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Journal of Molecular Catalysis A: Chemical 151 (2000) 17–28

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Mn-tetraarylporphyrins bearing *N*-alkyl sulphonamido tails: effect of the length and polarity of the chains on physical properties and reactivity

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Received 22 January 1999; received in revised form 16 April 1999; accepted 19 May 1999

Abstract

Manganese-complexes of a new series of tetraarylporphyrins, featuring both chlorine atoms in *ortho*, *ortho*′ positions and *N*-mono- or *N*,*N*-disubstituted sulphonamido groups in *meta* on the *meso*-phenyls, were used as catalysts in the epoxidation of α-olefines in the presence of diluted (17.5%) H_2O_2 as primary oxidant. The catalytic efficiency of these catalysts is related to the polarity of the chains and the *N*,*N*-dialkylsulphonamido porphyrins turned out to be more reactive than the robust Mn-TDClPP in the epoxidations of styrenes.

Keywords: Hydrogen-peroxide; Mn-tetraarylporphyrins; α-Olefines; Epoxidation

1. Introduction

Since the middle of the eighties, metallo-tetraarylporphyrins have been widely used as catalysts in oxidation reactions in the presence of a primary oxidant (oxygen donor, OD), with the purpose of obtaining a synthetic model of the enzymes of the cytochrome *P*-450 family [1–4]. Under well defined reaction conditions manganese- or iron-porphyrins can perform several hundred turnovers in α-olefin epoxidations or in alkane mono oxygenations and also reach thousand turnovers in the epoxidation of reactive alkenes (i.e., Cyclooctene, Styrenes); often these reactions are over in less than 1 h at room temperature or below [5–7].

By using an excess of oxidant with respect to the substrate, the efficiency of the catalytic system, meant as maximum turnover numbers (TN_{max}), depends on several factors such as the nature of the oxygen donor, the presence of cocatalysts, the structure of both substrate and of the catalyst itself; among these factors the last topic was the most widely studied throughout the last decade. Indeed, the inactivation of the catalyst, ascribed to the demolition of the tetrapyrrole macroring under drastic oxidation conditions, is the side of this catalytic system.

In the attempt to minimize this problem, the electronic and steric characteristics of tetraphen-

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1381-1169/00/$ - see front matter
PII: S1381-1169(99)00239-3

ylporphyrin were largely modified by the introduction of substituents on the catalyst periphery [8–11]. Thus, bulky and/or electronwithdrawing atoms or groups were introduced on the *meso*-phenyl rings and it was found that those placed in the *ortho* positions exerted a beneficial effect on porphyrin stabilities. As a consequence of these studies, in catalytic oxidations, the metallo complexes of the commonly used ''naked'' tetraphenylporphyrin have been replaced with the tetrakis(2,6-dichlorophenyl) porphyrin (**1**). The latter is a catalyst known as particularly robust and easily available, then metallo-complexes of **1** must be considered as reference model. All the newly synthetized porphyrins featuring different structure should be compared with it in order to unambiguously define their efficiency as oxidation catalysts.

More recently, halogens were placed on the β-pyrrole positions, thus producing a new class of porphyrins which was called ''third generation porphyrins'' to differentiate them from those bearing substituents only on the *meso* phenyls; the efficiency of such catalysts is currently under debate because the presence of sterically demanding atoms on the β-positions causes ruffling of the porphyrin plane, hence, both the reactivity and the stability are strongly affected [12–14]. Only in the case of metallo-tetramesitylporphyrin [M-tetrakis(2,4,6-trimethylphenyl-porphyrin)] the β-perchlorinated derivative was found more robust with respect of the not halogenated parent porphyrin, while it was experimentally and theoretically demonstrated that the same effect does not occur when eight chlorine atoms are introduced on β-pyrrole positions of **1** [15–17].

On the other hand, the presence of electron-withdrawing substituents placed in the *meta* or *para* positions of the phenyl rings of catalyst **1** further increases the stability of the macroring as it was found by us in the case of nitro groups [18–20]. Indeed, a few examples concern with the use of nitro substituted tetraarylporphyrins as catalysts; as a matter of fact, NO_2 groups are often introduced on the porphyrin frame mostly to be reduced to the corresponding amino groups which, in turn, are suitable for linkage of lateral chains through amido bond.

More appealing is the introduction of sulphonyl groups which show electronic effect comparable with that one of the NO_2 group and besides allow the linkage of tails without loss of the electronic effect. Furthermore, sulphonamides are fairly more stable than carboxyamides. The major drawbacks in the synthesis of sulphonated porphyrins is given either by the harsh reaction conditions employed for the sulphonation (fuming H_2SO_4) and by the work-up which give sulphonic acid or sulphonate derivatives, both insoluble in organic solvents. Actually sulphonyl substituents have been widely used to allow the solubility of both porphyrins and of phthalocyanines in water [21,22]. The sulphonic acid derivatives can be converted into the corresponding sulphonylchloride by the reaction with PCl_5 at 150°C [23]. Recently, a more convenient synthesis of sulphonylchloride functionalized porphyrins has been reported by Rocha Gonsalves et al.; in this case, the reaction is carried out on tetraarylporphyrins with neat chlorosulphonic acid, the work up directly producing the desired compound [24].

