Tailed Mn^{III}-tetraarylporphyrins Bearing an Axial Ligand and/or a Carboxylic Group: Self-consistent Catalysts for H_2O_2 or NaOCl Alkene Epoxidation

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Mn^{III}-tetraarylporphyrins bearing either a heterocyclic nitrogen base axial ligand or a carboxylic acid group, or both, covalently bonded to the porphyrin through a single flexible chain, have been synthesized. Their basic frame is that of the robust tetrakis(2,6-dichlorophenyl)porphyrin, and the chains are connected by ether or amido linkages to the *ortho*-positions of one *meso*-aryl group. Catalytic efficiency was tested in alkene epoxidations at 0 °C under aqueous CH_2Cl_2 two-phase conditions in the presence of NaOCl (pH 10.5) or 30% H_2O_2 (pH 4.5) as oxygen donors (ODs). Compound **4** bearing an imidazole ligand showed satisfactory catalytic activity in the presence of both ODs, whereas Mn^{III}-porphyrins **5a–d** bearing a covalently bonded carboxylate group are suitable for the activation of H_2O_2, and proved to be very efficient in the presence of an externally added axial ligand. Catalyst **6**, featuring an imidazole ligand and a carboxylate group bonded on the 2,6-positions of the same *meso*-aryl group, is particularly efficient in alkene epoxidations promoted by 30% H_2O_2 (initial rates up to 500 turnovers/min, overall turnovers up to 1200). A possible reaction mechanism for epoxidation catalysed by the bis-tailed Mn^{III}-porphyrins is discussed.

Metal complexes of synthetic tetraarylporphyrins, M(P), especially those of Fe^{III} and Mn^{III}, are efficient models of cytochrome *P*-450 monooxygenase enzymes in the presence of a single oxygen-atom donor (OD).[1]

Of the ODs tested, NaOCl and dilute H_2O_2 are particularly interesting.[1l,n] Both are cheap and clean oxidants, suitable for large-scale applications. The presence of a pyridine or imidazole nitrogen base (L) increases the rate and selectivity of the reactions promoted by these ODs. The base co-ordinates the metal of M(P) on the axial positions according to equilibria (1) and (2).

$$M(P) + L \overset{K_1}{\rightleftharpoons} M(P)L \quad (1)$$

$$M(PL) + L \overset{K_2}{\rightleftharpoons} M(P)L_2 \quad (2)$$

$$\beta_2 = K_1 \cdot K_2 \quad (3)$$

The mono-ligated M(P)L, where one of the axial co-ordination sites of the metal is free, easily forms an adduct with the oxygen donor, thus affording the high-valent metallo-oxo species that is the effective oxidizing species in the catalytic cycle. The non-ligated M(P) and the bis-ligated $M(P)L_2$ are catalytically less active and inactive, respectively.[1l,n]

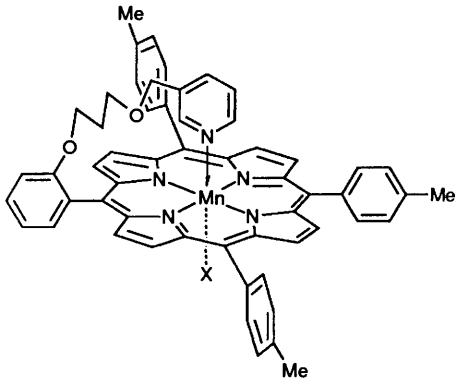
We previously found that in oxygenations carried out under aqueous/organic two-phase conditions the efficiency of the reaction strongly depends on the lipophilicity of the axial ligand, and is very high when the ligand is completely partitioned in the organic phase.[1l,n] With 30% H_2O_2 the reaction rates are strongly increased by adjusting the pH to 4.5–5.0 and adding catalytic amounts of a lipophilic carboxylic acid.[2] In the case of NaOCl, adjusting the pH of the aqueous phase within the range 9.5–10.5 leads to the formation of HOCl (pK_a 7.54) partitioned between the two phases. This allows very high reaction rates, even in the absence of a phase-transfer catalyst.[3]

In the natural cytochrome *P*-450 a thiolate residue of a cysteine is the axial ligand,[1b] whereas this role is played by the imidazole of a histidine residue in other haem proteins such as haemoglobin,[4] myoglobin,[4] and cytochrome *c* peroxidase.[5] A number of sophisticated models capable of closely reproducing the proximal effect of the natural enzymes have been obtained by covalently linking the axial ligand onto the porphyrin ring.[6,7] These synthetic models were generally used for an understanding of the catalytic cycle of cytochrome *P*-450; in only a few cases were they tested as oxygenation catalysts for synthetic purposes.[8]

Metallo-porphyrins to be used as oxygenation catalysts should have a very high catalytic efficiency together with high chemical stability. However, these features are difficult to combine in structured porphyrins whose catalytic activity depends on the preorganization degree of the system. In an effort to solve this problem we chose a model in which the axial ligand is covalently bonded to the porphyrin ring through only one flexible chain. In fact, the high binding constants between pyridines or imidazoles and Mn^{III}-porphyrins should be further increased in the intramolecular co-ordination because of a lower loss of conformational and rotational entropy of the ligand, which gives rise to a lower free energy of co-ordination.[7d] We have already reported that complexes **1** and **2** proved to be efficient catalysts in NaOCl-promoted alkene epoxidations, but they were completely bleached after 200 overall turnovers. The weak spot was the absence of sterically hindering or electron-withdrawing groups which increase the chemical stability of the porphyrin structure.[3a]

The main object of the present report is the design and synthesis of new structured Mn^{III}-porphyrins specific for the activation of either 30% H_2O_2 or NaOCl.

In designing these models the following points have been considered: (i) the porphyrin skeleton must be as similar as possible to that of the robust tetrakis(2,6-dichlorophenyl)-porphyrin **3**; (ii) the chemical bond between the flexible chain and one of the *meso* phenyl groups must be stable under oxidative conditions; (iii) in the case of the catalysts planned for H_2O_2-promoted reactions two different flexible chains connect the porphyrin with an axial ligand and a carboxyl group; links in positions 2 and 6 of the same phenyl ring ensure that, along



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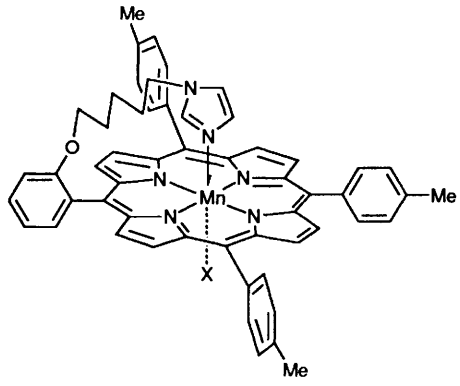

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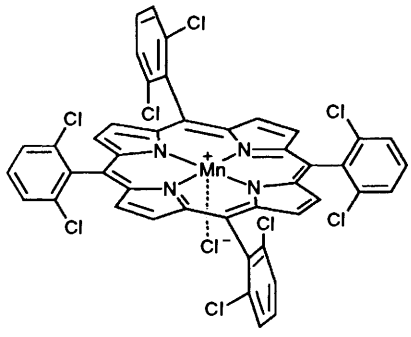

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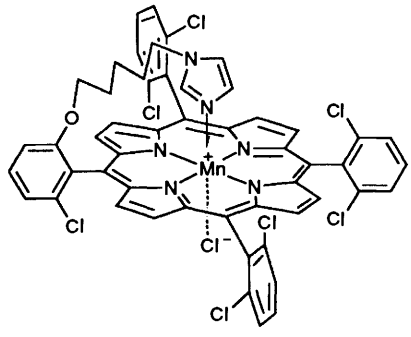

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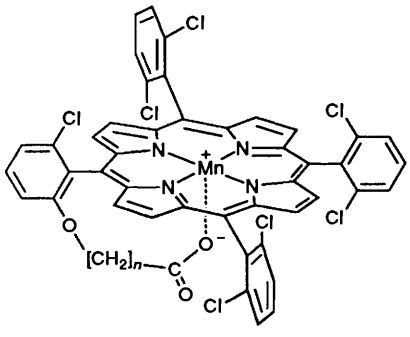
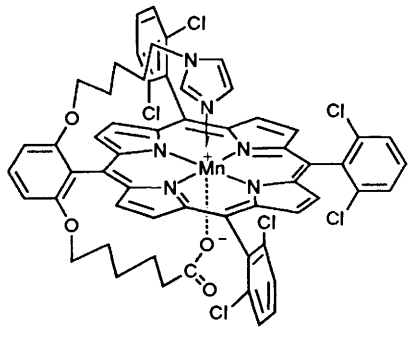


5a; n = 1
b; n = 3
c; n = 5
d; n = 7



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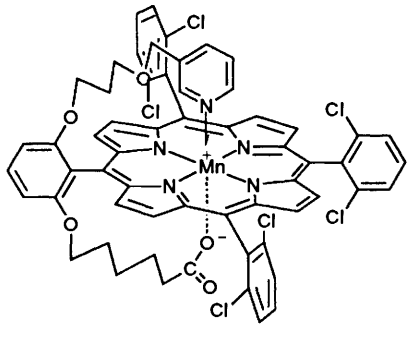

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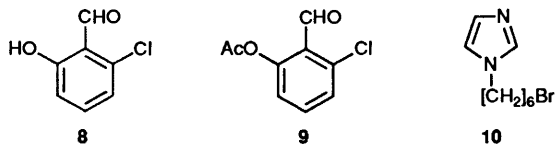
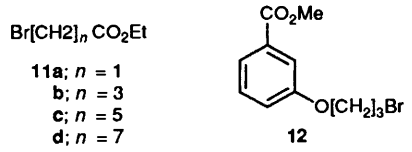
with improved synthetic simplicity, the axial ligand and the carboxyl group are juxtaposed on opposite sites of the porphyrin ring plane.[9] Among the catalysts reported, Mn^{III}-porphyrins **4**, **5b–d**, **6** and **7** turned out to be particularly efficient in alkene epoxidations promoted by 30% H_2O_2; some led to the highest overall turnover numbers reported up to now for H_2O_2 oxygenations mediated by metallo-porphyrins. Catalyst **4** could also be efficiently used for NaOCl-promoted epoxidations.

