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Epoxidation of Alkenes Under Liquid-Liquid Biphasic Conditions: Synthesis and Catalytic Activity of Mn(III)-Tetraarylporphyrins Bearing Perfluoroalkyl Tails.

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Abstract: Four tetraarylporphyrins bearing one *n*-C_8F_{17} chain on each *meso*-aryl group have been synthesized. The Mn(III)-complexes of these new compounds (Mn-**1** - Mn-**4**) were used as catalysts in alkene epoxidations carried out under aqueous-organic biphasic conditions. High epoxide yields were obtained with catalysts in which, along with perfluoroalkyl chains, bulky substituents were present at appropriate positions. The expected general enhancement of stability and catalytic activity due to the electron-withdrawing effect of *n*-C_8F_{17} substituents was not observed. However, Mn-**4** was found to be an exceptionally active catalyst for NaOCl promoted epoxidation of poorly reactive linear α-alkenes .

Introduction of electron-withdrawing substituents at the periphery of porphyrin ligands has a deep effect on the catalytic properties of the corresponding metal complexes. Electron-deficient metalloporphyrins have been found to be more active and stable catalysts for oxygenation reactions than related complexes devoid of electron-withdrawing substituents.[1,2] Such favourable results are usually ascribed to the activation of the high-valent metal intermediate involved in oxygen transfer and to the increase of the ionization potential (IP) of the porphyrin that protects the catalyst from oxidative degradation. Attempts to rationalize and possibly forecast the effects of electron-withdrawing substituents by means of computational tools and photoelectron spectroscopy have been recently reported.[3,4] These studies confirm that both the nature and the point of attachment of the substituents influence the catalytic activity of metalloporphyrins. Among the substituents examined, perfluoroalkyl groups (R_F) stand out for their unique properties. The presence of these strong electron-withdrawing groups with a neat -I character should drastically lower the energy of the porphyrin HOMO, thus increasing the stability of the ligand toward oxidation.

A new approach to liquid biphasic catalytic reactions ("fluorous biphasic system", FBS) based on the low miscibilities of fluorocarbons with most organic solvents has been recently described.[5] Efficient catalysts selectively soluble in fluorocarbons are required in order to carry out reactions according to the FBS technique: insertion of R_F segments in the structure of known active compounds has been proposed as a general strategy for the preparation of such catalysts.[5a]

These findings prompted us to investigate the properties of perfluoroalkyl-substituted tetraarylporphyrins, a class of compounds which was nearly neglected in the wide body of literature devoted to porphyrins. We previously reported the synthesis of two tetraarylporphyrins bearing R_F chains linked to the *meso*-phenyl rings

through amido bonds.[6] These compounds were found to be insoluble in perfluorocarbons, hence the catalytic activity of their Mn(III)-complexes was evaluated in the epoxidation of alkenes carried out under classical aqueous-organic conditions. Although the presence of amido bonds partly masks the true effect of the R_F substituents, the results obtained pointed to a beneficial influence of the latter on the catalytic efficiency of Mn(III)-tetraarylporphyrins, in agreement with theoretical predictions.

In this paper, we report the synthesis of tetraarylporphyrins **1-4** featuring *n*-C_8F_{17} chains directly linked to the *meso*-phenyl rings (Fig. 1). The Mn(III)-complexes of these new ligands were tested as catalysts for the epoxidation of alkenes in aqueous-organic biphasic systems. Steric and solvent effects, that have not been considered in computational studies, were found to overpower the electron-withdrawing effect of the R_F tails.

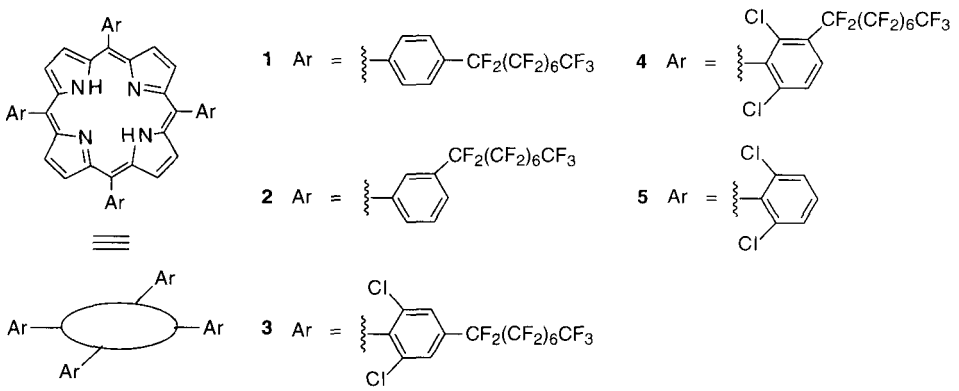


Figure 1. Structure of porphyrins **1-5**.

RESULTS AND DISCUSSION

*Synthesis of porphyrins **1-4***

Perfluoroalkyl-substituted tetraarylporphyrins could be synthesized in principle by two different pathways, namely: i) cyclization of perfluoroalkylated building blocks or ii) attachment of the R_F chains to a preformed porphyrin ring. The main advantage of the second synthetic strategy is the use of readily available starting compounds, as we already verified for the preparation of tetraarylporphyrins bearing perfluoroalkylamido tails.[6] Provided that selective perfluoroalkylation of the *meso*-phenyl groups of tetraarylporphyrins were possible, porphyrins **1** - **4** could be directly prepared from, for instance, 5,10,15,20-tetraphenylporphyrin (TPP) or 5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin **5**. On the other hand, the presence of perfluoroalkyl residues on the aromatic building-blocks could be troublesome for most cyclization procedures[7] and it can considerably lower the yields in the desired porphyrin.[8] Both pathways were investigated nonetheless and, rather unexpectedly, only cyclization of perfluoroalkylated building blocks was found to be effective for the synthesis of **1** - **4**.

Perfluoroalkylation of tetraarylporphyrins.

A number of methods of perfluoroalkylation of aromatic compounds have been described.[9] The only reported application to the preparation of perfluoroalkyl-tetraarylporphyrins is the claimed synthesis of **1** and **2** by coupling of $C_8F_{17}I$ with 5,10,15,20-tetrakis-(4-bromophenyl)porphyrin **6** and 5,10,15,20-tetrakis-(3-

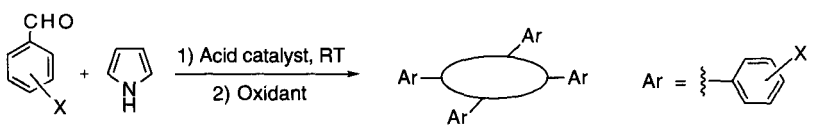
bromophenyl)porphyrin **7** in the presence of copper bronze.[10] In our hands, however, this procedure failed to give the same compounds. The coupling reaction of perfluoroalkylcopper reagents with aromatic halides is a well-known method of perfluoroalkylation,[11] it occurs exclusively at the halogen site and it is compatible with the presence of a wide range of functional groups. Since reactivity of aromatic halides follows the order ArI > ArBr >> ArCl, we also tried to synthesize **1** from 5,10,15,20-tetrakis-(4-iodophenyl)porphyrin **8** [12] by treatment with an excess of a preformed solution of perfluorooctylcopper in DMSO at 120 °C for 4 hours. Under these conditions **8** was completely converted into a mixture of products. According to mass spectrometry (FAB^+) the major component of the mixture was the copper complex of 5-(4-perfluorooctylphenyl)-10,15,20-tris-(4-iodophenyl)porphyrin, together with a similar compound bearing two R_F chains. Unfortunately, no tetraperfluorooctyl derivative was detected.