In this work, we report the synthesis of manganese-tetraarylporphyrins featuring one or two side chains linked through one sulphonamido group on each 2,6-dichlorophenyl rings. The catalytic efficiency of these catalysts in alkene epoxidations, with H_2O_2 as oxygen donor, will be discussed in relation to the number, polarity and length of the lateral chains.

2. Results and discussion

The free base 5,10,15,20-tetrakis(2,6-dichloro-3-chlorosulphonyl-phenyl)porphyrin **2** was obtained in 90% yield from H_2-TDClPP **1** with chlorosulphonic acid as reported in literature [24] and recovered as pure brown solid by re-

precipitation from $CHCl_3$/*n*-hexane = 1/5. The sulphonamido porphyrins **3**–**9** were synthetized in a 50–70% yield by heating under reflux **2** with an excess of the desired primary or secondary amine. Porphyrins **3**–**6** and **9** were obtained from **2** using commercially available amines, while the synthesis of compounds **7** and **8** required the preparation of the unprecedented amines **10** and **11**. The synthesis of **10** is reported in Scheme 1.

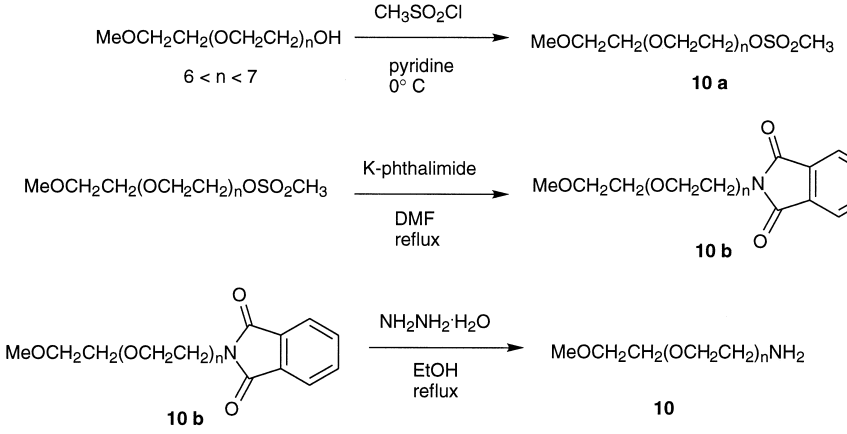
Amine **11** was obtained starting from tetraethylenglycol (TEG), firstly treated with one equivalent of sodium in dioxane and then reacted with an excess of 1-bromododecane; the tetraethylenglycol-monoether (TEG-OC_{12}) was then subjected to the same reaction sequences reported for **10**.

The corresponding manganese(III)-complexes (**Mn-3**–**Mn-9**) were prepared by standard methods refluxing free base porphyrins **3**–**9** in anhydrous DMF in the presence of $Mn(OAc)_2$ (Fig. 1) [25].

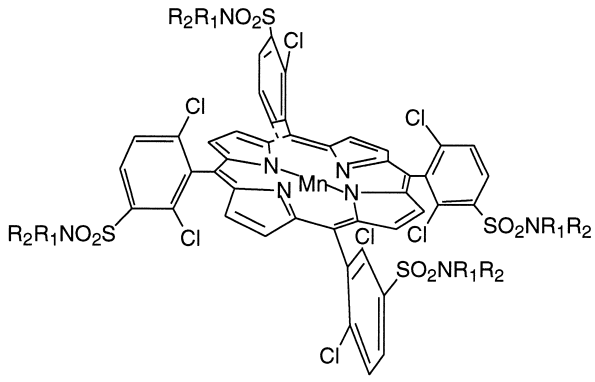
These metallo-complexes were tested in the epoxidations of 1-dodecene and 1-octene (alkene/Mn-porph = 500) carried out under two phase conditions (CH_2Cl_2/H_2O), following the procedure previously reported by us [18,26] at 0°C, in the presence of an excess of 17.5% H_2O_2 with respect to the substrate. *N*-hexylimidazole as axial ligand (L) and sodium benzoate (A) were also added as cocatalysts in few molarequivalent with respect to the catalyst (L/Mn-porph = 5; A/Mn-porph = 10). α-Olefins were chosen to emphasize the efficiency of the catalysts being the epoxidation of such substrates more difficult compared with that of di- or tri-substituted alkenes; furthermore, the epoxidations were carried out also in the presence of the known robust catalyst Mn-TDClPP (**Mn-1**) and its turnover numbers were considered as reference for the evaluation of the catalytic activities.

The results are reported in Tables 1 and 2. The most efficient among the new catalysts was then used in the epoxidation of some alkenes, once more comparing its activity with **Mn-1** (Table 3).