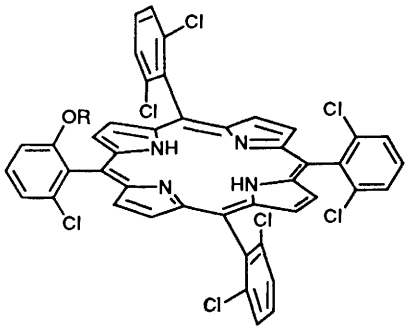


8 **9** **10**



11a; *n* = 1
b; *n* = 3
c; *n* = 5
d; *n* = 7

12

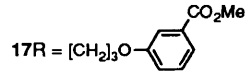


13 R = H

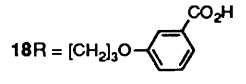
14R = $[CH_2]_6$-N

15a–d R = $[CH_2]_nCO_2Et$ (*n* = 1, 3, 5, 7)

16a–d Mn^{III} complexes of **15a–d**

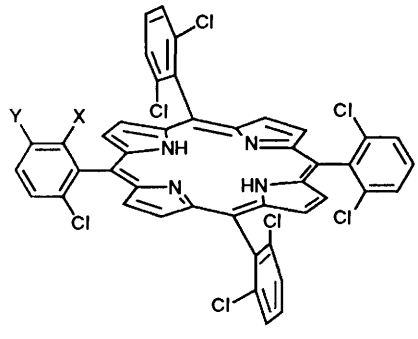


17R = $[CH_2]_3O$-



18R = $[CH_2]_3O$-

19 Mn^{III} complex of **18** (internal salt)
20 R = $[CH_2]_5Me$
21 Mn^{III} complex of **20**



22 X = NH_2, Y = H
23 X = $NHCO[CH_2]_2CO_2Me$, Y = H
24 X = $NHCO[CH_2]_2CO_2H$, Y = H
25 Mn^{III} complex of **24** (internal salt)
26 X = Cl, Y = NH_2
27 X = Cl, Y = $NHCO[CH_2]_8CO_2Et$
28 X = Cl, Y = $NHCO[CH_2]_8CO_2H$
29 Mn^{III} complex of **28** (internal salt)

Results

Synthesis of Mn^{III}*-Porphyrins bearing Ether-bonded Flexible Chains.*—Mono-tailed Mn^{III}-porphyrins **4**, **5a–d**, **19** and **21** were prepared from monohydroxy porphyrin **13**, which was synthesized in 14.7% yield by condensation of 2-acetoxy-6-chlorobenzaldehyde **9** with 2,6-dichlorobenzaldehyde and pyrrole (molar proportions 1 : 3 : 4, respectively), carried out in CH_2Cl_2 at room temperature, under the general synthetic conditions described by Lindsey.[10] The direct use of 2-chloro-6-hydroxybenzaldehyde **8**, instead of the corresponding hydroxy-protected aldehyde, for the preparation of compound **13** failed.

O-Alkylation of compound **13** with *N*-(6-bromohexyl)imidazole **10** carried out in dimethylformamide (DMF) with Cs_2CO_3 as base gave compound **14** (46%), which was converted into the Mn^{III}-complex **4** (88%) following reported procedures.[11]

O-Alkylation of compound **13** with a series of ω-bromo ethyl esters **11a–d** in DMF and solid Cs_2CO_3 at room temperature afforded porphyrins **15a–d** in almost quantitative yield. Complexation of compounds **15a–d** with $Mn(OAc)_2{\cdot}4H_2O$ and alkaline hydrolysis of the resulting complexes **16a–d** afforded Mn^{III}-porphyrins **5a–d** (70–99% yield) as internal salts, in spite of previous anion exchange of AcO^- for Cl^-. An identical protocol, starting from compound **13** and ethyl 3-(3-bromopropoxy)benzoate **12**, afforded the porphyrin **18**, which was converted into Mn^{III} complex **19** (internal salt) in 35% overall yield.

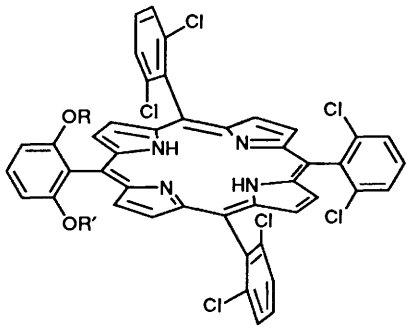
Catalyst **6**, bearing both the imidazole and the carboxyl group, was prepared as follows: condensation of 2,6-dimethoxybenzaldehyde, 2,6-dichlorobenzaldehyde and pyrrole, under the conditions described for compound **13**, afforded compound **30** in 9% yield after column chromatography. Demethylation of compound **30** with BBr_3 in CH_2Cl_2 (quantitative yield) and condensation of the resulting diol **31** with a stoichiometric amount of ethyl 6-bromohexanoate **10c** afforded the mono-*O*-alkylated porphyrin **32** in 20–25% yield, the remainder being mainly the starting product **31** and bis-*O*-alkylated porphyrin **33** (5–10%). Steps from compound **32** to and the target molecule **6**, which proceed in 45% overall yield *via* the porphyrin ester **34** and its Mn^{III} complex **35**, were carried out as described for the imidazole-tailed porphyrin **4**; similarly prepared were Mn^{III} complexes **37** and **7** in which a pyridine is the axial ligand (62 and 64% overall yield from **32**, respectively).

Synthesis of Mn^{III}*-Porphyrins bearing Amido-bonded Flexible Chains.*—Condensation of 5-(2-amino-6-chlorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin **22**[12] with commercial methyl 3-(chloroformyl)propanoate, carried out in CH_2Cl_2 and Et_3N as base, afforded ester **23** in 57% yield. Alkaline hydrolysis of ester **23**, and complexation of the resulting acid **24** with $Mn(OAc)_2{\cdot}4H_2O$, afforded the Mn^{III} complex **25** (internal salt) in 53% overall yield.

Starting from 5-(3-amino-2,6-dichlorophenyl)-10,15,20-tris-(2,6-dichlorophenyl)porphyrin **26**[12] and ethyl 9-(chloroformyl)nonanoate, and following an analogous series of reactions as described above, the Mn^{III} complex **29** (internal salt) was obtained in 24% overall yield.

Key steps in the preparation of compounds **25** and **29** are the alkaline hydrolyses **23** ⟶ **24** and **27** ⟶ **28** which must be carried out at room temperature in order to minimize the concomitant hydrolysis of the amido bridge. Nevertheless, the yield of reaction **27** ⟶ **28** is low (57%), the main side-product being the starting aminoporphyrin **26**.

Catalytic Efficiency of Mn^{III}*-Porphyrins bearing a Covalently Bonded Axial Ligand.*—Catalytic activity of complex **4** was tested in olefin epoxidations in the presence of an excess of either NaOCl or 30% H_2O_2 as oxygen donor and using cyclooctene



30 R = R′ = Me
31 R = R′ = H
32 R = H, R′ = $[CH_2]_5CO_2Et$
33 R = R′ = $[CH_2]_5CO_2Et$

34 R = $[CH_2]_6$–N⟨imidazole⟩
R′ = $[CH_2]_5CO_2Et$
35 Mn^{III} complex of **34**

36 R = CH_2–⟨pyridine⟩
R′ = $[CH_2]_5CO_2Et$

37 R = CH_2–⟨pyridine⟩
R′ = $[CH_2]_5CO_2^-$
Mn^{III} complex (internal salt)

38 R = $[CH_2]_3OCH_2$–⟨pyridine⟩
R′ = $[CH_2]_5CO_2Et$

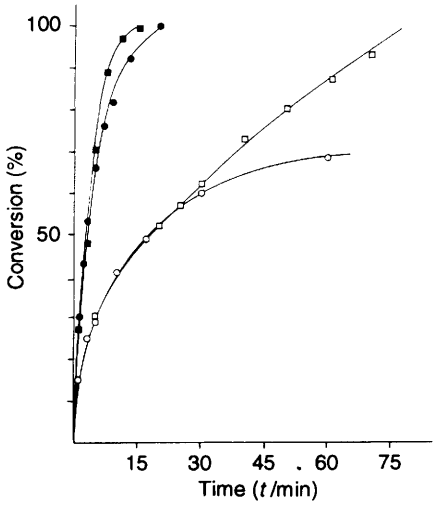


Fig. 1 Cyclooctene (full symbols) and dodec-1-ene (empty symbols) epoxidations promoted by NaOCl (OD) at pH 10.5 and 0 °C, catalysed by Mn^{III}-porphyrins (P) **4** (■, □) and **3** (●, ○), in the presence, for **3**, of *N*-hexylimidazole (L), with molar proportions P:L:alkene:OD 1:0–1:200:600

and dodec-1-ene as models of highly reactive and poorly reactive alkenes, respectively. Reactions were carried out under aq. CH_2Cl_2 two-phase conditions at 0 °C. The pH of the aqueous phase was adjusted at 10.5, with solid $NaHCO_3$ in the case of NaOCl,[3] and at 4.5–5.0 with sodium benzoate (A) in the

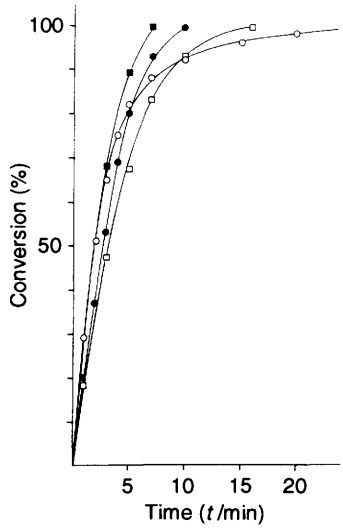


Fig. 2 Cyclooctene (full symbols) and dodec-1-ene (empty symbols) epoxidations promoted by 30% H_2O_2 (OD) at pH 4.5 and 0 °C, catalysed by Mn^{III}-porphyrins (P) **4** (■, □) and **3** (●, ○), in the presence of sodium benzoate (A) and, for **3** of *N*-hexylimidazole (L), with molar proportions P:L:A:alkene:OD 1:0–1:4:200:400

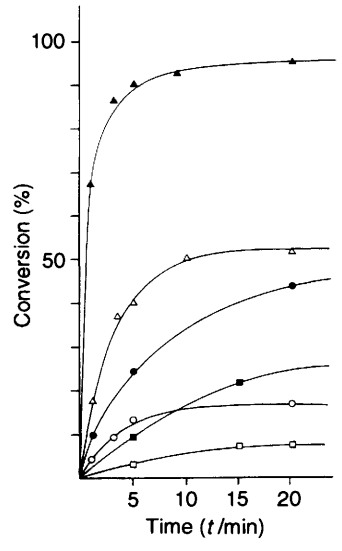


Fig. 3 Cyclooctene (full symbols) and dodec-1-ene (empty symbols) epoxidations promoted by 30% H_2O_2 (OD) at pH 4.5 and 0 °C, catalysed by Mn^{III}-porphyrins (P) **19** (■, □), **25** (●, ○) and **29** (▲, △), in the presence of *N*-hexylimidazole (L), with molar proportions P:L:alkene:OD 1:1:200:400

case of 30% H_2O_2.[2] The optimum molar ratios with respect to the metalloporphyrin (P) are A:P = 1 and 4 for cyclooctene and dodec-1-ene, respectively. Results with NaOCl are reported in Fig. 1; those referring to 30% H_2O_2 are reported in Fig. 2.

With both oxygen donors and under the same reaction conditions, the catalytic efficiency of complex **4** is comparable with that obtained with complex **3** in the presence of an equimolecular amount of *N*-hexylimidazole (L). Molar ratio L:P = 1 gives the highest initial rates in the range of concentration of complex **3** to which kinetic measurements are referred throughout this report.[3b] For this reason L:P = 1 is the ratio of choice for any comparison between complex **3** and a tailed porphyrin.