The coupling reaction was also carried out at a slightly higher temperature (140 °C) over a longer time (12 hours) for the sake of introducing four R_F chains. In this case the zinc complex of **8** was used as starting product in order to prevent copper complexation.[13] Indeed, copper is so tightly bonded in the porphyrin ring that sometimes it is removed only by methods so drastic as to cause decomposition of the porphyrin structure.[14] Under the above reaction conditions copper-transmetallation occurred. After removal of the unreacted copper reagent the crude mixture was treated with H_2SO_4/CF_3COOH at room temperature for 48 hours,[15] but ligated copper was not displaced. The solution was then heated to reflux for 3 hours affording a tarry mixture of compounds that did not contain porphyrin **1**.

Electrophilic perfluoroalkylation of electron rich aromatic compounds has been accomplished under mild conditions by using (perfluoroalkyl)phenyliodonium triflates (FITS reagents).[16] Although some deactivated molecules such as nitrobenzene and methyl benzoate can be perfluoroalkylated by FITS reagents, all attempts to obtain **1** through functionalization of TPP with (perfluorooctyl)phenyl-iodonium triflate (FITS-8) failed.

Other perfluoroalkylation methods that require forcing conditions, such as thermolysis of perfluoroalkyl iodides,[17] seemed to be too harsh to be applied to porphyrin substrates and were not explored.

Cyclization of aromatic perfluoroalkylaldehydes. Condensation of aromatic aldehydes and pyrrole is the oldest preparative route to tetraarylporphyrins.[2b] Lindsey and coworkers extensively studied this reaction and devised a gentle procedure that has been widely applied to the preparation of porphyrins bearing a variety of substituents on the *meso*-phenyl rings (Scheme 1).[18] Although versatile, this acid-catalyzed procedure has several limitations mainly related to the nature of the aldehyde, for instance the presence of bulky substituents can lower or even annihilate the yield in porphyrin. Careful choice of the reaction conditions can sometimes lessen these negative effects.



Scheme 1. Synthesis of tetraarylporphyrins according to Lindsey procedure.

5,10,15,20-Tetrakis-(4-trifluoromethylphenyl)porphyrin **9** and 5,10,15,20-tetrakis-(2-trifluoromethyl-phenyl)porphyrin **10** have been synthesized according to the Lindsey procedure, but 2,6-bis(trifluoromethyl)-benzaldehyde failed to yield the corresponding tetraarylporphyrin.[19] Apparently, condensation of aromatic

aldehydes bearing perfluoroalkyl substituents other than -CF_3 was never carried out. In order to assess the validity of this approach, condensation of 4-perfluorooctylbenzaldehyde **11** [20] with pyrrole was attempted. Under optimized conditions (Table 1, entry 4) the yield of porphyrin **1** was only 10%, which should be compared with the yield obtained in the synthesis of TPP (45%).

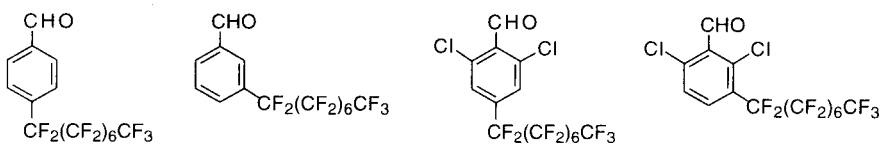
Table 1. Condensation of aldehyde **11** and pyrrole. Reaction conditions and yields in porphyrin **1**.

Entry	T (°C)	Solvent	Catalyst	Oxidant	[Substrates]	Yield (%)
1	20	CH_2Cl_2	CF_3COOH	DDQ[a]	10^{-2} M	traces
2	40	CH_2Cl_2	CF_3COOH	DDQ	10^{-2} M	traces
3	20	Hexane	CF_3COOH	DDQ	10^{-2} M	traces
4	20	CH_2Cl_2	$BF_3.Et_2O$	DDQ	10^{-2} M	10%
5	20	CH_2Cl_2	$BF_3.Et_2O$	*p*-chloranil[b]	10^{-2} M	traces
6[c]	140	CH_3CH_2COOH	/	O_2	10^{-2} M	3%
7[d]	140	CH_3CH_2COOH	/	$O_2/PhNO_2$	10^{-2} M	6%

[a] DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; [b] *p*-chloranil = 2,3,5,6-tetrachloro-1,4-benzoquinone; [c] Conditions described in Ref. 21; [d] Conditions described in Ref. 22.

Despite its negative influence on the condensation yields, the presence of the long R_F chain is compatible with the formation of the porphyrin ring. Synthesis of tetraarylporphyrins **2**, **3** and **4** was thus carried out by condensation of perfluoroalkyl-substituted benzaldehydes **12**, **13** and **14** respectively (Fig. 2).

*Synthesis of aromatic perfluoroalkylaldehydes **12-14**.* The synthesis of aldehyde **11** was previously reported by three independent groups.[20] None of the described procedures is suited for large scale preparation and for the synthesis of the poly-substituted benzaldehydes **13** and **14**.



11 **12** **13** **14**

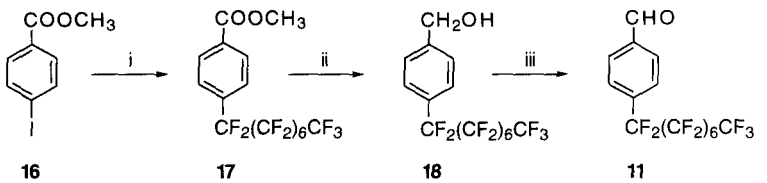
Figure 2. Starting compounds for the synthesis of perfluoroalkyl-substituted tetraarylporphyrins **1-4**.

Direct perfluoroalkylation methods were tested in the synthesis of **11** from benzaldehyde or 4-iodobenzaldehyde **15**. Electrophilic perfluoroalkylation of benzaldehyde by using FITS-8 [16] was unsuccessful. Attempts to functionalize benzaldehyde by treating the substrate with a mixture of $C_8F_{17}I$ and copper bronze in DMSO at 100 °C failed too.[23] Only the coupling of $C_8F_{17}I$ with 4-iodobenzaldehyde according to the general procedure described by McLoughlin and Thrower [11] gave a small amount of **11** (yield = 10%). Protection of the carbonyl group of **15** by conversion into acetal before the coupling reaction did not result in improved yields.