The epoxidations of both 1-octene and 1-dodecene indicate the reactivity of catalysts **Mn-3**–**Mn-9** strongly dependent on the nature of the sulphonylamino group; the *N*-monoalkyl substituted sulphonamido porphyrins are always less reactive than the *N,N*-dialkyl tailed ones featuring the same number of carbon atoms (compare **Mn-3** with **Mn-4** and **Mn-5** with **Mn-6**); among the dialkyl-sulphonamido porphyrins the length of the hydrocarbon chains does not particularly influence the reactivity as evidenced by the comparison between the *N*-dibutyl **Mn-4** and the *N*-dioctyl **Mn-6**, the former



Scheme 1.



Mn-3	R_1 = H; R_2 = nC_8H_{17}	**Mn-TDClSO$_2$NHC$_8$PP**
Mn-4	R_1 = R_2 = nC_4H_9	**Mn-TDClSO$_2$N,NC$_4$PP**
Mn-5	R_1 = H; R_2 = $nC_{16}H_{33}$	**Mn-TDClSO$_2$NHC$_{16}$PP**
Mn-6	R_1 = R_2 = nC_8H_{17}	**Mn-TDClSO$_2$N,NC$_8$PP**
Mn-7	R_1 = H; R_2 = $CH_2CH_2(OCH_2CH_2)_nOCH_3$; $6 < n < 7$	**Mn-TDClSO$_2$NHPEG-OMePP**
Mn-8	R_1 = H; R_2 = $CH_2CH_2(OCH_2CH_2)_nOCH_3$; $n = 3$	**Mn-TDClSO$_2$NHTEG-OC$_{12}$PP**
Mn-9	R_1 = R_2 = nC_2H_5	**Mn-TDClSO$_2$N,NC$_2$PP**

Fig. 1.

being only slightly more reactive than the latter. For the sake of knowledge, we have also synthetized the corresponding *N*-diethyl derivative (**Mn-9**) which, however, showed the same reactivity of **Mn-4** in the epoxidation of 1-dodecene, thus confirming the absence of effects that can be ascribed to the length of the chains. These results are partially in agreement with those reported in 1996 by Rocha Gonsalves et al., which, in the epoxidation of cyclooctene, found a lower reactivity of both mono *N*-alkyl substituted and *N*,*N*-diethylsulphonamidoporphyrins with respect to **Mn-1** [27].

The reactivity of new catalysts dramatically decreases when hydrophilic chains are present on the periphery of the macroring. Conversions are nil in the case of catalyst **Mn-7** which shows highly hydrophilic polyethylenglycol tails and are still very low with catalyst **Mn-8**, which features chains with hydrophilic section in the inner part (tetraethylenglycol moiety) and a lipophilic section due to the linear C12 hydrocarbon unit in the outer part.

These results can be explained considering two factors related to the presence of chains on the periphery of the tetraarylporphyrins: (i) steric

Table 1
Epoxidation of 1-dodecene catalyzed by **Mn-1**, **Mn-3**–**Mn-9**[a]

Catalyst	Time (min)	Conv.%[b]	Turnover numbers[c]	Time (min)	Conv.%[b]	Turnover numbers[c]
Mn-1	30	64	320	60	73	365
Mn-3	30	56	280	60	60	300
Mn-4	30	66	330	60	74	370
Mn-5	30	46	230	60	54	270
Mn-6	30	65	325	60	73	365
Mn-7	30	–	–	60	–	–
Mn-8	30	15	75	60	16	80
Mn-9	30	66	330	60	72	360

[a] In CH_2Cl_2, $T = 0$°C, in the presence of sodium benzoate (A) and *N*-hexylimidazole, as axial ligand (L). Molar ratios: Mn–P:alkene: A:L = 1:500:5:10. Aqueous phase at pH 4.5.
[b] Values obtained by GC analysis with internal standard; selectivity (epoxide/alkene reacted) ≥ 95%.
[c] mmol reacted alkene/mmol Mn–P.

hindrance and (ii) polarity of the reaction medium in the surroundings of the metal centre.

As far as it concerns the first point, from the results obtained with catalysts **Mn-4**, **Mn-6** and **Mn-9** in the epoxidation of 1-dodecene (Table 1), it is easily inferred that the steric hinderance is negligible; indeed not only these catalysts give a comparable TN_{max} but their catalytic activities are very close to that one of the unsubstituted **Mn-1** too. However, the alkyl tails grant to porphyrins **Mn-4** and **Mn-6** an extreme solubility in low polar solvent. Particularly the latter is even soluble in pure hydrocarbons while, generally, metallo-tetraarylporphyrins are partially soluble in chlorinated solvents only.