As shown in Figs. 1 and 2, with substrate (S): porphyrin, S:P = 200 molar ratio, and complex **4**, as catalyst, reactions are generally completed in 7–15 min. In the presence of NaOCl

Table 1 Alkene epoxidations promoted by 30% H_2O_2 catalysed by Mn^{III}-porphyrin **4**[a]

Alkene	Alkene (S)/ porphyrin (P)	Conversion (%)	Selectivity[b] (%)	Time (t/min)
Cyclooctene	1000	100	100	36
Dodec-1-ene	500	97	97	300
α-Methylstyrene	1000	89	100	120
p-Chlorostyrene	500	98	100	10
(*E*)-β-Methylstyrene	200	95	89	90
β,β-Dimethylstyrene	200	100	89	40
(*E*)-Oct-4-ene	500	98	78	130
α-Pinene	500	95	92[c]	80
Camphene	500	92	84[d]	90

[a] In CH_2Cl_2/30% H_2O_2 (OD), pH 4.5, 0 °C, in the presence of sodium benzoate (A), molar quotients: A/P 4, OD/S 2. [b] (Epoxide/converted alkene) × 100. [c] 3:1 Mixture of diastereoisomers. [d] 4:1 Mixture of diastereoisomers.

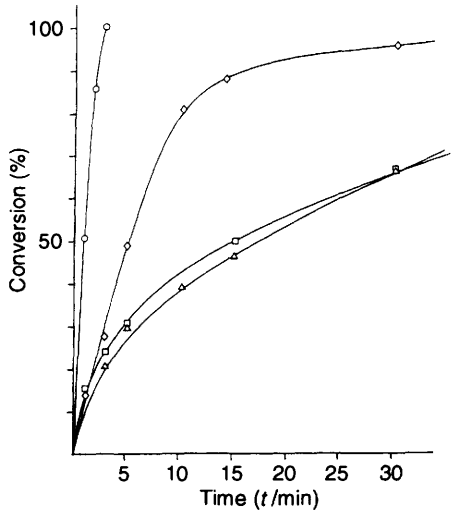


Fig. 4 Cyclooctene epoxidations promoted by 30% H_2O_2 (OD) at pH 4.5 and 0 °C, and catalysed by Mn^{III}-porphyrins (P) **6** (○), **3** (□), **4** (△) and **5c** (◇). Molar proportions P:cyclooctene:OD 1:1000:2000. For **3**, **4** and **5c**, *N*-hexylimidazole (L) and/or sodium benzoate (A) were also present with molar proportions **3**:L:A 1:1:1, **4**:A 1:1, **5c**:L 1:1, respectively.

and 30% H_2O_2, the reaction rates (calculated at 50% conversion) were 40 and 50 turnovers/min for cyclooctene and 6 and 33 turnovers/min for dodec-1-ene, respectively. With NaOCl, complete conversion of dodec-1-ene requires 75 min. However, the same reaction catalysed by complex **3** and an added axial ligand (L:P 1) stops at 70% conversion after the same time. The epoxidation of a series of alkenes has been carried out with catalyst **4**, using 30% H_2O_2 and A:P = 4, with very high conversions and selectivities and up to 1000 overall turnovers (Table 1).

Catalytic Efficiency of Mn^{III}*-Porphyrins bearing a Covalently Bonded Carboxyl Group.*—Mono-tailed Mn^{III}-porphyrins **5a–d**, **19**, **25** and **29**, designed for the activation of dil. H_2O_2, have been tested under the reaction conditions previously described,[2] in the presence of equimolecular amounts of *N*-hexylimidazole (L:P 1) in the absence of added carboxylic acid (A) (Figs. 3 and 4). A comparison with complex **3** (A:P 1, L:P 1) showed that catalysts **5b–d** have similar catalytic efficiency at low substrate:catalyst ratio (S:P 200), whereas at higher ratios they exhibit a noticeably greater efficiency, at least with electron-rich olefins. As an example, in the epoxidation of cyclooctene (S:P 1000) reaction rates (calculated at 50% conversion) were 98 and 28 turnovers/min for **5c** and for **3**, respectively (Fig. 4).

Table 2 Influence of the length of the spacer chain in alkene epoxidations catalysed by Mn^{III}-porphyrins **5a–d**[a]

Porphyrin (P)	Conversion (%) Cyclooctene[b]	Dodec-1-ene[c]
5a	22	23
5b	96	63
5c	84	66
5d	91	46

[a] In CH_2Cl_2/30% H_2O_2 (OD), pH 4.5, 0 °C, in the presence of *N*-hexylimidazole (L), molar proportions P:L:alkene:OD 1:1:200:400. [b] Conversion at 5 min; only slightly higher values were observed at 10 min. [c] Conversion at 15 min; almost the same values at 30 min.

The influence of the length of the spacer chain on the catalytic efficiency of complexes **5a–d** in the epoxidations of cyclooctene and dodec-1-ene is shown in Table 2. For cyclooctene there is no significant difference between complexes **5b–d** whereas **5d** is slightly less reactive in the case of dodec-1-ene; complex **5a**, bearing only one methylene unit, is a very poor catalyst, probably due to the lack of interaction of the carboxyl group with the H_2O_2–metal adduct (see Discussion section, below).

In addition, complexes **19** and **25** are poor catalysts, the first probably for the steric hindrance introduced by the carboxylated phenyl group, the latter due to the presence of the amido bond in the *ortho* position of a *meso*-aryl group, which is unstable under the reaction conditions and undergoes hydrolysis assisted by the metal.[13] Indeed, complex **29** is more efficient than complex **25**, since the relatively higher stability of the connecting *meta*-amido bond compensates for the more difficult interaction of the carboxyl group with the H_2O_2–metal adduct.

Catalytic Efficiency of Mn^{III}*-Porphyrins bearing both a Covalently Bonded Axial Ligand and a Carboxyl Group.*—Bis-tailed Mn^{III}-porphyrin **6** having the imidazole and the carboxylate group juxtaposed on opposite sides with respect to the plane of the aromatic macro-ring, and spaced from the connecting ether bridge by 6 and 5 methylene units, respectively, proved to be an extremely efficient catalyst for cyclooctene epoxidation with 30% H_2O_2 as oxygen donor, without requiring additional axial ligand and/or carboxylic acid as co-catalysts. In fact, in the presence of compound **6** and with molar proportions P:S:H_2O_2 of 1:1000:2000, cyclooctene was epoxidized in 3 min, with 100% conversion and selectivity, with an initial rate of 500 turnovers/min in the first min as shown in Fig. 4. The reaction rate of complex **6** is by far the fastest in comparison with those obtained with catalysts **3**, **4** and **5c**

Table 3 Alkene epoxidations promoted by 30% H_2O_2 catalysed by Mn^{III}-porphyrin **6**[a]

Alkene	Alkene (S)/ porphyrin (P)	Conversion (%)	Selectivity[b] (%)	Time (*t*/min)
α-Methylstyrene	1000	96	95	15
	500	100	100	8
p-Chlorostyrene	1000	75	100	35
	500	100	100	5
α-Pinene	1000	78	88[c]	30
	500	85	87	20
Camphene	1000	69	66[d]	60
	500	83	71	30
Dodec-1-ene	500	66	96	15

[a] In CH_2Cl_2/30% H_2O_2 (OD), pH 4.5, OD/S 2. [b] (Epoxide/converted alkene) × 100. [c] 3:1 Mixture of diastereoisomers. [d] 4:1 Mixture of diastereoisomers.

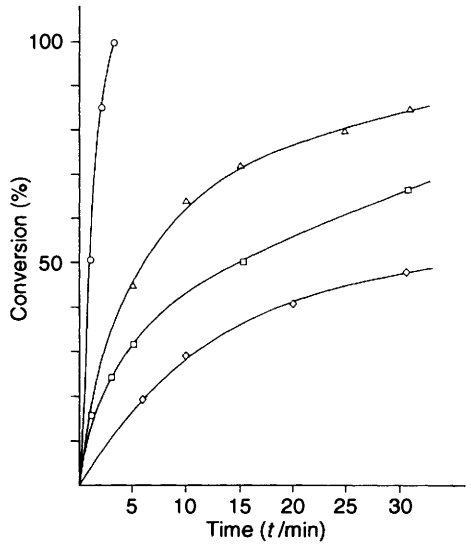


Fig. 5 Cyclooctene epoxidations promoted by 30% H_2O_2 (OD) at pH 4.5 and 0 °C, catalysed by Mn^{III}-porphyrins **3** (□), **6** (○), **37** (◇) and **7** (△), with molar proportions P:alkene:OD 1:1000:2000. For **3**, *N*-hexylimidazole (L) and sodium benzoate (A) were also present with molar proportions **3**: L:A 1:1:1.

under the same conditions and in the presence of equimolecular amounts, with respect to the Mn^{III}-porphyrins, of L and A for **3**, of A for **4**, and of L for **5c**.

With catalyst **6** α-methylstyrene, *p*-chlorostyrene, α-pinene and camphene were similarly oxidized with initial rates at 1 min of 200–270 turnovers/min and 700–1000 overall turnover numbers (Table 3). In the epoxidation of dodec-1-ene the reactions stopped after 330 turnovers, but the initial rate was still very high (170 turnovers/min). With cyclooctene, catalyst **6** afforded up to 1200 overall turnovers. The UV–VIS spectrum of the catalyst was, at the end of the reaction, substantially unchanged, probably indicating that the porphyrin ring is not involved in deactivation of the catalyst. This same behaviour has been observed with Mn^{III}-porphyrins **3**, **4** and **5a–d**. Our feeling is that the main deactivation path is due to the oxidative decomposition of the axial ligand either covalently bonded or externally added (see Discussion section, below).

The bis-tailed complex **7**, in which a covalently bonded pyridine is the axial ligand, has also shown catalytic efficiency, increased with respect to that found with complex **3** but lowered in comparison with that of complex **6**. This is in agreement with our and other observations that imidazole is a better axial ligand than is pyridine for unfunctionalized Mn^{III}-porphyrins.[2,3,14] Finally, catalyst **37**, in which the spacing chain bearing the axial ligand is too short to allow co-ordination with the metal, showed low catalytic efficiency (Fig. 5).