Although at the end of the reaction the mixture was rich in the perfluorooctyl acetal of **11** (50% as evaluated by ^{1}H-NMR), during the work-up most of the product underwent decomposition into several perfluoroalkylated compounds.

As already pointed out, the presence of substituents such as -COOH, -OH, -R, -NR_2 on the aromatic halide do not hamper the perfluoralkylation process. Some substituents even enhance the yields obtained, in particular -COOR.[11] Since aldehydes can be easily obtained from esters, the coupling reaction was carried out between methyl 4-iodobenzoate **16** and $C_8F_{17}I$ in DMF at 130 °C. Perfluorooctyl ester **17** was easily recovered from the reaction mixture in good yield (80%). Reduction with $LiAlH_4$ in Et_2O followed by oxidation with MnO_2 afforded aldehyde **11** in 65% overall yield with respect to **16** (Scheme 2).[24]

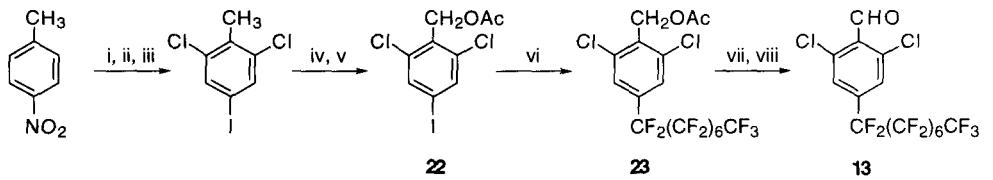
Aldehyde **12** was synthesized in 70% overall yield from methyl 3-iodobenzoate **19** following the same three-steps procedure .



Scheme 2. Synthesis of aldehyde **11**. Reaction conditions: i) $C_8F_{17}I$/Cu, DMF, 130 °C, 80%; ii) $LiAlH_4$, Et_2O, 95%; iii) MnO_2, $CHCl_3$, reflux, 85%.

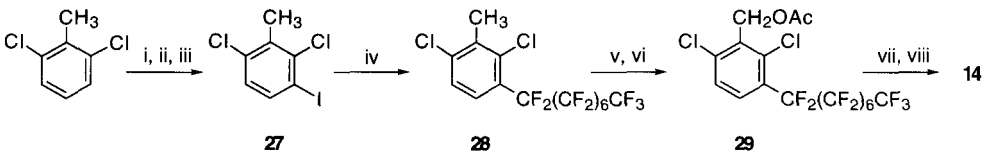
Chlorine is usually inert toward coupling reaction with perfluoroalkylcopper,[11] therefore 2,6-dichloro-4-iodo- and 2,6-dichloro-3-iodo-methylbenzoate would be useful intermediates for the synthesis of **13** and **14**. Unfortunately, the two esters were not available and a slightly different approach was then followed.

We had already devised a procedure for the synthesis of 2,6-dichloro-4-iodobenzaldehyde that involves ester **22** (Scheme 3) as an intermediate.[25] This compound was found to be a good substrate for the coupling reaction with $C_8F_{17}I$/Cu. Hydrolysis of the ester function followed by oxidation gave aldehyde **13** in 54% yield with respect to **22**.



Scheme 3. Synthesis of aldehyde **13**. Reaction conditions: i) Cl_2, $SbCl_3$, 70 °C, 70%; ii) $SnCl_2$, HCl, 95%; iii) $NaNO_2$, H^+, KI_{aq}, 65%; iv) NBS, CCl_4, hv, reflux, 75%; v) AcOK, TEBA·HSO_4, CH_3CN, 100%; vi) $C_8F_{17}I$/Cu, DMF, 130 °C, 86%; vii) KOH_{aq}, MeOH, 90%; viii) MnO_2, $CHCl_3$, reflux, 70%.

Aldehyde **14** was prepared starting from 2,6-dichlorotoluene as reported in Scheme 4. The order of the bromination/esterification and perfluoroalkylation steps was inverted with respect to the synthesis of **13**, because upon reaction with NBS, 2,6-dichloro-3-iodotoluene **26** lost iodine. Although still acceptable (50%), the yield of the coupling reaction was lower than that previously obtained in the presence of -CH_2OAc (86 %, Scheme 3). Sterical hindrance, besides the nature of the substituents, could account for the reduced yield.



Scheme 4. Synthesis of aldehyde **14**. Reaction conditions: i) HNO_3/H_2SO_4, CH_2Cl_2, 95%; ii) $SnCl_2$, HCl, 92%; iii) $NaNO_2$, H^+, KI_{aq}, 70%; iv) $C_8F_{17}I$/Cu, DMF, 130 °C, 50%; v) NBS, CCl_4, hv, reflux, 90%; vi) AcOK, $TEBAHSO_4$, CH_3CN,100%; vii) KOH_{aq}, MeOH, 90%; viii) MnO_2, $CHCl_3$, reflux, 81%.

Condensation of aldehydes **12**, **13**, **14** with pyrrole under the synthetic conditions reported in entry 4, Table 1, afforded compounds **2**, **3**, **4** in 14%, 2% and 15% yield, respectively. The very low yield in the synthesis of **3** was mainly due to loss of compound during the purification step, which requires column chromatography followed by complexation with zinc, further chromatography and removal of the metal (see Experimental). Perfluoroalkyl-substituted tetraarylporphyrins **1**-**4** were converted into the corresponding Mn(III)-complexes (Mn-**1** - Mn-**4**) following reported procedures.[26]

Catalytic activity of Mn-1 - Mn-4

Metal complexes of tetraarylporphyrins are well-known catalysts for hydrocarbon oxygenation reactions. Despite their distance from the core of the macrocycle, electron-withdrawing substituents on the phenyl rings modulate efficiently the catalytic properties of the complexes.[2] Both *ab initio* Hartree-Fock (HF)[3] and local density functional (LDF) calculations,[4] successfully predict the influence of the substitution on the IPs of tetraarylporphyrins, and the agreement between computational and X-ray Photoelectron Spectroscopical (XPS) data is good.[4]

As far as R_F substituents are concerned, the validity of the computational forecasts has been checked in the case of porphyrins bearing trifluoromethyl or pentafluoropropyl groups linked at the β-pyrrolic positions. These compounds have been known for some years,[3,27] and the electrochemical oxidation potential of some of them have been reported.[28] The experimental results agree qualitatively with the computational data, although these latter overestimate the substituent effect.[4] To the best of our knowledge, hydrocarbon oxygenation reactions catalyzed by metal complexes of β-perfluoroalkyl-substituted porphyrins have never been reported. *Meso*-tetrakis(perfluoroalkyl)porphyrins are a new class of highly electron-deficient compounds which is the object of current interest.[7,29] Metal complexes of these ligands are efficient catalysts for the oxidation of isobutane to *tert*-butyl alcohol.[30] The above cited theoretical studies, suggest that *meso*-R_F substituents exert a higher stabilizing effect than the same substituents placed at the β-positions. Electrochemical and XPS data, do confirm that *meso*-tetrakis(perfluoroalkyl)porphyrins have peculiar redox and electronic properties.[29e] Whereas XPS core ionization potentials are in good agreement with the the enormous stabilizing effect predicted by HF[3] and LDF calculations,[4] the magnitudes of the substituent effects evaluated electrochemically are again lower than those calculated.

