Mn(TDCPN$_6$P) (Table 2). With the three Mn-porphyrin catalysts, *para*-hydroxy anisole and α-naphthol were predominent (*para*-/*ortho*-hydroxyanisole ratio between 7 and 9.6; α-/β-naphthol ratio between 6 and 12), and hydroxylation of ethylbenzene exclusively occurred at benzylic position. However, higher hydroxylation yields were observed with Mn(TDCPP)Cl as catalyst, and Mn(OEPy$_4$P) appears to be closer to Mn(TDCPN$_6$P) than to Mn(TDCPP)Cl as a catalyst of hydroxylation of aromatic compounds by $H_2O_2$. In that regard, it is noteworthy that the samples of Mn(OEPy$_4$P) and Mn(TDCPN$_6$P) used for those reactions mainly existed under the Mn(II) state, whereas Mn(TDCPP)Cl is a Mn(III) complex.

Mn(OEPy$_4$P) is a new biomimetic Mn-porphyrin catalyst that exhibits catalytic properties towards hydroxylation of hydrocarbons by PhIO comparable to those of Mn(TDCPP)Cl and much better than those of the other previously described tetracationic Mn-porphyrin Mn(T4MPyP) (Table 1). It also acts as a catalyst for the hydroxylation of aromatic compounds by $H_2O_2$, with a lower efficiency than Mn(TDCPP)Cl. For the latter reactions, it exhibits characteristics similar to those of

β-polynitro–Mn(TDCPP) complexes bearing 5 and 6 nitro substituents [10]. However, when compared to Mn(TDCPP)Cl or its β-polynitro derivatives, $Mn(OEPy_4P)$ has the great advantage to be soluble both in aprotic, relatively hydrophobic solvents such as $CH_2Cl_2$ and $CH_3CN$, and in water at pH > 5. In that regard, preliminary experiments concerning the oxidation of the drug diclofenac by oxone, $KHSO_5$, in water (phosphate buffer pH 6), in the presence of catalytic amounts of $Mn(OEPy_4P)$, showed that this reaction led to the quinone-imine related to 5-hydroxydiclofenac, a classical metabolite of diclofenac in humans [22,23] (Eq. (1)). A 50% yield (based on starting diclofenac) of this product was obtained upon reaction of two oxone equivalent relative to diclofenac under those conditions. Its reduction by ascorbate or $NaBH_4$ quantitatively led to 5-hydroxydiclofenac [22,23]. Further experiments to study the catalytic properties of $Mn(OEPy_4P)$ in various solvents and with various kinds of oxygen atom donors are required before to conclude about its potential interest related to its solubility in very different media and the presence of four positive charges close to the metallic centre.




(1)

## Acknowledgements

The authors thank Dr. P. Leduc (UMR 8601) for his help for the electrochemical part of this study, and Dr. A. Giraudeau, A. Brisach-Wittmeyer and L. Ruhlmann (UMR 7512, Strasbourg) for their important help for the synthesis of $Zn(OEPy_4P)(PF_6)_4$.

## References

[1] B. Meunier, Chem. Rev. 92 (1992) 1411.
[2] D. Mansuy, Coord. Chem. Rev. 125 (1993) 129.
[3] J.R. Lindsay Smith, in: R.A. Sheldon (Ed.), Metalloporphyrins in Catalytic Oxidations, Marcel Dekker, New York, 1994, p. 325.
[4] D. Dolphin, T.G. Taylor, L. Xie, Acc. Chem. Res. 30 (1997) 251.
[5] B. Meunier, A. Robert, G. Pratviel, J. Bernadou, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 4, Academic Press, New York, 2000, p. 119.
[6] J.T. Groves, in: P. Ortiz de Montellano (Ed.), Cytochrome P450: Structure, Mechanism and Biochemistry, Plenum Press, New York, 2005, p. 1.
[7] C.K. Chang, M.S. Kuo, J. Am. Chem. Soc. 101 (1979) 3413.
[8] A. Giraudeau, S. Lobstein, L. Ruhlmann, D. Melamed, K.M. Barkigia, J. Fajer, J. Porphyr. Phthalocyan. 5 (2001) 793.
[9] M. Palacio, V. Mansuy-Mouries, G. Loire, K. Le Barch-Ozette, P. Leduc, K.M. Barkigia, J. Fajer, P. Battioni, D. Mansuy, J. Chem. Soc. Chem. Commun. (2000) 1907.
[10] J.F. Bartoli, V. Mansuy-Mouries, K. Le Barch-Ozette, M. Palacio, P. Battioni, D. Mansuy, J. Chem. Soc. Chem. Commun. (2000) 827.
[11] P. Hoffmann, A. Robert, B. Meunier, Bull. Soc. Chim. Fr. 129 (1992) 85.
[12] K.A. Campbell, E. Yikilmaz, C.V. Grant, W. Gregor, A.-F. Miller, R.D. Britt, J. Am. Chem. Soc. 121 (1999) 4714.
[13] K.A. Campbell, M.R. Lashley, J.K. Wyatt, M.H. Nantz, R.D. Britt, J. Am. Chem. Soc. 123 (2001) 5710.
[14] D. Mansuy, J.F. Bartoli, P. Battioni, D.K. Lyon, R.G. Finke, J. Am. Chem. Soc. 113 (1991) 7222.
[15] P. Battioni, J.P. Renaud, J.F. Bartoli, M. Reina-Artiles, M. Fort, D. Mansuy, J. Am. Chem. Soc. 110 (1988) 8462.
[16] J.T. Groves, W.J. Kruper, R.C. Haushalter, J. Am. Chem. Soc. 102 (1980) 6375.
[17] C.K. Chang, F. Ebina, J. Chem. Soc. Chem. Commun. (1981) 778.
[18] J.R. Lindsay-Smith, P.R. Sleath, J. Chem. Soc. Perkin Trans. 2 (1982) 1009.
[19] S. Tsuchiya, M. Seno, Chem. Lett. (1989) 236.
[20] M.N. Carrier, C. Scheer, P. Gouvine, J.F. Bartoli, P. Battioni, D. Mansuy, Tetrahedron Lett. 31 (1990) 6645.
[21] K. Ikida, M. Nango, K. Okada, S. Matsumoto, M. Matsuura, K. Yamashita, K. Tsuda, Y. Kuruno, Y. Kimura, Chem. Lett. (1994) 1307.
[22] A. Mancy, M. Antignac, C. Minoletti, S. Dijols, V. Mouries, N.T. Ha Duong, P. Battioni, P.M. Dansette, D. Mansuy, Biochemistry 38 (1999) 14264.
[23] S. Othman, V. Mouries-Mansuy, C. Bensoussan, P. Battioni, D. Mansuy, CR Chim./Chem. 3 (2000) 751.