Discussion

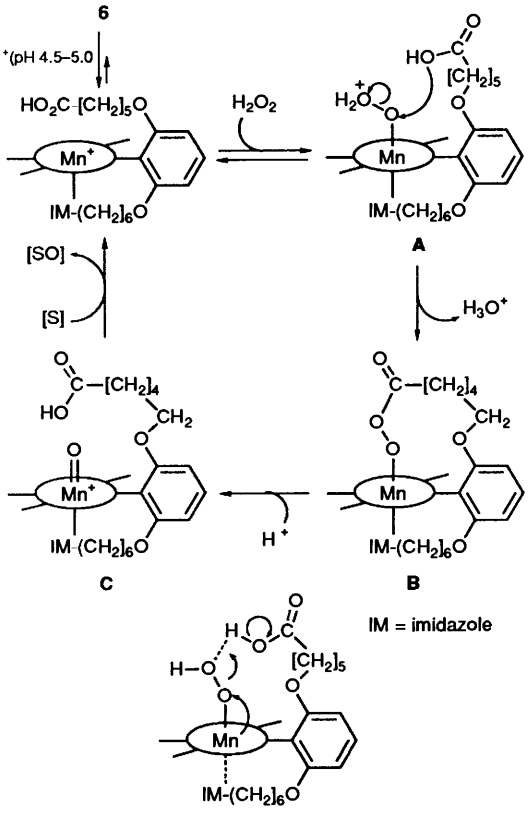
As reported above, Mn^{III}-porphyrin **4** is a 'self consistent' catalyst for alkene epoxidations in which NaOCl is the oxygen donor, nor does it require the addition of an external axial ligand. In contrast to the previously reported catalysts **1** and **2**, in complex **4**, the axial ligand is covalently bonded to a porphyrin ring which is itself intrinsically stable towards oxidative degradation. Indeed, complex **4** can also be used to catalyse epoxidations in the presence of 30% H_2O_2 which, as already demonstrated,[2,14] can be performed only with highly robust porphyrins. In a previous approach we introduced an amido bond as the connecting linkage, because of its synthetic accessibility. However, only modest catalytic activities could be achieved, due to the fast degradation of this linkage by the metal.[12,13] A similar behaviour was also observed with catalysts **25** and **29** bearing a covalently bonded carboxylate group, prepared in an early stage of this investigation.

Activation of dil. hydrogen peroxide by the chemically robust Mn^{III}-porphyrin **3** requires the presence of externally added lipophilic heterocyclic base and lipophilic carboxylic acid.[2] In the absence of the latter, reactions still occur; however, they are slower and either a huge amount of base (up to 60% with respect to the substrate), or a large excess of substrate with respect to the oxygen donor is needed.[14] With complex **3** and the co-catalytic species under CH_2Cl_2–water two-phase conditions at 0 °C, alkene epoxidations were achieved with initial rates up to 125 turnovers/min and up to 800 overall turnover numbers.[2c]

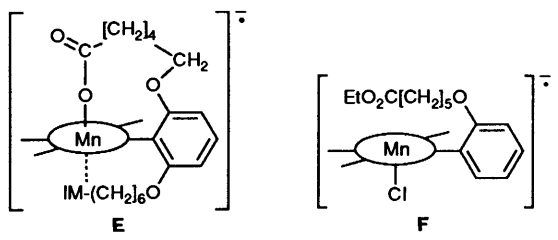
It must be pointed out that hydrogen peroxide is slightly soluble in CH_2Cl_2. With CH_2Cl_2:30% H_2O_2 6:1 (v/v), as in the reaction conditions, we found 8.5 mmol dm^{-3} H_2O_2 in CH_2Cl_2 at 0 °C. This amount is 6.8 times that of the Mn^{III}-porphyrin used (1.25 mmol dm^{-3}).

The combination of these experimental observations and synthetic improvements resulted in the self-consistent model compounds **6** and **7**: compound **6** proved to be a particularly efficient catalyst, specific for alkene oxygenations in the presence of dil. H_2O_2 under the same mild conditions described above, affording up to 1200 overall turnovers in few minutes at 0 °C, at initial rates up to 500 turnovers/min.

The mechanism that we tentatively propose for the H_2O_2-promoted oxygenations catalysed by the doubly tailed Mn^{III}-porphyrins **6** and **7** is reported in Scheme 1, and is derived from the mechanism proposed for the oxygenations catalysed by complex **3** with externally added axial ligands and carboxylic acids.[2] The co-catalytic effect of the carboxylic group can be explained through the formation of an acylperoxy-Mn^{III} intermediate (**B**) in which the heterolytic cleavage of the O–O bond, affording the high-valent metallo-oxo species (**C**),



Scheme 1



responsible for oxygen transfer to the substrate, is favoured by the good leaving ability of the carboxylate.*

The alternative possibility that the acylperoxy intermediate **B** is the active species in this catalytic cycle was excluded since: (i) under these conditions only the *Z*-isomer of stilbene was easily oxidized, while the *E*-isomer was not, a typical behaviour of porphyrin-catalysed oxygenation reactions; (ii) with complex **3** and the two externally added co-catalytic species, the Bayer–Villiger rearrangement did not take place. Furthermore, optically active carboxylic acids, such as (+)-camphoric acid or (+)-camphorcarboxylic acid, behave as good co-catalysts, but the epoxides obtained starting from prochiral alkenes were racemic.[2c] The same alkenes, epoxidized by the corresponding optically active peroxy acids, afforded optically active products.[17]

According to the same mechanism, the covalently bonded axial ligand in the doubly tailed Mn^{III}-porphyrins **6** *and* **7** displays only the 'push' effect,[18] namely, its co-ordination increases the electronic density of the metal, thus stabilizing the high-valent Mn-oxo porphyrin **C**. Owing to the action of the carboxylate group, the addition of an extra amount of free heterocyclic base, usually requested to assist heterolytic O–O bond cleavage *via* general acid/base catalysis ('pull' effect),[8b,14] is no longer necessary.

The proposal for the role played by the two functionalized tails is further supported by the following observations: (i) fast-atom bombardment mass spectrometry operating in negative ion mode (MS–FAB$^-$) showed that catalysts **5b–d** and **6** are in the form of carboxylate internal salts **E**, whereas in the ethyl ester of **5c** (**F**) Cl^- is present as a counter-ion to the metal cation.† (ii) co-ordination constants K_1 and β_2 [defined in equation (3)] of *N*-hexylimidazole to Mn^{III}-porphyrin **21** in a homogeneous CH_2Cl_2 solution (10^{-5} mol dm^{-3}) have been calculated by using a non-linear computer-fitting of data obtained from UV–VIS spectrophotometric titrations at 477 nm, following equation (4), according to a procedure previously followed for the porphyrin **3**.[11,2c,20] The titration of complex **21** afforded $K_1 = 2.02 \times 10^3$ dm^3 mol^{-1} and $\beta_2 = 4.55 \times 10^6$ dm^6 mol^{-2}, values comparable with those found for complex **3**.

$$A = [P]_0\left(\frac{\varepsilon_0 + \varepsilon_1 K_1[L] + \varepsilon_2\beta_2[L]^2}{1 + K_1[L] + \beta_2[L]^2}\right) \quad (4)$$

A = absorbance; $[P]_0$ = initial concentration of the Mn-porphyrin; [L] = axial ligand concentration at equilibrium, *i.e.* $[L] = [L]_0 - [Mn(P)L] - 2[Mn(P)L_2]$; ε_0, ε_1, ε_2 = molar absorptivities of non-ligated, mono- and bis-ligated porphyrins, respectively.

However, it turned out to be impossible to apply the same procedure to complex **4**, due to the presence of two bands at 477 and 485 nm (the second one attributable to the intramolecular co-ordination of the ligand), whose relative intensities remained unchanged over a wide concentration range (0.2×10^{-5}–4.0×10^{-5} mol dm^{-3}), thus excluding the presence of aggregates, formed by intermolecular co-ordination. Since the absorbance coalesced in one band at high added ligand concentrations, a comparison between species **4** and **21** was made in the final part of the titration, when the change of absorbance as a function of the ligand concentration flattens. It was observed for complex **21** that the bis-ligated species $M(P)L_2$ represented 86 and 91% when, respectively, 320 and 500 molar equivalents of ligand, with respect to the porphyrin, were added (Fig. 6). In this range of added ligand the variation of absorbance was $\Delta A = 0.0079$. For complex **4** this same variation occurred in the range 120–500 molar equivalents of ligand. Assuming that the concentration of the bis-ligated species of complex **4** was 86% in the presence of 120 molar equivalents of *N*-hexylimidazole, the estimated value of β_2 for complex **4** is 2.95×10^7 dm^6 mol^{-2}, which is almost 6 times that of the Mn^{III}-porphyrin **21**. We can then conclude that the proximity effect imposed by the covalent linking of the axial ligand increases the binding capability by at least 6 times.

Within the same catalytic cycle reported in Scheme 1, other possibilities cannot be, *a priori*, ruled out, *e.g.* a proton-transfer mechanism which assists the heterolysis of the O–O bond as

* The formation of acylperoxy-metalloporphyrins is well documented. Indeed, in the adduct between dioxygen and Fe^{II}- or Mn^{II}-porphyrins, acylation of distal oxygen favours the heterolytic cleavage of the O–O bond, affording a high-valent Mn-oxo porphyrin.[15] These same acylperoxy derivatives are obtained by reaction of metallo-porphyrins with peroxy acids or with alkyl hydroperoxides.[7l,16]

A referee suggested that path **A** ⟶ **B** in the catalytic cycle seems to be unlikely to occur at a rate sufficient to explain the turnover rate of the catalyst under the mild conditions employed. This reaction would be favoured by strong acids as in the reaction between carboxylic acids and H_2O_2. In the referee's opinion path **A** ⟶ **D** (see later) is more consistent with the obtained results. However, up to now we have no compelling evidence supporting either of the two possible intermediates.

† A detailed investigation of MS–FAB$^-$ characterization of Mn^{III}-tailed porphyrins will be reported elsewhere.[19]

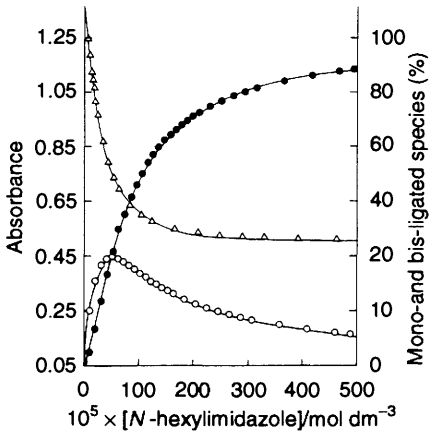


Fig. 6 UV–VIS spectrophotometric titration of a 1×10^{-5} mol dm^{-3} CH_2Cl_2 solution of Mn^{III}-porphyrin **21** with *N*-hexylimidazole. Absorbance at 478 nm (△); Mn(P)L % (○); $Mn(P)L_2$ % (●).

indicated in formula **D**. This alternative mechanism recalls the role played by the imidazole as base[14] promoting the heterolytic cleavage of the O–O bond of metallo-porphyrin/H_2O_2 adduct.

A last comment concerns the catalase activity of metallo-porphyrin complexes.[21] As shown by Momenteau and Meunier[22] it depends on the natures of the metal and axial ligand: the association of a Mn^{III}-porphyrin and a nitrogen base as axial ligand is the most effective in performing hydrogen peroxide dismutation, but at the same time it also shows the highest monooxygenase activity. The competition between these two kinds of catalytic activity does not affect hydrocarbon oxygenations performed with the models described in the present report, in fact we never observed a significant loss of H_2O_2 due to its dismutation catalysed by tailed Mn^{III}-porphyrins, as well as by complex **3**.*

Conclusions

A major challenge for the realization of efficient synthetic models of cytochrome *P*-450 based on metallo-porphyrins is the control of the interactions between the metal and the co-catalytic species. We developed a series of models in which the problem is faced by linking the co-catalytic species to the porphyrin structure through a flexible chain. These models were tested in oxygenation reactions promoted by 30% H_2O_2 or NaOCl, which are the more convenient among the possible ODs although they require high chemical stability of the catalyst.