Metal-complexes of perfluoroalkyl-substituted tetraarylporphyrins have never been used as catalyst for hydrocarbon oxygenation. However, the IP of 5,10,15,20-tetrakis-(4-trifluoromethylphenyl)porphyrin **9** evaluated by LDF calculations is 0.72 eV higher than the evaluated IP of 5,10,15,20-tetraphenylporphyrin (TPP) and the experimental difference between IPs, evaluated by XPS, is equal to 0.65 eV.[4] This means that introduction of R_F tails on the *meso*-phenyl rings should result in a significant degree of porphyrin stabilization

under oxidizing conditions. Theoretical and XPS studies take into account only the purely electronic effects of the peripheral substituents, but steric and solvent effects are as much important for determining the catalytic activity of metal-porphyrins. In other words, empirical reactivity studies are required in order to verify the validity of the computational hint.

*Solubility of porphyrins **1-4**.* Choice of the proper organic solvent is central to the outcome of catalytic reactions carried out under aqueous-organic biphasic conditions.[31] On the other hand, solubility of the catalyst in perfluorocarbons is the main concern for reactions carried out under FBS conditions.[5] The presence of four long R_F tails was expected to impart fluorophilic character to porphyrins **1-4**, which should result in decreased solubility in common organic solvents and increased solubility in perfluorocarbons.

It was previously found that porphyrins **29** and **30** (Figure 3) were insoluble in perfluorocarbons.[6] The location of the R_F substituents on the *meso*-phenyl rings strongly affected the solubility of the two ligands in common organic solvents. Porphyrins **29** was sparingly soluble in AcOEt, DMF and ethers, whereas porphyrin **30** was easily solubilized in most organic solvents at concentrations $\leq 10^{-3}$ M. The same trends applied also to the respective Mn(III)-complexes.

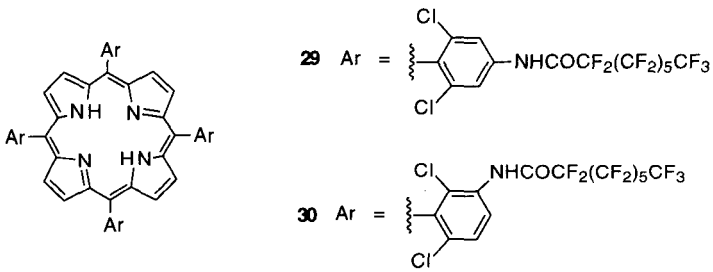


Figure 3. Structure of porphyrins **29** and **30**.

A similar behaviour was observed in the case of porphyrins **1-4**. Compounds **1** and **3** bearing perfluorooctyl chains in the *para*-position of the phenyl rings were sparingly soluble in AcOEt, DMF, $CF_2ClCFCl_2$ and ethers. Compounds **2** and **4** were soluble in solvents ranging from CH_2Cl_2 to hot cyclohexane, even if solubility was quantitatively limited ($< 10^{-2}$ M) as observed for most tetraarylporphyrins. None of the new porphyrins was soluble in perfluorocarbons.

These results strenghten the conclusions we tentatively drew in our previous paper: i) introduction of four C_7 or C_8 perfluoroalkyl tails at the periphery of a tetraarylporphyrin is not sufficient for ensuring solubility in perfluorocarbons;[32] ii) ethers are among the few good solvents for perfluoroalkyl derivatives and the unusual solubility of tetraarylporphyrins **1-4** in ethers (Et_2O, dimethoxyethane and *t*-butyl methyl ether) can be ascribed to the favourable interaction of these solvents with the R_F tails;[33] iii) the lower degree of symmetry of compounds **2**, **4** and **30** with respect to **1**, **3** and **29** is the main reason for the different solubility of these two series of porphyrins in organic solvents. It should be also noted that **4** and **30** were synthesized as mixtures of atropoisomers because of hindered rotation of the aryl groups.[6,34] This feature further prevents π-π interactions among porphyrin rings and the consequent aggregation in solution.[35]

Epoxidation of alkenes under aqueous/organic two-phase conditions. Catalytic activity of Mn-**1** - Mn-**4** was tested in the epoxidation of two model compounds, cyclooctene and dodec-1-ene, which are representative

of easily oxidized and poorly reactive alkenes respectively. Reactions were carried out at 0 °C under aqueous/organic two-phase conditions, using NaOCl as oxygen donor in the presence of N-hexylimidazole as axial ligand for the Mn complexes. The pH of the aqueous solution was adjusted to 10.0 with solid $NaHCO_3$ before starting the reaction.[2b] Yields were determined by gas-chromatographic analysis of the organic phase.

In order to correctly compare the catalytic efficiency of Mn-**1** - Mn-**4** it was necessary to choose a solvent able to dissolve all four Mn-complexes at concentration = 10^{-4} M. Both ethers and AcOEt served this purpose, but previous experiments carried out with Mn-**29** and Mn-**30** had already shown that *t*-butyl methyl ether, the most attractive ether, was unsuitable as the organic phase and ethyl acetate was used. Results obtained are shown in Table 2.

Table 2. Alkene Epoxidations by HOCl/OCl^-: Comparison among Catalysts Mn-**1** - Mn-**4** and Mn-**5**.[a,b]

Entry	Catalyst (P)	Olefin (S)	Time (min)	Yield in Epoxide [c] (%)	Selectivity [c,d] (%)
1	Mn-**1**	Cyclooctene	60 [e]	8	95
2	Mn-**2**	Cyclooctene	60 [e]	5	95
3	Mn-**3**	Cyclooctene	180	35	67
4	Mn-**4**	Cyclooctene	180	90	92
5	Mn-**5**	Cyclooctene	180	80	88
6	Mn-**3**	Dodec-1-ene	180	/	/
7	Mn-**4**	Dodec-1-ene	180	14	72
8	Mn-**5**	Dodec-1-ene	180	15	84

[a] Reaction conditions: T = 0 °C; pH = 10.0, in the presence of N-hexylimidazole (L). $[P]_0 = 1 \times 10^{-4}$ M. Solvent = AcOEt. Molar ratios: S/P = 1000, L/P = 3; NaOCl/S = 2. [b] Average values over 3 runs. [c] Determined by gas-chromatographic analysis of the organic phase. Epoxides were identified by comparison with authentic samples.[d] Selectivity = (moles of epoxide)/(moles of substrate converted). [e] Yields were not increased on longer reaction times.