Catalysts **Mn-7** and **Mn-8** feature chains of comparable length with respect to **Mn-5** (mono N-C16) but with higher polarity, and as said before, they show a limited or nil catalytic activity. These catalysts were synthetized with the aim to facilitate interaction between the oxidant aqueous phase and catalyst active centre through a pseudo reverse micellar system composed by the amphiphilic catalyst, H_2O_2/H_2O and organic layer. The absence of reactivity could be imputed to the excess of hydrophilic moieties of the porphyrins which does not allow the approach of the substrate to the metal centre, probably shielded by the presence of water molecules. **Mn-7** and **Mn-8** are not soluble in water, however it has been reported that free base porphyrins bearing only one polyethyleneglycol tail, although longer than those positioned on catalyst **7**, spontaneously distribute

Table 2
Epoxidation of 1-octene catalyzed by **Mn-1**, **Mn-3**–**Mn-8**[a]

Catalyst	Time (min)	Conv.%[b]	Turnover numbers[c]	Time (min)	Conv.%[b]	Turnover numbers[c]
Mn-1	30	70	350	60	80	400
Mn-3	30	59	295	60	63	315
Mn-4	30	70	350	60	78	390
Mn-5	30	42	210	60	45	225
Mn-6	30	66	330	60	78	390
Mn-7	30	–	–	60	–	–
Mn-8	30	18	90	60	21	105

[a] In CH_2Cl_2, $T = 0$°C, in the presence of sodium benzoate (A) and *N*-hexylimidazole, as axial ligand (L). Molar ratios: Mn–P:alkene: A:L = 1:500:5:10. Aqueous phase at pH 4.5.
[b] Values obtained by GC analysis with internal standard; selectivity (epoxide/alkene reacted) ≥ 95%.
[c] mmol reacted alkene/mmol Mn–P.

Table 3
Epoxidation of styrenes catalyzed by **Mn-1** and **Mn-6**[a]

Catalyst	Time (min)	Styrene conv.%[b] (turnovers)[c]	3-Nitrostyrene conv.%[b] (turnovers)[c]	4-Methystyrene conv.%[b] (turnovers)[c]
Mn-1	5	28 (140)	25 (125)	13 (65)
Mn-6	5	70 (350)	70 (350)	50 (250)
Mn-1	10	61 (305)	46 (230)	30 (150)
Mn-6	10	100 (500)	75 (375)	82 (410)
Mn-1	20	100 (500)	71 (355)	54 (270)
Mn-6	20	–	78 (390)	88 (440)

[a] In CH_2Cl_2, $T = 0$°C, in the presence of sodium benzoate (A) and *N*-hexylimidazole as axial ligand (L). Molar ratios: Mn–P:alkene: A:L = 1:500:5:10. Aqueous phase at pH 4.5.
[b] Values obtained by GC analysis with internal standard; selectivity (epoxide/alkene reacted) $\geq$ 95%.
[c] mmol reacted alkene/mmol Mn–P.

between benzene/water phases after some hours under stirring and the rate depends on the conformation of the PEG chain; it is known that PEG can exhibit two different conformations, one *trans* with non polar character and another *gauche* which is polar, the latter conformer being favoured by low temperature [28]. As confirmation of the low catalytic efficiency of PEG tethered metallotetraarylporphyrins, Monti et al. [29] recently reported few turnovers (up to 10) in the epoxidations of cyclooctene and 1-dodecene carried out in micellar system.

Catalysts **Mn-6** and **Mn-1** were also used in the epoxidations of styrenes; with these alkenes the reactivity of the former porphyrin is by far higher than that one showed by the reference catalyst (Table 3). With **Mn-6** the conversion of styrene, 3-nitro-styrene and 4-methyl-styrene are 100, 75 and 82%, respectively after 10 min, while the epoxidations catalyzed by **Mn-1** reach comparable conversion only at higher reaction times (about 20 min later).

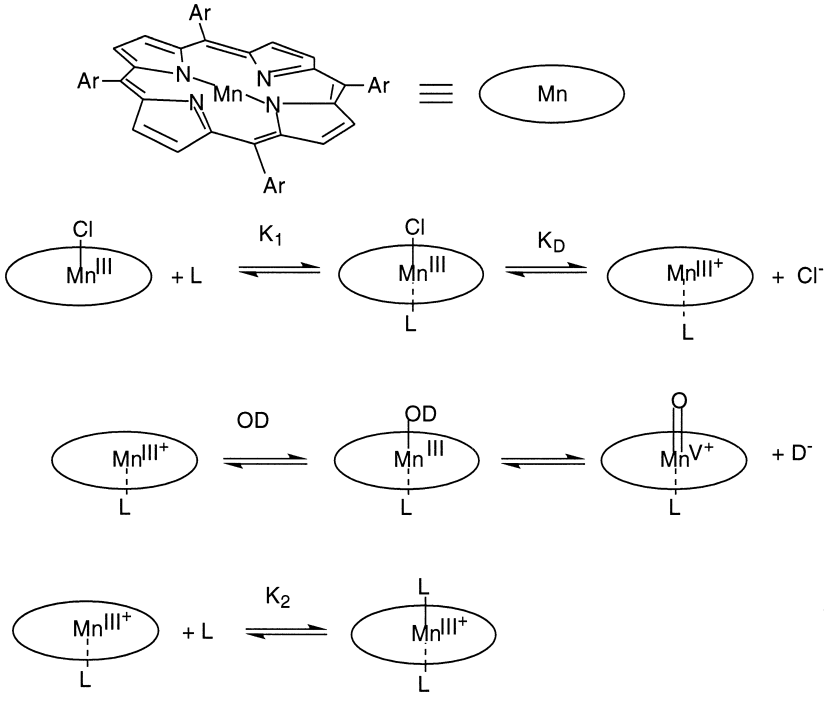
Probably, the eight lipophilic chains provide a microenviromental effect which favours the approach of the double bond to the catalytic centre, similarly to what reported by Groves and Neumann [30] in the case of membrane spanning steroidal metalloporphyrin.