A first improvement, with respect to similar models that we previously synthesized, was the introduction of structural features, affording robustness to the catalyst (choice of ether linkage instead of the easier accessible amido bond and protection of the porphyrin structure by chlorine atoms in the *ortho*-positions of the *meso*-aryl group).

Catalyst **4**, bearing an imidazole moiety covalently linked, afforded results comparable to those found with the chemically stable Mn^{III}-porphyrin **3** employed in the presence of *N*-hexylimidazole; in the same way, catalysts bearing a carboxylic acid group, which are specific for 30% H_2O_2 activation, afforded results comparable to those found with complex **3** in the presence of benzoic acid. Under particular conditions (*e.g.*, high substrate:catalyst molar ratio, poorly reactive substrate) mono-tailed catalysts afforded slightly better results than did complex **3**.

It is worthwhile noting that the lack of protection even in only one of the *ortho*-positions significantly decreases the stability of catalyst **3**,[24] so that the better interactions between the metal and the co-catalytic species in mono-tailed Mn^{III}-porphyrins can be deemed responsible for filling the stability gap due to the substitution of one of the chlorine atoms in the structure of complex **3** with ether-linked chains.

A more impressive demonstration of this statement is that doubly tailed Mn^{III}-porphyrins **6** and **7** are more efficient catalysts than complex **3** in 30% H_2O_2-promoted alkene epoxidation. In these self-consistent models of cytochrome *P*-450 the unfavourable absence of two chlorine atoms is overcome by the synergistic effect of the increased co-ordinative ability of the axial ligand and of the proximity of the carboxylic acid group to the metal centre.

Mn^{III}-porphyrin **6** allows rates of up to 500 turnovers/min at 0 °C with 30% H_2O_2 as OD, while the natural cytochrome *P*-450 performs oxygenations with O_2 affording 1–100 turnovers/min at room temperature.[16,25] However, complex **6** is deactivated after 700–1200 overall turnovers, accomplished in a very short time: this is a major drawback not only for this model, but also for all those metallo-porphyrins, including **3**, claimed to be 'robust' when used with 30% H_2O_2 as OD. In fact, in comparison with those obtained with complex **6**, only lower reaction rates and a few tens of overall turnovers are reported in the literature.[14,26]

A last comment we would like to make concerns the chemical stability of the axial ligand under oxidative conditions. Destruction of the axial ligand, covalently bonded or externally added, could be responsible for the end of the catalytic activity of the studied Mn^{III}-porphyrins that occurs even when, as indicated by UV–VIS spectroscopy, the porphyrin skeleton seems to be unaffected. The use of an excess of axial ligand simply slows down the reaction rate by increasing at equilibrium the concentration of the di-co-ordinated species $M(P)L_2$, whereas the ligand is rapidly oxidized together with the substrate.[3b] The addition of further ligand at the end of the reaction is ineffective, the catalyst being apparently poisoned by the destroyed ligand *via* an unknown mechanism.

Experimental

^1H NMR spectra were recorded on Bruker WP80SY and Varian XL300 spectrometers, with $CDCl_3$ as solvent. UV–VIS spectra were obtained with a Varian Cary 219 spectrophotometer. GC analyses were performed on a Varian Model 3700 gas chromatograph flame ionization instrument (20 × 0.125 in, OV-101-5% on CHP 100-125 mesh column). Light petroleum refers to the fraction boiling in the range 40–60 °C.

The pH of aqueous solution was measured using an Orion pH meter model SH 250 with a PH electrode model 91-03 (semi-micro glass body).

2-Chloro-6-hydroxybenzaldehyde **8**.—A suspension of 2-chloro-6-fluorobenzaldehyde (10 g, 63 mmol) in aq. 0.3 mol dm^{-3} NaOH (700 cm^3) was magnetically stirred at 75 °C for 40 h. The mixture was cooled at room temperature and extracted with Et_2O (2 × 150 cm^3) in order to separate the unchanged substrate. The aqueous phase was acidified with conc. HCl and extracted with Et_2O (2 × 150 cm^3). The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. The product was purified by column chromatography (silica gel;

* Alkene epoxidations catalysed by Mn^{III}-tetraphenylporphyrin and *N*-methylimidazole as axial ligand, promoted by H_2O_2 prepared *in situ* by electrochemical reduction of dioxygen in CH_2Cl_2 in the presence of benzoic acid, have been reported.[23] The authors have suggested that benzoic acid acts as both proton source and, somehow, as co-catalyst, by increasing the reaction rate and/or the stability of oxo-porphyrin/olefin adducts. Although no explanation was given we would like to stress that there is a relevant agreement with our previous results.[2]

Et_2O–light petroleum, 50:50) to afford compound **8** (3.97 g, 40%), as a white solid, m.p. 52 °C (lit.,[27] 51.5–52.0 °C; δ_H(80 MHz) 6.70–7.60 (3 H, m), 10.40 (1 H, s) and 11.90 (1 H, s, D_2O exchange).

2-Acetoxy-6-chlorobenzaldehyde **9**.—A solution of acetyl chloride (0.75 cm^3, 10.5 mmol) in $CHCl_3$ (10 cm^3) was slowly added to a stirred solution of 2-chloro-6-hydroxybenzaldehyde **8** (1.56 g, 10 mmol) and Et_3N (1.11 g, 11 mmol) in $CHCl_3$ (30 cm^3) cooled at 0 °C. During the addition, which took 30 min, the temperature was maintained at 0–5 °C. The reaction mixture was stirred at 0–5 °C for 1 h and, upon addition of water (20 cm^3), the organic phase was separated, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; CH_2Cl_2) to afford compound **9** (1.19 g, 60%) as a thick, yellow oil (Found: C, 54.2; H, 3.4. $C_9H_7ClO_3$ requires C, 54.42; H, 3.52%); δ_H(80 MHz) 2.30 (3 H, s), 6.90–7.60 (3 H, m) and 10.40 (1 H, s). This product undergoes hydrolysis during chromatography on silica gel and this is responsible for the low yield.

5-(2-Chloro-6-hydroxyphenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin **13**.—A solution of 2,6-dichlorobenzaldehyde (2.62 g, 15 mmol), 2-acetoxy-6-chlorobenzaldehyde **9** (1.0 g, 5 mmol), pyrrole (1.34 g, 20 mmol) and BF_3·Et_2O (1.87 g, 13.2 mmol) in CH_2Cl_2 (freshly distilled over P_2O_5; 2000 cm^3) was stirred at room temperature for 15 h. After addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (3.68 g, 16 mmol), the reaction mixture was stirred for a further 2 h, then Et_3N (1 cm^3) was added and the solvent was evaporated off. The residue was supported on Florisil (80 g) and purified by column chromatography (neutral alumina). Elution with light petroleum–CH_2Cl_2 (50:50) gave 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (540 mg); then with 10% MeOH–CH_2Cl_2 as eluent, crude porphyrin **13** (700 mg) was obtained. Column chromatography (silica gel; light petroleum–Et_2O, 50:50) of this crude product yielded pure compound **13** (640 mg, 14.7%) as a bright blue powder; δ_H(300 MHz) −2.55 (2 H, br s, D_2O exchange), 4.80 (1 H, br s, D_2O exchange), 7.20–7.83 (12 H, m) and 8.64–8.63 (8 H, m); MS–FAB$^+$, *m/z* cluster 872 (100%) ($C_{44}H_{23}Cl_7N_4O$ requires M, 871.8).

5-{2-Chloro-6-[6-(imidazol-1-yl)hexyloxy]phenyl}-10,15,20-tris(2,6-dichlorophenyl)porphyrin **14**.—A suspension of the porphyrin **13** (200 mg, 0.23 mmol), *N*-(6-bromohexyl)imidazole dihydrochloride **7** (304 mg, 1 mmol), and Cs_2CO_3 (1.3 g, 4 mmol) in dry DMF (15 cm^3) was stirred at room temperature for 72 h. The solvent was evaporated off under reduced pressure and the residue was taken up with CH_2Cl_2 (200 cm^3) and washed with water (150 cm^3). The organic phase was dried over $MgSO_4$ and then evaporated. Column chromatography of the residue (silica gel; CH_2Cl_2–MeOH, 90:10) afforded the product (278 mg), which was dissolved in CH_2Cl_2 (10 cm^3) and reprecipitated by addition of pentane. This procedure was repeated twice to afford pure compound **14** (187 mg, 80%); MS–FAB$^+$, *m/z* 1019, lowest mass peak of isotope cluster ($C_{53}H_{37}Cl_7N_6O$ requires M, 1022.0).

5-{2-Chloro-6-[6-(imidazol-1-yl)hexyloxy]phenyl}-10,15,20-tris(2,6-dichlorophenyl)porphyrin Mn^{III} *Chloride Complex* **4**.—A solution of the porphyrin **14** (130 mg, 0.127 mmol) in DMF (50 cm^3) was stirred at reflux with $Mn(OAc)_2$·$4H_2O$ (200 mg, 0.816 mmol) for 6 h. After evaporation of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 (150 cm^3) and washed with water (2 × 50 cm^3). Column chromatography (silica gel; $CHCl_3$–MeOH, 90:10) of the residue afforded a dark green powder (130 mg). This product was dissolved in CH_2Cl_2 (100 cm^3) and the solution was stirred for 30 min at room temperature with saturated aq. NaCl (50 cm^3), dried over $MgSO_4$, and evaporated to afford pure complex **4** (125 mg, 88%); $\lambda_{max}(CH_2Cl_2)$/nm 384 (ε/dm^3 mol^{-1} cm^{-1} 52 400), 486 (71 500) and 575 (11 400); MS–FAB$^+$, *m/z* 1071, lowest mass peak of isotope cluster ($C_{53}H_{35}Cl_7MnN_6O$ requires M, 1075.0).

5-{2-Chloro-6-[(ethoxycarbonyl)methoxy]phenyl}-10,15,20-tris(2,6-dichlorophenyl)porphyrin **15a**.—A suspension of the porphyrin **13** (150 mg, 0.172 mmol), ethyl 2-bromoacetate **11a** (302 mg, 1.72 mmol) and solid Cs_2CO_3 (561 mg, 1.72 mmol) in DMF (10 cm^3) was stirred at room temperature for 26 h. Evaporation of the solvent and column chromatography (silica gel; CH_2Cl_2–light petroleum, 50:50) afforded *ester* **15a** as a purple powder (156 mg, 95%); δ_H(300 MHz) −2.55 (2 H, br s, D_2O exchange), 0.85 (3 H, t), 3.70 (2 H, q), 4.10 (2 H, s), 7.10–7.90 (12 H, m) and 8.60–8.90 (8 H, m); MS–FAB$^+$, *m/z* cluster 958 (100%) ($C_{48}H_{29}Cl_7N_4O_3$ requires M, 957.9).