The presence of bulky *ortho*-chlorine atoms on the phenyl rings turned out to be indispensable for achieving the required resistance of the catalyst: despite the presence of four strong electron-withdrawing R_F chains, Mn-**1** and Mn-**2** were readily degraded under the strong oxidizing conditions employed and poor yields in epoxide were obtained (entries 1, 2).

It was previuosly found that Mn-**29** was a poor catalyst with respect to Mn-**30**.[6] Comparison of data reported in entries 3-8 confirms that the introduction of R_F tails in the *para*-positions of the *meso*-phenyl rings has a negative effect on the catalytic activity of Mn-complexes of perfluoroalkyl-substitued tetraarylporphyrins. The effect is not related to the nature of the bond between R_F and the phenyl ring as previously inferred. Mn-**5**, devoid of R_F substituents, performed much better than catalyst Mn-**3** bearing four R_F substituents in the *para*-positions of the phenyl rings (entries 3, 5 and 6, 8).

The presence of R_F tails in the *meta*-positions did not particularly influence the catalytic activity of Mn-**4**. Reactions carried out in the presence of Mn-**4** (entries 4, 7) gave yields in epoxide similar to those obtained with Mn-**5** (entries 5, 8), except for a small increase in the yield of cyclooctene oxide.

Dichloromethane is commonly used as the organic phase in hydrocarbon oxygenations catalyzed by metallo-tetraarylporphyrins.[31] Further experiments carried out using CH_2Cl_2 instead of AcOEt (Table 3) showed that Mn-**4** was especially active in the epoxidation of the poorly reactive dodec-1-ene (entries 1, 2). The epoxide yield obtained with the pefluoroalkyl-substituted catalyst doubled with respect to that obtained with Mn-**5**, selectivity being also improved. This result could not be related to increased stability of Mn-**4**, because at the end of the reactions UV-Vis measurements showed that both catalysts were degraded to the same extent (60%). It is worth noting that Mn-**5** gave a slightly higher yield in epoxide than Mn-**4** when cyclooctene was examined (entries 3, 4).

Table 3. Alkene Epoxidations by $HOCl/OCl^-$: Comparison between Catalysts Mn-**4** and Mn-**5**.[a,b]

Entry	Catalyst (P)	Olefin (S)	Time (min)	Yield in Epoxide [c] (%)	Selectivity [c,d] (%)
1	Mn-**4**	Dodec-1-ene	360	67	96
2	Mn-**5**	Dodec-1-ene	360	33	69
3	Mn-**4**	Cyclooctene	180	82	100
4	Mn-**5**	Cyclooctene	180	95	100
5	Mn-**4**	Dec-1-ene	360	65	86
6	Mn-**5**	Dec-1-ene	360	54	80
7	Mn-**4**	Hexadec-1-ene	360	63	70
8	Mn-**5**	Hexadec-1-ene	360	18	45
9	Mn-**4**	2-Methylundec-1-ene[e]	180	41	41
10	Mn-**4**	1-Methylcyclohexene[e]	240	15	23
11	Mn-**4**	Norbornene[e]	240	60	60
12	Mn-**4**	4-Chlorostyrene[e]	180	36	36

[a] Reaction conditions: T = 0 °C; pH = 10.0, in the presence of N-hexylimidazole (L). $[P]_0 = 1 \times 10^{-4}$ M. Solvent = CH_2Cl_2. Molar ratios: S/P = 1000, L/P = 3; NaOCl/S = 2. [b] Average values over 3 runs. [c] Determined by gas-chromatographic analysis of the organic phase. Epoxides were identified by comparison with authentic samples or by GC-MS. [d] Selectivity = (moles of epoxide)/(moles of substrate converted). [e] S/P = 500.

Mn-**4** was singularly effective in the epoxidation of other (usually) poorly reactive linear α-alkenes such as dec-1-ene and hexadec-1-ene (entries 5 - 8). This finding was even more striking in the light of the result obtained with 2-methylundec-1-ene (entry 9). Yield and selectivity in the epoxidation of the methyl-substituted

terminal alkene were lower than those observed with dec-1ene and dodec-1-ene, although the opposite usually holds.[2b] Other reactive substrates (entries 10 - 12) were epoxidized less efficiently than terminal alkenes.

The catalytic activity of Mn-**4** and Mn-**5** was also compared in the epoxidation of cyclooctene and dodec-1-ene promoted by 30% H_2O_2 (Table 4). Reactions were carried out at 0 °C in a CH_2Cl_2/H_2O two-phase system, in the presence of N-hexylimidazole and benzoic acid. The pH of the aqueous solution was adjusted to 4.5 with NaOH before starting the reaction.[2b] Only a few robust metallo-tetraarylporphyrins are able to withstand this highly oxidizing environment and to catalyze the oxygen transfer to the substrate.[2a,31] Both Mn-**4** and Mn-**5** belongs to this selected group.

Table 4. Alkene Epoxidations by 30% H_2O_2: Comparison between Catalysts Mn-**4** and Mn-**5**.[a,b]

Entry	Catalyst (P)	Olefin (S)	Time (min)	Yield in Epoxide [c] (%)	Selectivity [c,d] (%)
1	Mn-**4**	Cyclooctene	180	74	88
2	Mn-**5**	Cyclooctene	180	100	100
3	Mn-**4**	Dodec-1-ene	240	35	94
4	Mn-**5**	Dodec-1-ene	240	25	98

[a] Reaction conditions: T = 0 °C; pH = 4.5, in the presence of N-hexylimidazole (L) and benzoic acid (A). $[P]_0 = 1 \times 10^{-4}$ M. Solvent = CH_2Cl_2. Molar ratios: S/P = 1000, L/P = 3; A/P = 4; $H_2O_2/S = 2$. [b] Average values over 3 runs. [c] Determined by gas-chromatographic analysis of the organic phase. [d] Selectivity = (moles of epoxide)/(moles of substrate converted).

As already found for reactions promoted by aqueous NaOCl, the catalyst bearing four R_F tails was less efficient than Mn-**5** in the epoxidation of cyclooctene and gave better results than the latter in the case of dodec-1-ene. However, the relative increase in epoxide yield (+20 %, entries 3,4 Table 4) was much lower than that previously observed (+100 %, entries 1, 2 Table 3).