The peculiar solubility of **Mn-4** and **Mn-6** prompted us to carry out the oxidations in the absence of toxic chlorinated solvent, just stirring the catalyst and the alkene with H_2O_2, in the presence of usual cocatalysts. Unfortunately, no conversion was observed even after long reaction time. We believe the absence of reactivity have to be ascribed to the missed formation of the high valent metallo-oxo species (M=O), which is actually the active species.

There are two possible explanations why the metallo-oxo species is not generated in apolar medium: (a) the aqueous oxidant hardly dissolve in the organic phase, then its concentration is too low to give M=O with reasonable rate; (b) the formation of M=O is hampered by the undissociation of the metallo counterion in the low polar medium.

Point (a) was confuted by the addition of a highly lipophilic phase-transfer catalyst (dicyclohexane-18-crown-6, 10 molarequiv. with respect to the porphyrin), thus ensuring the interaction between the aqueous oxidant and the catalyst; nevertheless, no conversion was observed. (Under the standard conditions set up by our group, the polarity of CH_2Cl_2 is adequate to dissolve a sufficient amount of H_2O_2 or HOCl in the organic phase [31,32].) The second important factor which can bias the reaction outcome is the effect of the low polar alkene solution on the porphyrin itself. In the case of manganese(III)-tetraarylporphyrins, the mechanism of the metallo-oxo species formation is known in its fundamental aspects (Scheme 2).

The key step is the coordination of a molecule of heterocyclic nitrogen ligand (L) on the metal atom at the free side of the planar macroring, followed by the dissociation (K_D) of the counter



Scheme 2.

anion, which leaves the metal free to react with the primary oxygen donor (OD). In this last step, the molecule of catalyst changes from uncharged to a zwitterionic form, the positive charge being placed on the metal with the anion free in solution. The zwitterionic form is favoured by solvents with high dielectric constants but is inhibited in apolar solutions.

In order to get experimental evidences on this aspect of the reaction mechanism, we have measured, by means of spectrophotometric titrations in the visible region, the binding constants between **Mn-6** and *N*-hexylimidazole both in CH_2Cl_2 and cyclooctane [10,31,32].

According to the same considerations reported above for the reaction between metalloporphyrin and oxidant, the binding constant of bis-coordination (K_2) of the axial ligand on the metal should be largely decreased in apolar solvent, while the first coordination constant (K_1) is unaffected; indeed, we have found that β_2 value ($\beta_2 = K_2$) obtained in hydrocarbon is two orders of magnitude lower than the one calculated in CH_2Cl_2 (log $\beta_2 = 6.8$ and 4.6, respectively), thus strongly indicating that, in apolar solvent, Mn-porphyrins exist as stable, neutral hexacoordinate complexes in which both axial positions are occupied, one by the counterion and the other by the nitrogen base. In confirmation of the importance of the polarity of reaction medium, we run a set of reactions increasing the alkene/CH_2Cl_2 *V*/*V* ratio from 9/1 up to 1/9; the results indicate a constant increase of reaction rates, the maximum being obtained with the 1/9 ratio. This ratio corresponds to an [alkene] = 0.6 M, which is very close to the standard conditions employed by us in the kinetic investigations.

3. Conclusions

In the epoxidation of α-olefins promoted by 17.5% H_2O_2, among the unprecedently reported manganese-3-sulphonamido-2,6-dichlorophenyl-porphyrins (**Mn-4**–**Mn-9**), the

N,N-dialkyl tailed (**Mn-4**, **Mn-6** and **Mn-9**) showed a catalytic efficiency comparable or higher than that one of the robust Mn-TDClPP (**Mn-1**). The alkyl chains do not interfere with the manganese centre, the main feature of catalysts **Mn-4** and **Mn-6** being an enhanced solubility in pure hydrocarbons; this feature should allow to lead the reactions in the absence of chlorinated solvents. Unfortunately, no reactivity was observed in alkene medium; the explanation of such inertness was found in the ionic pair, made by Mn^{+}(III) atom and its counterion, which cannot dissociate in low polar solvent, thus preventing the coordination of the primary oxidant (OD) on the metal centre. Catalysts featuring polyethyleneglycole chains were found completely unreactive under standard reaction conditions; nevertheless, these amphiphilic catalyst could find application under reverse micellar or microemulsion conditions. Studies on this topic are under investigations.

4. Experimental

4.1. General methods and materials

The alkenes and the other products used in the synthesis were high purity commercial products and were used as received. The CH_2Cl_2 used for the epoxidations was a ''Baker analyzed'' reagent stabilized with amylene. A 17.5% H_2O_2 was obtained diluting portions of 2 ml of 35% H_2O_2 (Fluka) with an equivalent volume of distilled water just before use. ^{1}H NMR were obtained on either Bruker 80 MHz or 300 MHz instruments. MS-FAB spectra were registered on a Finningan MAT90 instrument with 3-nitrobenzyl alcohol as matrix. Analytical LC was carried out on a 5890 Hewlett-Packard instrument, with a flame ionization detector (FID-250°C) and fitted with a 30 m × 0.53 mm RSL-200 column, using the internal standard method to determine alkene conversions and epoxide formations. The injector temperature was kept at 150°C. UV–Vis analyses were performed on a Lambda 6 Perkin-Elmer spectrophotometer.