5-{2-Chloro-6-[3-(ethoxycarbonyl)propoxy]phenyl}-10,15,20-tris(2,6-dichlorophenyl)porphyrin **15b**.—The *compound* was obtained in 98% yield from substrate **13** and ethyl 4-bromobutanoate as reported for **15a**; δ_H(300 MHz) −2.50 (2 H, br s, D_2O exchange), 0.85 (3 H, t), 1.10–1.40 (4 H, m), 3.70 (2 H, q), 3.95 (2 H, t), 7.10–7.90 (12 H, m) and 8.60–8.90 (8 H, m); MS–FAB$^+$, *m/z* cluster 986 (100%) ($C_{50}H_{33}Cl_7N_4O_3$ requires M, 986.0).

5-{2-Chloro-6-[5-(ethoxycarbonyl)pentyloxy]phenyl}-10,15,20-tris(2,6-dichlorophenyl)porphyrin **15c**.—The *compound* was obtained in 94% yield starting from substrate **13** and ethyl 6-bromohexanoate **11c** as reported for **15a**; δ_H(300 MHz) −2.50 (2 H, br s, D_2O exchange), 0.85 (3 H, t), 1.10–1.50 (8 H, m), 3.70 (2 H, q), 3.95 (2 H, t), 7.10–7.90 (12 H, m) and 8.60–8.90 (8 H, m); MS–FAB$^+$, *m/z* cluster 1014 (100%) ($C_{52}H_{37}Cl_7N_4O_3$ requires M, 1014.0).

5-{2-Chloro-6-[7-(ethoxycarbonyl)heptyloxy]phenyl}-10,15,20-tris(2,6-dichlorophenyl)porphyrin **15d**.—The *compound* was obtained in 90% yield starting from substrate **13** and ethyl 8-bromooctanoate **11d** as reported for **15a**; δ_H(300 MHz) −2.50 (2 H, br s, D_2O exchange), 0.30–1.30 (10 H, m), 1.10 (3 H, t), 1.80 (2 H, t), 3.70–4.10 (4 H, q + t), 7.10–7.90 (12 H, m) and 8.50–8.80 (8 H, m); MS–FAB$^+$, *m/z* cluster 1042 (100%) ($C_{54}H_{41}Cl_7N_4O_3$ requires M, 1042.1).

5-[2-(Carboxymethoxy)-6-chlorophenyl]-10,15,20-tris(2,6-dichlorophenyl)porphyrin Mn^{III} *Internal Salt* **5a**.—A solution of *compound* **15a** (156 mg, 0.163 mmol) in DMF (30 cm^3) was stirred and refluxed with $Mn(OAc)_2$·$4H_2O$ (490 mg, 2 mmol) for 6 h. After evaporation of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 (150 cm^3) and washed with water (2 × 50 cm^3). TLC [silica gel; CH_2Cl_2–MeOH (95:5)] showed only one spot, corresponding to complex **16a** with R_f 0.34, and the complete disappearance of the starting material. The solvent was evaporated off and the residue, dissolved in EtOH (40 cm^3) and 10% aq. NaOH (15 cm^3), was refluxed with magnetic stirring for 2 h. The solvent was evaporated off and the residue was taken up with water (50 cm^3), acidified with 10% aq. HCl, then extracted with CH_2Cl_2 (3 × 100 cm^3). Column chromatography [silica gel; CH_2Cl_2–MeOH (95:5)] afforded a dark brown powder (180 mg), which was dissolved in CH_2Cl_2 (100 cm^3) and stirred with saturated aq. NaCl (100 cm^3). The organic phase was dried over $MgSO_4$ and the solvent was evaporated off, to afford pure *complex* **5a** (175 mg, 99%); $\lambda_{max}(CH_2Cl_2)$/nm 370 (ε/dm^3 mol^{-1} cm^{-1} 46 500), 470 (98 100) and 574 (11 800); MS–FAB$^+$, *m/z* cluster 982 (100%) ($C_{46}H_{23}Cl_7MnN_4O_3$ requires M, 982.8).

5-[2-(3-*Carboxypropoxy*)-6-*chlorophenyl*]-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* Mn^{III} *Internal Salt* **5b**.—The *compound* was obtained in 70% yield starting from substrate **15b** through **16b**, as reported for **5a**; $\lambda_{max}(CH_2Cl_2)$/nm 374 (ε/dm^3 mol^{-1} cm^{-1} 38 600), 479 (77 400) and 578 (9300); MS–FAB$^+$, *m*/*z* cluster 1010 (100%) ($C_{48}H_{27}Cl_7MnN_4O_3$ requires M, 1010.9).

5-[2-(5-*Carboxypentyloxy*)-6-*chlorophenyl*]-10,15,20-*tris*-(2,6-*dichlorophenyl*)*porphyrin* Mn^{III} *Internal Salt* **5c**.—The *compound* was obtained in 97% yield starting from compound **15c** through **16c**, as reported for **5a**; $\lambda_{max}(CH_2Cl_2)$/nm 373 (ε/dm^3 mol^{-1} cm^{-1} 48 200), 478 (100 000) and 578 (11 100); MS–FAB$^+$, *m*/*z* cluster 1038 (100%) ($C_{50}H_{31}Cl_7MnN_4O_3$ requires M, 1039.0).

5-[2-(7-*Carboxyheptyloxy*)-6-*chlorophenyl*]-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* Mn^{III} *Internal Salt* **5d**.—The *compound* was obtained in 98% yield starting from compound **15d**, through **16d**, as reported for **5a**; $\lambda_{max}(CH_2Cl_2)$/nm 372 (ε/dm^3 mol^{-1} cm^{-1} 62 800), 479 (112 100) and 681 (11 700); MS–FAB$^+$, *m*/*z* cluster 1066 (100%) ($C_{52}H_{35}Cl_7MnN_4O_3$ requires M, 1067.0).

Methyl 3-(3-*Bromopropoxy*)*benzoate* **12**.—A sample of 60% NaH (1 g, 25 mmol) in mineral oil was added to a stirred solution of commercial methyl 3-hydroxybenzoate (3.04 g, 20 mmol) in tetrahydrofuran (THF) (100 cm^3) at room temperature. The mixture was stirred for 30 min, then tetrabutylammonium bromide (322 mg, 1 mmol) and 1,3-dibromopropane (20 g) were added. After 8 h the reaction mixture was filtered over Celite, the solid was washed thoroughly with Et_2O (50 cm^3), and the solvent was evaporated off. Distillation of the excess of 1,3-dibromopropane, and column chromatography (silica gel, light petroleum–Et_2O, 70:30) of the residue afforded ester **12** (2.24 g, 68%) as a liquid; δ_H(80 MHz) 2.10–2.50 (2 H, q), 3.50–3.70 (2 H, t), 3.90 (3 H, s), 4.10–4.30 (2 H, t) and 7.00–7.70 (4 H, m).

5-(2-*Chloro*-6-{3-[3-(*methoxycarbonyl*)*phenoxy*]*propoxy*}-*phenyl*)-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* **17**.—This *compound* was obtained in 98% yield starting from substrate **13** and ester **12** as reported for **15a**; δ_H(300 MHz) −2.50 (2 H, br s, D_2O exchange), 1.20–1.60 (2 H, q), 2.80–3.10 (2 H, t), 3.75 (3 H, s), 3.95–4.25 (2 H, t), 7.20–7.90 (16 H, m) and 8.60–8.80 (8 H, m); MS–FAB$^+$, *m*/*z* cluster 1063 (100%) ($C_{55}H_{35}Cl_7N_4O_4$ requires M, 1064.0).

5-{2-[3-(3-*Carboxyphenoxy*)*propoxy*]-6-*chlorophenyl*}-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* **18**.—A solution of the porphyrin **17** (216 mg, 0.203 mmol) in EtOH (40 cm^3) and 10% aq. NaOH (10 cm^3) was refluxed with magnetic stirring for 2.5 h. The solvent was evaporated off and the residue was dissolved in CH_2Cl_2 (150 cm^3) and washed successively with 10% aq. HCl (50 cm^3) and water (100 cm^3). The organic phase was dried with $MgSO_4$ and evaporated. Column chromatography (silica gel; CH_2Cl_2 and CH_2Cl_2–MeOH, 90:10) of the residue afforded starting material (133 mg) and the acid **18** (75 mg, 35%); δ_H(300 MHz) −2.55 (2 H, br s, D_2O exchange), 1.10–1.40 (2 H, m), 3.00 (2 H, t), 4.10 (2 H, t), 6.00–6.20 (1 H, m), 6.60 (1 H, t), 7.10–7.90 (14 H, m) and 8.70–8.90 (8 H, m); MS–FAB$^+$, *m*/*z* cluster 1049 (100%) ($C_{54}H_{33}Cl_7N_4O_4$ requires M, 1050.0).

5-{2-[3-(3-*Carboxyphenoxy*)*propoxy*]-6-*chlorophenyl*}-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* Mn^{III} *Internal Salt* **19**.—A solution of compound **18** (75 mg, 0.071 mmol) in DMF (30 cm^3) was stirred and refluxed wih $Mn(OAc)_2{\cdot}4H_2O$ (490 mg, 2 mmol) for 6 h. The solvent was evaporated off under reduced pressure, the residue was dissolved in CH_2Cl_2–water, and the organic phase was washed with brine and dried over $MgSO_4$. Column chromatography (silica gel; CH_2Cl_2–MeOH, 90:10) of the residue afforded pure complex **19** (78 mg, 97%); $\lambda_{max}(CH_2Cl_2)$/nm 370 (ε/dm^3 mol^{-1} cm^{-1} 44 000), 478 (109 900) and 581 (88 200); MS–FAB$^+$, *m*/*z* cluster 1102 (100%) ($C_{54}H_{31}Cl_7MnN_4O_4$ requires M, 1103.0).

5-[2-*Chloro*-6-[3-(*methoxycarbonyl*)*propanamido*]*phenyl*]-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* **23**.—A solution of commercial methyl-3-(chloroformyl)propanoate (374 mg, 2.5 mmol) in CH_2Cl_2 (10 cm^3) was added during 10 min to a solution of the porphyrin **22** (220 mg, 0.25 mmol) and dry Et_3N (303 mg, 3.0 mmol) in CH_2Cl_2 (90 cm^3). After being stirred for 2 h at room temperature, the solution was washed with water (20 cm^3) and dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by column chromatography (silica gel; $CHCl_3$ then 2% EtOAc–$CHCl_3$) afforded *compound* **23** (140 mg, 57%) as a bluish powder; δ_H(300 MHz) −2.68 (2 H, br s), 1.52 (2 H, t), 1.90 (2 H, t), 2.60 (3 H, s), 6.84 (1 H, br s), 7.60–7.88 (12 H, m) and 8.60–8.80 (8 H, m); MS–FAB$^+$, *m*/*z* 981, lowest mass peak of isotope cluster ($C_{49}H_{30}Cl_7N_5O_3$ requires M, 984.9).