CONCLUSIONS

For the first time Mn(III)-tetraarylporphyins bearing perfluoroalkyl substituents directly linked on the *meso*-phenyl rings have been synthesized and tested as catalysts in the epoxidation of alkenes. This complements theoretical and XPS studies, which take into account only the electronic effects of peripheral substituents on the porphyrin ring. The mere presence of electro-withdrawing R_F tails do not suffice to enhance the stability and catalytic activity of Mn-**1** - Mn-**4** in the aqueous-organic biphasic systems employed. The location of the R_F tails and the steric protection provided by bulky *ortho*-substituents on the *meso*-phenyl rings are additional factors that effectively rule the performance of these new catalysts. Comparison between the results obtained with Mn-**4**, the best of the perfluoroalkyl-substituted catalysts, and Mn-**5** show that the presence of four R_F tails has a clear beneficial influence only on the epoxidation of poorly reactive linear α-olefins with aqueous NaOCl as oxygen donor and CH_2Cl_2 as solvent.

Stability as well as catalytic efficiency of metallo-tetraarylporphyrins under oxidative conditions are governed by a variety of factors. In addition to steric and electronic effects related to the nature of the ligand, reaction conditions (kind of solvent, use of an excess or defect of oxidant with respect to the substrate, presence of co-catalysts etc.) also play a major role. In our opinion, attempts at drawing conclusions of general validity about the effect of peripheral substitution on the catalytic activity of metallo-tetraarylporphyrins are likely to be deceptive. The experimental behaviour of Mn-**1** - Mn-**4** in the epoxidation of alkenes is in full agreement with this picture.

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EXPERIMENTAL SECTION

UV-VIS spectra were measured using a Lambda 6 Perkin-Elmer spectrometer in Et_2O or CH_2Cl_2 solution. ^{1}H-NMR (300 MHz), ^{13}C-NMR (75.4 MHz) and ^{19}F-NMR (282 MHz) spectra were recorded on a Varian XL 300 spectrometer with tetramethylsilane, $CDCl_3$ (δ = 77) and $CFCl_3$ (δ = 0) as internal standard respectively. Mass spectra were obtained using an Analytical VG 7070 EQ spectrometer. GC analyses were performed on Varian Model 3700 (20 x 0.125 in. OV-101-5% on CHP 100-125 mesh column) and Hewlett-Packard 5890 (30 x 0.5 mm RSL-200 polymethylsiloxane column) gas chromatographs. All the commercially available reagents were used as received; solvents for column chromatography were distilled over $CaCl_2$ before the use. CH_2Cl_2 used in porphyrin syntheses was a "Baker analyzed" reagent (0.01% of water) stabilized with amylene.

*Methyl 4-perfluorooctylbenzoate (**17**).* A few crystals of iodine were added under stirring to a suspension of copper bronze (3.18 g, 50 mmol) in acetone (20 ml). After 30 min the liquid phase was eliminated and the copper washed with HCl in acetone, followed by acetone alone. The activated copper was added to a solution of 4-iodobenzoic acid methylester **16** (2.53 g, 9.6 mmol) in DMF (25 ml). The suspension was heated under stirring at 130 °C and purged with N_2. $C_8F_{17}I$ (3.17 ml, 12 mmol) was dropped into the stirred suspension over 10 min. After 15 h the suspension was cooled at RT. Water (20 ml) and Et_2O (50 ml) were added and the suspension stirred for 30 min. The solid was removed by filtration on a Büchner funnel and washed with Et_2O (3 x 30 ml). The aqueous phase was extracted with Et_2O (20 ml). The combined ether layers were washed with brine (30 ml) and dried over $MgSO_4$. The solvent was evaporated and the residue purified by column chromatography (silica-gel, light petroleum/Et_2O 85/15), affording **17** (4. 28 g, yield = 80%) as colourless solid (mp = 57-59 °C). ^{1}H NMR ($CDCl_3$): δ = 3.94 (s, 3H), 7.67 (d, J = 7.5 Hz, 2H), 8.15 (d, J = 7.5 Hz, 2H); ^{13}C{H} NMR ($CDCl_3$) δ = 52.6, 105-120 (m, C_8F_{17}), 126.9 (t, $J_{C\text{-}F}$ = 6 Hz), 129.8, 133.0 (t, $J_{C\text{-}F}$ = 24 Hz), 133.5, 165.9; ^{19}F NMR ($CDCl_3$) δ = -81.3 (t, J = 10 Hz, 3F), -111.3 (t, J = 13 Hz, 2F), -121.6 (br s, 2F), -122.2 (br s, 2F), -122.4 (br s, 4F), -123.2 (br s, 2F), -126.6 (br s, 2F); Anal. Calcd for $C_{16}H_7F_{17}O_2$: C, 34.68; H, 1.27; F, 58.27. Found: C, 34.42; H, 1.31; F, 57.95.

*(4-perfluorooctylphenyl)methanol (**18**).* A solution of ester **17** (2.49 g, 4.5 mmol) in dry Et_2O (10 ml) was addded, under a N_2 atmosphere, to a suspension of $LiAlH_4$ (114 mg, 3 mmol) in Et_2O (5 ml). This mixture was stirred at RT for 2 h, then AcOEt (1 ml) was added. The solid was removed by filtration, suspended in Et_2O

(10 ml) and H_2O (1 ml) and heated at reflux for 20 min. After removing the salts by filtration the ether layers were combined, washed with brine (10 ml) and dried over $MgSO_4$. The solvent was evaporated and the residue purified by column chromatography (silica-gel, light petroleum/Et_2O 7/3), affording **18** (2.25 g, yield = 95%) as colourless solid (mp = 60-62 °C). ^1H NMR ($CDCl_3$): δ = 1.98 (br s, 1H), 4.72 (s, 2H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H); $^{13}C\{H\}$ NMR ($CDCl_3$) δ = 64.4, 105-120 (m, C_8F_{17}), 126.7, 127.1 (t, J_{C-F} = 6 Hz), 128.1 (t, J_{C-F} = 24 Hz), 145.0; ^{19}F NMR ($CDCl_3$) δ = -81.2 (t, *J* = 10 Hz, 3F), -111.1 (t, *J* = 13 Hz, 2F), -121.7 (br s, 2F), -122.4 (br s, 6F), -123.2 (br s, 2F), -126.6 (br s, 2F); Anal. Calcd for $C_{15}H_7F_{17}O$: C, 34.24; H, 1.34; F, 61.37. Found: C, 34.55; H, 1.27; F, 60.97.

*4-perfluorooctylbenzaldehyde (**11**).* Finely powdered MnO_2 (4.87 g, 56 mmol) was added to a solution of alcohol **18** (2.63 g, 5 mmol) in $CHCl_3$. The mixture was heated at reflux under stirring for 8 h. The solid was filtered off, washed with $CHCl_3$ (3 x 15 ml) and the combined liquid phases were evaporated under reduced pressure. The solid residue was purified by column chromatography (silica-gel, light petroleum/Et_2O 7/3), affording **11** (2.22 g, yield = 85%) as colourless solid (mp = 52-53 °C). ^1H NMR ($CDCl_3$): δ = 7.79 (d, *J* = 8 Hz, 2H), 8.03 (d, *J* = 8 Hz, 2H), 10.12 (s, 1H); $^{13}C\{H\}$ NMR ($CDCl_3$) δ = 105-118 (m, C_8F_{17}), 127.8 (t, J_{C-F} = 6 Hz), 129.7, 134.3 (t, J_{C-F} = 24 Hz), 138.7, 191.1; ^{19}F NMR ($CDCl_3$) δ = -81.2 (t, *J* = 10 Hz, 3F), -112.7 (t, *J* = 14 Hz, 2F), -121.7 (br s, 2F), -122.2 (br s, 4F), -122.4 (m, 2F) -123.2 (br s, 2F), -126.6 (br s, 2F); Anal. Calcd for $C_{15}H_5F_{17}O$: C, 34.38; H, 0.96; F, 61.61. Found: C, 34.02; H, 1.05; F, 61.18.