4.1.1. Synthesis of amines

4.1.1.1. O-(2-Aminoethyl)-O′-methylpolyethylene glycol 350 (aminopolyethylene glycol 350-monomethyl ether) ***10***. Synthesis of *O*-(2-methanesulphonylethyl)-*O′*-methylpolyethylene glycol 350 (Ms-PEG350-OMe) **10a**. To a solution of 10.5 g (0.03 mol) of polyethylene glycol 350-monomethyl ether in 40 ml of anhydrous pyridine, cooled with an ice bath, were slowly added 3.1 ml (4.57 g, 0.04 mol) of freshly distilled methanesulfonylchloride, keeping the temperature below 5°C. After addition, the solution was stirred for 1 h at the same temperature, then the reaction mixture was brought at pH 1.0 carefully adding HCl conc. at a such rate to keep the temperature below 15°C. The acid layer was extracted with CH_2Cl_2 (3 × 30 ml) and the organic phase was washed twice with 20 ml of 10% HCl and then with water to neutral pH, dried with Na_2SO_4 and evaporated. The raw material was purified by column chromatography (silica-gel, $CHCl_3$/EtOH 9/1) to give the methanesulphonyl-derivative in 90% yield (11.5 g, pale yellow oil; $n_D^{20} = 1.459$). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.05$ (3H, s), 3.30 (3H, s), 3.50 (2H, m), 3.60 (22H, br s), 3.70 (2H, m), 4.35 (2H, m).

Synthesis of *O*-(2-phthalimidoethyl)-*O′*-methylpolyethylene glycol 350 (Phth-PEG350-OMe) **10b**. Ms-PEG350-OMe (4.1 g) was treated with potassium-phthalimide (5.5 g, 0.03 mol.) in refluxing DMF for 18 h. The mixture was cooled, filtered on sintered buchner funnel and the solvent evaporated in vacuo. The residue was diluted with CH_2Cl_2 and again filtered to eliminate the unreacted potassium-phthalimide. The organic solvent was then dried over Na_2SO_4 and evaporated; the residue was purified by column chromatography (silica-gel, $CHCl_3$/EtOH 9/1) to give 3.0 g (65% yield) of the phthalimido-derivative as yellow oil; $n_D^{20} =$

1.514. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.35$ (3H, s), 3.50–3.60 (24H, m), 3.70 (2H, t), 3.85 (2H, t), 7.65 (2H, m), 4.82 (2H, m).

Amine **10** was finally obtained refluxing the phthalimido compound (0.92 g, 2 mmol) with an excess of hydrazine hydrate (4 mmol) for 5 h in ethanol. The solvent was then eliminated in vacuo and the residue taken up into CH_2Cl_2 and filtered. The organic solution was washed with diluted HCl and the acid aqueous layer was again brought to basic pH with NaOH and extracted with CH_2Cl_2. The amine was obtained as pure sticky yellow oil (450 mg, 65% yield; $n_D^{25} = 1.457$) after column chromatography (silica-gel, acetone/EtOH 7/3). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.70$ (2H, br s, D_2O exchange) 2.85 (2H, t), 3.35 (3H, s), 3.45–3.55 (4H, m), 3.62 (24H, s).

4.1.1.2. O-(2-Aminoethyl)-O′-dodecyltetraethylene glycol (aminotetraethylene glycol-monododecyl ether) ***11***. Synthesis of tetraethylene glycol monododecyl ether (TEG-OC12): Na (2.3 g, 0.1 mol) was added in portion to 70 ml of tetraethylene glycol (TEG) kept under vigorous stirring, at room temperature and under nitrogen. When sodium was completely consumed, 1-bromododecane (24 ml, 0.1 mol) was added and the reaction mixture heated at 100°C. Stirring was maintained for 24 h then the reaction mixture was cooled, diluted with Et_2O (200 ml) and filtered to eliminate the salts. The organic layer was thoroughly washed with water and dried over $MgSO_4$. After evaporation of the solvent, column chromatography (silica-gel, Et_2O/AcOEt 2/1) afforded 9.0 g (25%) of the TEG-monododecyl ether (TEG-OC12) as clear oil ($n_D^{20} = 1.451$). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.80$ (3H, t) 1.20–1.30 (18H, br s), 1.55 (2H, m), 2.78 (1H, br t, D_2O exchange), 3.40 (2H, t), 3.50–3.70 (16H, m).

This compound undergone the reactions reported above in the case of the PEG350-OMe; thus, in the sequence, it was reacted with CH_3SO_2Cl in pyridine then with potassium phthalimide in DMF and, as last, with hydrazine in EtOH. The characteristics of the intermediates are reported here.