5-[2-(3-*Carboxypropanamido*)-6-*chlorophenyl*]-10,15,20-*tris*-(2,6-*dichlorophenyl*)*porphyrin* **24**.—A solution of ester **23** (110 mg, 0.11 mmol) in EtOH (25 cm^3) and 10% aq. NaOH (5 cm^3) was stirred at room temperature for 2 h. After evaporation of the solvent under reduced pressure without heating, the residue was dissolved in CH_2Cl_2–water and the pH of the aqueous layer was adjusted to 3 with 3 mol dm^{-3} aq. HCl, and the organic phase was washed with water, dried over $MgSO_4$, and evaporated. Column chromatography (silica gel; $CHCl_3$ then 5% MeOH–$CHCl_3$) gave acid **24** (95 mg, 89%) as a bluish powder; δ_H(300 MHz) −2.55 (2 H, br s), 1.46 (2 H, t), 1.95 (2 H, t), 6.78 (1 H, br s), 7.58–7.80 (12 H, m) and 8.53–8.70 (8 H, m). The carboxylic acid proton could not be detected. It was probably broadened to such an extent as to be missing in the baseline; MS–FAB$^+$, *m*/*z* 967, lowest mass peak of isotope cluster ($C_{48}H_{28}Cl_7N_5O_3$ requires M, 970.9).

5-[2-(3-*Carboxypropanamido*)-6-*chlorophenyl*]-10,15,20-*tris*-(2,6-*dichlorophenyl*)*porphyrin* Mn^{III} *Internal Salt* **25**.—A solution of acid **24** (92 mg, 0.095 mmol) in DMF (25 cm^3) was stirred and refluxed with $Mn(OAc)_2{\cdot}4H_2O$ (245 mg, 1.0 mmol) for 2 h. After evaporation of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2–water and the organic phase was washed with brine and dried over $MgSO_4$. Column chromatography (silica gel; 2% MeOH–$CHCl_3$) and anion exchange of a $CHCl_3$ solution of the complex with saturated aq. NaCl afforded *complex* **25** (59 mg, 58%) as a dark green powder; MS–FAB$^+$, *m*/*z* cluster 1023 (100%) ($C_{48}H_{26}Cl_7MnN_5O_3$ requires M, 1023.9).

5-[3-(9-*Ethoxycarbonylnonanamido*)-2,6-*dichlorophenyl*]-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* **27**.—A solution of ethyl 9-(chloroformyl)nonanoate (400 mg, 1.61 mmol) in CH_2Cl_2 (10 cm^3) was added during 10 min to a solution of the porphyrin **26**[12b] (270 mg, 0.28 mmol) and dry Et_3N (364 mg, 3.61 mmol) in CH_2Cl_2 (90 cm^3) and the mixture was stirred at room temperature for 16 h. The reaction mixture was washed successively with 3 mol dm^{-3} aq. HCl (50 cm^3), saturated aq. $NaHCO_3$ (50 cm^3) and water (50 cm^3); the organic phase was dried over $MgSO_4$ and the solvent was evaporated off under reduced pressure. The residue was purified by column chromatography (silica gel; light petroleum–CH_2Cl_2, 50:50) to yield *ester* **27** (194 mg, 62%) as a dark blue powder; δ_H(300 MHz) −2.55 (2 H, br s), 1.00–1.90 (15 H, m), 2.25 (2 H, t), 2.47 (2 H, t), 3.35 (1 H, br s), 4.05 (2 H, q), 7.50–7.85 (11 H, m) and

8.55–8.95 (8 H, m); MS–FAB$^+$, *m/z* cluster 1115 (100%) ($C_{56}H_{43}Cl_8N_5O_3$ requires M, 1117.6).

5-[3-(9-*Carboxynonanamido*)-2,6-*dichlorophenyl*]-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* **28**.—A sample of ester **27** (194 mg, 0.17 mmol) was dissolved in hot EtOH (100 cm^3). After the mixture had cooled to room temperature aq. 10% NaOH (20 cm^3) was added, and the reaction mixture was stirred for 16 h. The solvent was evaporated off at room temperature under reduced pressure and the residue was dissolved in CH_2Cl_2–water. The pH of the aqueous phase was adjusted to 3 with aq. 3 mol dm^{-3} HCl, then the organic phase was washed with water and dried over $MgSO_4$. Evaporation of the solvent and column chromatography (silica gel; 5% MeOH–CH_2Cl_2) of the residue afforded *acid* **28** as a blue powder (105 mg, 57%); δ_H(300 MHz) −2.55 (2 H, br s), 1.20–1.85 (12 H, m), 2.30 (2 H, t), 2.46 (2 H, t), 4.10 (1 H, br s), 7.50–7.85 (11 H, m) and 8.65–8.90 (8 H, m); MS–FAB$^+$, *m/z* cluster 1087 (100%) ($C_{54}H_{39}Cl_8N_5O_3$ requires M, 1089.5).

5-[3-(9-*Carboxynonanamido*)-2,6-*dichlorophenyl*]-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* Mn^{III} *Complex* **29**.—This compound was prepared from acid **28** as described for complex **25**. Column chromatography (silica gel; MeOH–CH_2Cl_2, 10:90 afforded *complex* **29** (69%); MS–FAB$^+$, *m/z* cluster 1140 (100%) ($C_{54}H_{37}Cl_8MnN_5O_3$ requires M, 1142.5).

5,10,15-*Tris*(2,6-*dichlorophenyl*)-20-(2,6-*dimethoxyphenyl*)-*porphyrin* **30**.—A solution of 2,6-dichlorobenzaldehyde (1.575 g, 9 mmol), 2,6-dimethoxybenzaldehyde (0.498 g, 3 mmol), pyrrole (0.8 g, 12 mmol) and BF_3·Et_2O (1.12 g, 7.92 mmol) in CH_2Cl_2 (1200 cm^3 freshly distilled over P_2O_5) and absolute EtOH (12 cm^3) was stirred at room temperature for 15 h. After addition of DDQ (1.5 g, 6.6 mmol), the reaction mixture was stirred for a further 2 h, then Et_3N (1 cm^3) was added and the solvent was evaporated off. The residue was supported on Florisil (60 g) and purified by column chromatography (neutral alumina). Elution with light petroleum–CH_2Cl_2 (50:50), resulted in 5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin (197 mg), then using CH_2Cl_2 and CH_2Cl_2–MeOH 90:10 as eluent, pure *compound* **30** (250 mg, 9.4%) was obtained as a blue powder; δ_H(300 MHz) −2.55 (2 H, br s, D_2O exchange), 3.31 (6 H, s), 6.90–7.90 (12 H, m) and 8.50–8.90 (8 H, m); MS–FAB$^+$, *m/z* cluster 881 (100%) ($C_{46}H_{28}Cl_6N_4O_2$ requires M, 881.4).

5,10,15-*Tris*(2,6-*dichlorophenyl*)-20-(2,6-*dihydroxyphenyl*)-*porphyrin* **31**.—A solution of compound **30** (85 mg, 0.096 mmol) in CH_2Cl_2 (60 cm^3; freshly distilled over $CaCl_2$) and BBr_3 (4.5 cm^3 of 1 mol dm^{-3} solution in CH_2Cl_2) was stirred at room temperature under an inert atmosphere for 24 h. The reaction mixture was then added to crushed ice (150 g), then was vigorously stirred for 30 min, and the organic phase was separated. The aqueous layer was extracted twice with CH_2Cl_2 (50 cm^3), and the combined organic phases were dried over $MgSO_4$ and evaporated to afford *diol* **31** (83 mg, 100%); δ_H(300 MHz) −2.55 (2 H, br s, D_2O exchange), 4.80 (2 H, br s, D_2O exchange), 6.90–7.90 (12 H, m) and 8.50–9.00 (8 H, m); MS–FAB$^+$, *m/z* cluster 853 (100%) ($C_{44}H_{24}Cl_6N_4O_2$ requires M, 853.4).

5,10,15-*Tris*(2,6-*Dichlorophenyl*)-20-{2-[5-(*ethoxycarbonyl*)-*pentyloxy*]*phenyl*}*porphyrin* **32**.—A solution of diol **31** (84 mg, 0.098 mmol) and ethyl 6-bromohexanoate **11c** (26.2 mg, 0.118 mmol) in DMF (7 cm^3) was stirred for 5 days at room temperature with solid Cs_2CO_3 (32 mg, 0.098 mmol). The solvent was evaporated off under reduced pressure and the residue was dissolved in CH_2Cl_2 (50 cm^3) and washed successively with 10% aq. HCl (20 cm^3) and with water (3 × 20 cm^3). Evaporation of the solvent and column chromatography (silica gel; light petroleum–CH_2Cl_2, 50:50 and then pure CH_2Cl_2) afforded starting porphyrin **31** (21 mg recovery), the *porphyrin* **32** (22 mg, 22%); δ_H(300 MHz) −2.55 (2 H, br s, D_2O exchange), 0.30–1.80 (11 H, m), 3.70–4.00 (4 H, m), 4.80 (1 H, br s, D_2O exchange), 6.90–7.90 (12 H, m) and 8.50–8.90 (8 H, m); MS–FAB$^+$, *m/z* cluster 994 (100%) ($C_{52}H_{38}Cl_6N_4O_4$ requires M, 995.6), and *disubstituted diol* **33** (7.7 mg); δ_H(300 MHz) −2.55 (2 H, br s, D_2O exchange), 0.30–1.80 (26 H, m), 3.70–4.00 (4 H, m), 6.90–7.90 (12 H, m) and 8.60–8.90 (8 H, m); MS–FAB$^+$, *m/z* cluster 1137 (100%) ($C_{60}H_{52}Cl_6N_4O_6$ requires M, 1137.8).

5,10,15-*Tris*(2,6-*dichlorophenyl*)-20-{2-[5-(*ethoxycarbonyl*)-*pentoxy*]-6-[6-(*imidazol*-1-*yl*)*hexyloxy*]*phenyl*}*porphyrin* **34**.—A solution of ester **32** (40 mg, 0.040 mmol) and *N*-(6-bromohexyl)imidazole dihydrochloride (120 mg, 0.40 mmol) in DMF (15 cm^3) was stirred at room temperature with solid Cs_2CO_3 (196 mg, 0.8 mmol) for 4 days. The mixture was evaporated to dryness and the residue was purified by column chromatography (silica gel; CH_2Cl_2–MeOH, 90:10) to afford pure *compound* **34** (21 mg, 46%); MS–FAB$^+$, *m/z* cluster 1144 (100%) ($C_{61}H_{52}Cl_6N_6O_4$ requires M, 1145.8).

5,10,15-*Tris*(2,6-*dichlorophenyl*)-20-{2-[5-(*ethoxycarbonyl*)-*pentyloxy*]-6-[6-(*imidazol*-1-*yl*)*hexyloxy*]*phenyl*}*porphyrin* Mn^{III} *Acetate Complex* **35**.—A suspension of compound **34** (15 mg, 0.013 mmol) and $Mn(OAc)_2$·$4H_2O$ (490 mg, 2 mmol) in DMF (40 cm^3) was refluxed for 16 h with magnetic stirring. Evaporation of the solvent and column chromatography (silica gel; CH_2Cl_2–MeOH, 90:10) afforded pure *complex* **35** (15.6 mg, 95%); MS–FAB$^+$, *m/z* cluster 1197 (100%) ($C_{61}H_{50}Cl_6MnN_6O_4$ requires M, 1198.8).