*5,10,15,20-tetrakis-(4-perfluorooctylphenyl)porphyrin (**1**).* A solution of aldehyde **11** (2.62 g, 5 mmol), pyrrole (0.34 g, 5 mmol) and $BF_3{\cdot}Et_2O$ (0.23 g, 1.65 mmol) in CH_2Cl_2 (500 ml), was stirred at rt for 7 h. After addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.85 g, 3.75 mmol) the reaction mixture was stirred for 2 h, then Et_3N (0.5 ml) was added and the solvent evaporated. The residue was washed with MeOH, dissolved in warm Et_2O and passed through a short pad of neutral Al_2O_3 (eluant Et_2O/light petroleum 9/1). The raw material was chromatographed again (silica-gel, Et_2O/light petroleum 9/1) affording pure **1** as purple-red solid (282 mg, yield = 10 %). ^1H NMR (Et_2O-d_{10}) δ = -1.9 (br s, 2H), 8.11 (d, *J* = 8,4 Hz , 8H), 8.46 (d, *J* = 8,4 Hz, 8H), 8.84 (br s, 8H); ^{19}F NMR (Et_2O-d_{10}) δ = -81.3 (br s, 3F), -111.2 (br s, 2F), -121.4 (m, 2F), -121.8 (m, 2F), -122.2 (m, 4F), -123.1 (m, 2F), -126.6 (m, 2F); UV-Vis (Et_2O) λ_{max} (log ε) = 414 nm (5.45); MS (FAB$^+$): for $C_{76}H_{26}F_{68}N_4$ m/z 2286 (100%); Anal. Calcd for $C_{76}H_{26}F_{68}N_4$: C, 39.92; H, 1.15; F, 56.48, N, 2.45. Found: C, 39.60; H, 1.18; F, 56.03, N, 2.37.

*{Mn(III)-[5,10,15,20-tetrakis-(4-perfluorooctylphenyl)porphyrin]}chloride (Mn-**1**).* A solution of porphyrin **1** (205 mg, 0.09 mmol) in DMF (50 ml) was stirred under reflux with $Mn(OAc)_2{\cdot}4H_2O$ (220 mg, 0.9 mmol) for 7 h. After evaporation of the solvent *in vacuo*, the residue was taken up in Et_2O (50 ml) and filtered. The liquid phase was washed with water (2 x 15 ml), saturated aqueous NaCl (2 x 15 ml) and then dried over $MgSO_4$. After column chromatography (silica-gel, $CHCl_3$/MeOH 9/1) Mn-**1** was obtained as a dark brown powder (165 mg, yield = 71%). UV-Vis (Et_2O) λ_{max} (log ε) = 474 nm (4.90); MS (FAB$^+$): for $[C_{76}H_{24}F_{68}N_4Mn]^+$ m/z 2339 (100%); Anal. Calcd for $[C_{76}H_{24}F_{68}N_4Mn]^+Cl^-$: C, 38.43; H, 1.02; F, 54.38, N, 2.36. Found: C, 38.11; H, 1.11; F, 53.90, N, 2.44.

Methyl 3-perfluorooctylbenzoate (20). Synthesized starting from methyl 3-iodobenzoate **19** according to the procedure described for ester **17**. Yield = 90 %. Colourless solid (mp = 40 °C). ^{1}H NMR ($CDCl_3$): δ = 3.96 (s, 3H), 7.60 - 8.25 (m, 4H); ^{13}C{H} NMR ($CDCl_3$) δ = 52.6, 105-120 (m, C_8F_{17}), 128.1 (t, J_{C-F} = 6 Hz), 129.0, 129.5 (t, J_{C-F} = 24 Hz), 131.0, 131.1, 133.1, 165.8; ^{19}F NMR ($CDCl_3$) δ = -81.2 (t, J = 10 Hz, 3F), -111.3 (t, J = 13 Hz, 2F), -121.7 (br s, 2F), -122.2 (m, 6F), -123.2 (br s, 2F), -126.6 (br s, 2F); Anal. Calcd for $C_{16}H_7F_{17}O_2$: C, 34.68; H, 1.27; F, 58.27. Found: C, 34.35; H, 1.34; F, 57.89.

(3-perfluorooctylphenyl)methanol (21). Synthesized starting from **20** according to the procedure described for alcohol **18**. Yield = 95 %. Colourless solid (mp = 59-60 °C). ^{1}H NMR ($CDCl_3$): δ = 1.82 (t, J = 5.7 Hz, 1H), 4.78 (d, J = 5.7 Hz, 2H), 7.46 - 7.60 (m, 4H); ^{13}C{H} NMR ($CDCl_3$) δ = 64.5, 106-120 (m, C_8F_{17}), 125.0 (t, J_{C-F} = 6 Hz), 126.1 (t, J_{C-F} = 6 Hz), 128.8, 129.0 (t, J_{C-F} = 24 Hz), 130.3, 141.6; ^{19}F NMR ($CDCl_3$) δ = -81.1 (t, J = 10 Hz, 3F), -111.1 (t, J = 14 Hz, 2F), -121.8 (br s, 2F), -122.4 (m, 6F), -123.2 (br s, 2F), -126.6 (br s, 2F); Anal. Calcd for $C_{15}H_7F_{17}O$: C, 34.24; H, 1.34; F, 61.37. Found: C, 34.13; H, 1.39; F, 61.05.

3-perfluorooctylbenzaldehyde (12). Synthesized starting from **21** according to the procedure described for aldehyde **11**. Yield = 82 %. Colourless solid (mp = 50-52 °C). ^{1}H NMR ($CDCl_3$): δ = 7.68 - 8.12 (m, 4H), 10.09 (s, 1H); ^{13}C{H} NMR ($CDCl_3$) δ = 105-119 (m, C_8F_{17}), 128.1, 129.6, 130.3 (t, J_{C-F} = 24 Hz), 132.3, 132.8, 136.8, 190.6; ^{19}F NMR ($CDCl_3$) δ = -81.3 (t, J = 10 Hz, 3F), -111.4 (t, J = 13 Hz, 2F), -121.7 (br s, 2F), -122.3 (m, 6F), -123.2 (br s, 2F), -126.6 (m, 2F); Anal. Calcd for $C_{15}H_5F_{17}O$: C, 34.38; H, 0.96; F, 61.61. Found: C, 34.52; H, 1.01; F, 61.17.