Ms-TEG-OC12: oil, 65% yield after column chromatography (silica-gel, CH_2Cl_2/EtOH 99/1), $n_D^{20} = 1.456$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.80$ (3H, t) 1.20–1.30 (20H, br s), 3.05 (3H, s), 3.43 (2H, t), 3.55–3.80 (14H, m), 4.38 (2H, dd).

Phth-TEG-OC12: yellow oil, 60% yield after column chromatography (silica-gel, $CHCl_3$/EtOH 9/1), $n_D^{20} = 1.497$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.85$ (3H, t) 1.20–1.30 (18H, br s), 1.55 (2H, m), 3.40 (2H, t), 3.50–3.65 (14H, m), 3.70 (2H, t), 3.84 (2H, t), 7.68 (2H, m), 7.82 (2H, m).

Amine **10**: pale orange oil, 65% yield after column chromatography (silica-gel, acetone/EtOH 7/3), $n_D^{20} = 1.453$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.85$ (3H, t) 1.20–1.30 (18H, br s), 1.55 (2H, m), 1.70 (2H, br s, D_2O exchange), 2.85 (2H, t), 3.40 (2H, t), 3.50 (2H, t), 3.53–3.65 (12H, m).

4.1.2. Synthesis of free-base porphyrins

H_2-tetrakis-(2,6-dichlorophenyl)porphyrin **1** was synthetized following literature procedure [33] and H_2-tetrakis-(2,6-dichloro-3-chlorosulphonyl-phenyl)porphyrin **2** was obtained according to the method described by Rocha Gonsalves et al. [24].

4.1.2.1. General method for the synthesis of H_2-tetrakis-(2,6-dichloro-3-sulphonamido-phenyl) porphyrins ***3–9***. Batches of about 100–150 mg (0.078–0.117 mmol) of **2** were refluxed in $CHCl_3$ in the presence of a 5–10 molar-equivalents of the desired amine. The disappearance of starting porphyrin was followed by TLC on silica-gel, and the crude products were purified by column chromatography followed by a crystallization from CH_2Cl_2/hexane. Compound **3–9** were obtained in 50–80% yield and were characterized by ^{1}H NMR, MS-FAB$^+$ and molar extinction coefficient in the visible range.

H_2-tetrakis-(2,6-dichloro-3-*N*-octylsulphonamidophenyl) porphyrin (H_2-TDClSO$_2$-NHC$_8$-

PP) **3**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.53$ (2H, s) 0.85 (12H, t), 1.23–1.32 (40H, m), 1.60 (8H, m), 3.17 (8H, m), 5.00 (4H, m), 7.96 (4H, d), 8.58 (12H, s + d); MS-FAB$^+$: m/z 1654 highest peak of molecular cluster; $C_{76}H_{90}N_8O_8S_4Cl_8$ requires 1650 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 419 (283).

H_2-tetrakis-(2,6-dichloro-3-*N*,*N*-dibutylsulphonamidophenyl) porphyrin (H_2-TDClSO$_2$-N,NC$_4$PP) **4**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.53$ (2H, s) 0.90 (12H, t), 1.20–1.30 (8H, m), 1.45–1.53 (8H, m), 3.35 (8H, m), 5.00 (4H, m), 7.92 (4H, d), 8.52 (12H, s + d); MS-FAB$^+$: m/z 1654 highest peak of molecular cluster; $C_{76}H_{90}N_8O_8S_4Cl_8$ requires 1650 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 419 (285).

H_2-tetrakis-(2,6-dichloro-3-*N*-hexadecylsulphonamidophenyl) porphyrin (H_2-TDClSO$_2$-NHC$_{16}$PP) **5**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.53$ (2H, s) 0.85 (12H, t), 1.23–1.32 (104H, m), 1.60 (8H, m), 3.20 (8H, m), 4.96 (4H, m), 7.96 (4H, d), 8.58 (12H, s + d); MS-FAB$^+$: m/z 2104 highest peak of molecular cluster; $C_{104}H_{154}N_8O_8S_4Cl_8$ requires 2098 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 419 (241).

H_2-tetrakis-(2,6-dichloro-3-*N*,*N*-dioctylsulphonamidophenyl) porphyrin (H_2-TDClSO$_2$-N,NC$_8$PP) **6**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.52$ (2H, s) 0.78–0.92 (24H, m), 1.15–1.40 (80H, m), 1.40–1.65 (16H, m), 3.30–3.40 (16H, m), 7.92 (4H, d), 8.52 (12H, s + d); MS-FAB$^+$: m/z 2104 highest peak of molecular cluster; $C_{104}H_{154}N_8O_8S_4Cl_8$ requires 2098 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 419 (294).

H_2-tetrakis-(2,6-dichloro-3-*N*-polyethyleneglycol-monomethylether-sulphonamidophenyl) porphyrin (H_2-TDClSO$_2$NHPEG-OMePP) **7**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.55$ (2H, s) 3.25–3.72 (124H, m), 6.28 (4H, br t), 7.96 (4H, d), 8.58 (12H, s + d); MS-FAB$^+$: 2495 highest peak of molecular cluster; $C_{104}H_{146}N_8O_{36}S_4Cl_8$ requires 2490 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 419 (296).