5-{2-(5-*Carboxypentyloxy*)-6-[6-(*imidazol*-1-*yl*)*hexyloxy*]-*phenyl*}-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* Mn^{III} *Internal Salt* **6**.—A solution of complex **35** (15.6 mg, 0.0124 mmol) in EtOH (25 cm^3) and 10% aq. NaOH (10 cm^3) was stirred and refluxed for 3 h. The solvent was evaporated off and the residue, taken up with water (50 cm^3), was acidified with 10% aq. HCl and extracted with CH_2Cl_2 (3 × 50 cm^3). The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. Purification of the crude product by column chromatography (silica gel; CH_2Cl_2–MeOH, 90:10) afforded a dark brown powder (18 mg). This product was dissolved in CH_2Cl_2 (100 cm^3) and the solution was stirred for 30 min with saturated aq. NaCl (100 cm^3) to afford pure *complex* **6** (15 mg, 100%); $\lambda_{max}(CH_2Cl_2)$/nm 380 (ε/dm^3 mol^{-1} cm^{-1} 36 000), 477 (64 100) and 574 (9500); MS–FAB$^+$, *m/z* cluster 1169 (100%) ($C_{59}H_{46}Cl_6MnN_6O_4$ requires M, 1170.7).

5,10,15-*Tris*(2,6-*dichlorophenyl*)-20-{2-[5-(*ethoxycarbonyl*)-*pentyloxy*]-6-(3-*pyridylmethoxy*)*phenyl*}*porphyrin* **36**.—A solution of the porphyrin **32** (15 mg, 0.015 mmol) and 3-(chloromethyl)pyridine hydrochloride (25 mg, 0.15 mmol) in DMF (10 cm^3) was stirred with solid Cs_2CO_3 (50 mg, 0.15 mmol) at room temperature for 4 days. The mixture was evaporated to dryness and the residue was purified by column chromatography (silica gel; CH_2Cl_2–MeOH, 90:10) to afford pure *compound* **36** (12 mg, 73%); δ_H(300 MHz) −2.55 (2 H, br s, D_2O exchange), 0.30–1.80 (11 H, m), 3.80–3.90 (4 H, m), 4.90 (2 H, s), 6.35 (2 H, d), 7.05–7.10 (2 H, m), 7.40–7.80 (10 H, m), 8.00 (1 H, s), 8.15 (1 H, s) and 8.50–8.80 (8 H, m); MS–FAB$^+$, *m/z* 1083, lowest mass peak of isotope cluster ($C_{58}H_{43}Cl_6N_5O_4$ requires M, 1086.7).

5-[2-(5-*Carboxypentyloxy*)-6-(3-*pyridylmethoxy*)*phenyl*]-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* Mn^{III} *Internal Salt* **37**.—The *compound* was isolated in 85% yield starting from

ester **36**, after complexation with $Mn(OAc)_2 \cdot 4H_2O$ and hydrolysis with 10% aq. NaOH in EtOH as described for compounds **35** and **6**, respectively; MS–FAB$^+$, *m/z* 1108, lowest mass peak of isotope cluster ($C_{56}H_{37}Cl_6MnN_5O_4$ requires M, 1111.6).

5,10,15-*Tris*(2,6-*dichlorophenyl*)-20-{2-[5-(*ethoxycarbonyl*)*pentyloxy*]-6-[3-(3-*pyridylmethoxy*)*propoxy*]*phenyl*}*porphyrin* **35**.—The *compound* was isolated in 80% yield starting from compound **32** and 3-[(3-chloropropoxy)methyl]pyridine as described for compound **36**; δ_H(300 MHz) −2.55 (2 H, br s, D_2O exchange), 0.45–1.80 (11 H, m), 2.00 (2 H, m), 3.60–3.70 (2 H, m), 3.80–4.00 (6 H, m), 4.50 (2 H, s), 6.70–7.00 (4 H, m), 7.25–7.50 (1 H, m), 7.60–7.80 (9 H, m), 8.17 (1 H, s), 8.30 (1 H, s) and 8.50–8.80 (8 H, m); MS–FAB$^+$, *m/z* 1141, lowest mass peak of isotope cluster ($C_{61}H_{49}Cl_6N_5O_5$ requires M, 1144.8).

5-{2-(5-*Carboxypentoxy*)-6-[3-(*pyridylmethoxy*)*propoxy*]-*phenyl*}-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* Mn^{III} *Internal Salt* **7**.—The *compound* was isolated in 80% yield starting from compound **38**, after complexation with $Mn(OAc)_2 \cdot 4H_2O$ and hydrolysis with 10% aq. NaOH in EtOH as described for complexes **6** and **35**, respectively; MS–FAB$^+$, *m/z* 1166, lowest mass peak of isotope cluster ($C_{59}H_{43}Cl_6MnN_5O_5$ requires M, 1169.7).

5-(2-*Chloro*-6-*hexyloxyphenyl*)-10,15,20-*tris*(2,6-*dichlorophenyl*)-*porphyrin* **20**.—A suspension of the porphyrin **13** (87 mg, 0.1 mmol), 1-bromohexane (165 mg, 1.0 mmol) and solid Cs_2CO_3 (326 mg, 1.0 mmol) in DMF (20 cm^3) was stirred at room temperature for 26 h. Evaporation of the solvent and column chromatography (silica gel; CH_2Cl_2–light petroleum, 50:50) afforded *compound* **20** as a purple powder in quantitative yield; δ_H(300 MHz) −2.50 (2 H, br s, D_2O exchange), 0.20–1.00 (11 H, m), 3.85 (2 H, t), 7.10–7.90 (12 H, m) and 8.50–8.80 (8 H, m); MS–FAB$^+$, *m/z* 955, cluster (100%) ($C_{50}H_{35}Cl_7N_4O$ requires M, 956.0).

5-(2-*Chloro*-6-*hexyloxyphenyl*)-10,15,20-*tris*(2,6-*dichlorophenyl*)*porphyrin* Mn^{III} *Chloride Complex* **21**.—A solution of compound **20** (96 mg, 0.1 mmol) in DMF (30 cm^3) was stirred and refluxed with $Mn(OAc)_2 \cdot 4H_2O$ (250 mg, 2.0 mmol) for 6 h. After evaporation of the solvent under reduced pressure the residue was dissolved in CH_2Cl_2 (100 cm^3) and washed with water (2 × 50 cm^3). Column chromatography [silica gel; CH_2Cl_2–MeOH (95:5)] afforded a dark brown powder (100 mg). This product was dissolved in CH_2Cl_2 (100 cm^3) and stirred with brine (80 cm^3), dried over $MgSO_4$, and evaporated to afford pure complex **21** (95 mg, 95%); $\lambda_{max}(CH_2Cl_2)$/nm 370 (ε/dm^3 mol^{-1} cm^{-1} 54 200), 477 (108 700) and 500 (10 600); MS–FAB$^+$, *m/z* 1006, lowest mass peak of isotope cluster ($C_{50}H_{33}Cl_7MnN_4O$ requires M, 1009.0).

General Procedure of Olefin Epoxidation.—Oxidations were carried out in a 20 cm^3 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 speed was maintained at 1300 ± 50 rpm. The flask was charged with: (i) 1 cm^3 of a 2.5 × 10^{-3} dm^{-3} CH_2Cl_2 solution of Mn^{III}-porphyrin; (ii) 1 cm^3 of a 0.5 mol dm^{-3} (S/P 200) or 2.5 mol dm^{-3} (S/P 1000) CH_2Cl_2 solution of alkene, containing decane as internal standard, 0.25 or 1.25 mol dm^{-3} respectively; (iii) when an external axial ligand was required, the calculated volume of a 0.25 or 1.0 mol dm^{-3} CH_2Cl_2 solution of *N*-hexylimidazole was added (*i.e.*, 1 × 10^{-2} cm^3 of the 0.25 mol dm^{-3} solution for L/P 1).

The oxidant, 2–3 mol equiv. with respect to the substrate, was then added to the reaction mixture. When 30% H_2O_2 (10 mol dm^{-3}) was used its pH was adjusted to 4.5–5.0 with solid $NaHCO_3$ or, when required, by the addition of sodium benzoate in order to have the desired A/P ratio in the volume of H_2O_2 used in the reaction. These solutions were generally prepared on a 5 cm^3 scale, stored at 0 °C, and used within 1 h from their preparation. When 0.4 mol dm^{-3} aq. NaOCl was used, its pH was lowered to 10.5 by the addition of solid $NaHCO_3$ just before use.

The mixture was stirred and samples were taken at different times and analysed by GLC.

The observed rates are indicated as turnovers/min (see Tables 1 and 3). The error is evaluated as ± 2%.

Titration of H_2O_2 *in the Organic Phase.*—Samples of CH_2Cl_2 (50 cm^3) and 30% H_2O_2 (5 cm^3) were stirred for 15 min at 0 °C. The phases were separated and aliquots of 10 cm^3 of the organic phase were mixed with acidic aq. KI and vigorously stirred. The I_2 produced was titrated with standard 0.005 mol dm^{-3} $Na_2S_2O_3$. The result of six titrations indicated that the H_2O_2 concentration in CH_2Cl_2 was 8.5 × 10^{-3} mol dm^{-3}.

Evaluation of Catalase Activity in Cyclooctene Epoxidation.—The reaction was carried out as described in the general procedure for alkene epoxidation, by using Mn^{III}-tetrakis(2,6-dichlorophenyl)porphyrin **3** as catalyst (2.5 × 10^{-3} mmol), cyclooctene (2.5 mmol, S/P 1000), and 30% H_2O_2 (0.75 cm^3) containing sodium benzoate (1 × 10^{-2} mmol) (A/P 4). After 30 min, stirring was stopped and a sample (1 × 10^{-2} cm^3) of the organic phase was withdrawn and analysed by GLC to evaluate the conversion of cyclooctene (50%). In the meantime the reaction mixture was poured into acidic aq. KI and subsequently titrated with 0.05 mol dm^{-3} $Na_2S_2O_3$. The value of this titration was the same as that obtained from 0.75 cm^3 of H_2O_2 corrected for the amount of oxidant consumed in the formation of cyclooctene epoxide. The same titration was repeated on a solution of Mn^{III}-porphyrin stirred in the presence of H_2O_2 (0.75 cm^3) but in the absence of substrate. This last value was exactly the same of that for H_2O_2 alone, thus confirming that no catalase effect occurs under the reaction conditions used. Identical behaviour was observed with Mn^{III}-porphyrin **6**.

Determination of Binding Constants (K_1 *and* β_2) *between* Mn^{III}-*Porphyrin* **3** *and* N-*Hexylimidazole.*—Samples (5 cm^3) of a 2 × 10^{-5} mol dm^{-3} CH_2Cl_2 solution of complex **3** were placed in 10 cm^3 volumetric flasks (class A) by means of a Metrohm 655 Dosimat. To these flasks was then added a CH_2Cl_2 solution of *N*-hexylimidazole (0.25–5.0 cm^3 of the required molarity), in order to reach the desired axial ligand: Mn-porphyrin ratio (L/P 0.5–500). The volume of each volumetric flask was then brought to 10 cm^3 and the absorbance of the resulting solutions was measured at 477 nm. The titration data were analysed by using the least-squares curve-fitting routine of equation (4) (see text).

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