H_2-tetrakis-(2,6-dichloro-3-*N*-tetraethyleneglycol-monododecylether-sulphonamidophenyl) porphyrin (H_2-TDClSO$_2$NHTEG-OC$_{12}$PP) **8**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.55$ (2H, s), 0.83 (12H, t), 1.10–1.30 (80H), 1.35–1.53 (8H, m), 3.20–3.50 (64H, m), 6.28 (4H, t), 7.96 (4H, d), 8.58 (12H, s + d); MS-FAB$^+$: 2583 highest peak of molecular cluster; $C_{124}H_{186}N_8O_{24}S_4Cl_8$ requires 2578 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 420 (235).

H_2-tetrakis-(2,6-dichloro-3-*N*,*N*-diethylsulphonamidophenyl) porphyrin (H_2-TDClSO$_2$-N,NC$_2$PP) **9**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.54$ (2H, s) 1.23 (24H, t), 3.48 (16H, m), 7.94 (4H, d), 8.57 (12H, s + d); MS-FAB$^+$: m/z 1430 highest peak of molecular cluster; $C_{60}H_{58}N_8O_8S_4Cl_8$ requires 1426 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 418 (270).

*4.1.3. Synthesis of manganese-complexes of porphyrins **3**–**9***

Metallation of the free base porphyrins was obtained refluxing the substrates in DMF in the presence of a large excess of Mn(OAc)$_2$ [25]. The formation of the complexes was monitored by TLC (silica-gel, CH_2Cl_2/EtOH 9/1) and by UV–Vis spectroscopy. Catalysts **Mn-3**–**Mn-9** were purified by column chromatography up to a single spot and analyzed with MS-FAB$^+$ and spectrophotometrically.

Mn-3: MS-FAB$^+$: m/z 1707 highest peak of molecular cluster; $C_{76}H_{88}N_8O_8S_4Cl_8Mn^+$ requires 1703 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 479 (92).

Mn-4: MS-FAB$^+$: m/z 1707 highest peak of molecular cluster; $C_{76}H_{88}N_8O_8S_4Cl_8Mn^+$ requires 1703 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 478 (115).

Mn-5: MS-FAB$^+$: m/z 2155 highest peak of molecular cluster; $C_{104}H_{152}N_8O_8S_4Cl_8Mn^+$

requires 2151 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 479 (85).

Mn-6: MS-FAB$^+$: *m/z* 2155 highest peak of molecular cluster; $C_{104}H_{152}N_8O_8S_4Cl_8Mn^+$ requires 2151 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 478 (98).

Mn-7: MS-FAB$^+$: 2547 highest peak of molecular cluster; $C_{104}H_{144}N_8O_{36}S_4Cl_8Mn^+$ requires 2543 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 478 (80).

Mn-8: MS-FAB$^+$: 2636 highest peak of molecular cluster; $C_{124}H_{184}N_8O_{24}S_4Cl_8Mn^+$ requires 2631 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 479 (126).

Mn-9: MS-FAB$^+$: MS-FAB$^+$: *m/z* 1483 highest peak of molecular cluster; $C_{60}H_{56}N_8O_8S_4Cl_8Mn$ requires 1479 as lowest isotope molecular mass; UV–Vis (CH_2Cl_2): λ_{max}/nm [ε/(mmol l^{-1})] 478 (118).

*4.1.4. General method for alkene epoxidations with 17.5% H_2O_2 catalyzed by **Mn-1**, **Mn-3**–**Mn-9***

Reactions were carried out in a 10 ml flask equipped with a Teflon-lined screw cap and magnetic stirrer, thermostatted at 0 ± 0.2°C with circulating ethanol by a Haake F3 Cryostat; stirring was maintained at 1300 ± 50 rpm. The flask was charged with the following CH_2Cl_2 solution:

(a) 1 ml of a 10^{-3} M solution of catalyst (Mn–P);

(b) 1 ml of a 0.5 M solution of alkene, containing *ortho*-dichlorobenzene (0.5 M) as internal standard (molar ratio alkene/Mn–P = 500);

(c) 0.1 ml of a 0.1 M solution of *N*-hexylimidazole as axial ligand (L) (molar ratio L/Mn–P = 10).

(d) 0.9 ml of pure solvent to bring the total volume of the organic phase at 3 ml. The reaction concentrations of catalyst, alkene, and axial ligand become 3.3×10^{-4} M, 1.65 $\times 10^{-1}$ M and 3.3×10^{-3} M, respectively.

The solution was stirred for about 5 min, then 0.2 ml of the oxidant were added (molar ratio alkene/oxidant = 2.3). The pH of the H_2O_2 aqueous phase was previously adjusted to 4.5 adding 8 mg of sodium benzoate (A) to 2 ml of 17.5% H_2O_2 (molar ratio A/Mn–P = 5).

The mixture was stirred and samples of 0.1 ml were taken at different time and analysed by G.C. Before injecting the organic phase in the G.C. column, the samples were diluted with 0.4 ml of CH_2Cl_2, washed with distilled water and dried with Na_2SO_4.

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