5,10,15,20-tetrakis-(3-perfluorooctylphenyl)porphyrin (2). Synthesized starting from aldehyde **12** and pyrrole, according to the procedure described for porphyrin **1**. Yield = 14 %. ^{1}H NMR ($CDCl_3$) δ = -2.1 (br s, 2H), 7.89 - 8.44 (m , 16H), 8.87 (s, 8H); ^{19}F NMR ($CDCl_3$) δ = -81.2 (t, J = 10 Hz, 3F), -106.7 (t, J = 13 Hz, 2F), -120.0 (br s, 2F), -121.8 (br s, 2F), -122.2 (m, 4F), -123.1 (br s, 2F), -126.6 (br s, 2F); UV-Vis (CH_2Cl_2) λ_{max} (log ε) = 416 nm (5.51); MS (FAB$^+$): for $C_{76}H_{26}F_{68}N_4$ m/z 2286 (100%); Anal. Calcd for $C_{76}H_{26}F_{68}N_4$: C, 39.92; H, 1.15; F, 56.48, N, 2.45. Found: C, 39.71; H, 1.22; F, 56.16, N, 2.49.

{Mn(III)-[5,10,15,20-tetrakis-(3-perfluorooctylphenyl)porphyrin]}chloride (Mn-2). Synthesized according to the general procedure described for Mn-**1**. Yield = 84 %. UV-Vis (CH_2Cl_2) λ_{max} (log ε) = 474 nm (4.94); MS (FAB$^+$): for $[C_{76}H_{24}F_{68}N_4Mn]^+$ m/z 2339 (100%); Anal. Calcd for $[C_{76}H_{24}F_{68}N_4Mn]^+Cl^-$: C, 38.43; H, 1.02; F, 54.38, N, 2.36. Found: C, 38.35; H, 1.09; F, 54.72, N, 2.41.

2,6-dichloro-4-(perfluorooctyl)benzyl acetate (23). Synthesized starting from 2,6-dichloro-4-iodobenzyl acetate **22** [25] according to the procedure described for ester **17**. Yield = 86 %. Colourless solid (mp = 62-63 °C). ^{1}H NMR ($CDCl_3$): δ = 2.09 (s, 3H), 5.38 (s, 2H), 7.56 (s, 2H); ^{13}C{H} NMR ($CDCl_3$) δ = 20.5, 60.7, 105-120 (m, C_8F_{17}), 126.8 (t, J_{C-F} = 6 Hz), 131.5 (t, J_{C-F} = 24 Hz), 135.6, 137.7, 170.4; ^{19}F NMR ($CDCl_3$) δ = -81.3 (t, J = 10 Hz, 3F), -111.7 (t, J = 12 Hz, 2F), -121.8 (m, 4F), -122.3 (m, 4F), -123.2 (br s, 2F), -126.7 (br s, 2F); Anal. Calcd for $C_{17}H_7Cl_2F_{17}O_2$: C, 32.05; H, 1.11; F, 50.69. Found: C, 32.12; H, 1.20; F, 50.46.

*(2,6-dichloro-4-perfluorooctylphenyl)methanol (**24**).* A solution of KOH (0.66 g, 11.7 mmol) in H_2O (2 ml) was added under vigorous stirring to a suspension of acetate **23** (3.82 g, 6 mmol) in EtOH (100 ml). After 4 h most of the solvent was eliminated by evaporation under reduced pressure. Upon addition of 10% aqueous HCl to the residue, a pale yellow solid precipitated. The solid was dissolved in CH_2Cl_2 and the solution was washed with brine and dried over $MgSO_4$. The solvent was evaporated affording **24** (3.23 g, yield = 90%) as colourless solid (mp = 130 °C). ^{1}H NMR ($CDCl_3$): δ = 1.95-2.15 (br s, D_2O exchange, 1H), 4.98 (s, 2H), 7.55 (s, 2H); ^{13}C{H} NMR ($CDCl_3$) δ = 59.9, 108-115 (m, C_8F_{17}), 126.9 (t, $J_{C\text{-}F}$ = 6 Hz), 130.8 (t, $J_{C\text{-}F}$ = 24 Hz), 136.7, 139.5; ^{19}F NMR ($CDCl_3$) δ = -81.3 (t, J = 10 Hz, 3F), -111.7 (t, J = 12 Hz, 2F), -121.8 (m, 4F), -122.4 (m, 4F), -123.2 (br s, 2F), -126.6 (br s, 2F); Anal. Calcd for $C_{15}H_5Cl_2F_{17}O$: C, 30.28; H, 0.85; F, 54.27. Found: C, 30.03; H, 0.91; F, 53.98.

*2,6-dichloro-4-perfluorooctylbenzaldehyde (**13**).* Synthesized starting from **24** according to the procedure described for aldehyde **11**. Yield = 70 %. Colourless solid (mp = 60 °C). ^{1}H NMR ($CDCl_3$): δ = 7.60 (s, 2H), 10.46 (s, 1H); ^{13}C{H} NMR ($CDCl_3$) δ = 105-120 (m, C_8F_{17}), 128.1 (t, $J_{C\text{-}F}$ = 6 Hz), 133.6, 134.0 (t, $J_{C\text{-}F}$ = 24 Hz), 137.1, 187.7; ^{19}F NMR ($CDCl_3$) δ = -81.3 (t, J = 10 Hz, 3F), -111.8 (t, J = 12 Hz, 2F), -121.8 (m, 4F), -122.3 (m, 4F), -123.1 (br s, 2F), -126.6 (br s, 2F); Anal. Calcd for $C_{15}H_3Cl_2F_{17}O$: C, 30.38; H, 0.51; F, 54.45. Found: C, 30.15; H, 0.62; F, 54.17.

*5,10,15,20-tetrakis-(2,6-dichloro-4-perfluorooctylphenyl)porphyrin (**3**).* Condensation of aldehyde **13** (1.75 g, 3 mmol) and pyrrole (0.20 g, 3 mmol) was carried out as described for porphyrin **1**. The solid obtained was chromatographed twice (neutral Al_2O_3, Et_2O/light petroleum 9/1, then silica-gel, light petroleum/AcOEt 95/5). To the crude porphyrin (95 mg) dissolved in MeOH/$CHCl_3$ 1/4 (50 ml), $Zn(OAc)_2{\cdot}2H_2O$ (15 mg) was added. The mixture was refluxed for 8 h. The solvent was evaporated under reduced pressure and the residue was purified by column-chromatography (silica-gel, light petroleum/AcOEt 95/5) affording 45 mg of **3** under the form of zinc complex (Zn-**3**, yield = 2.3 %). ^{1}H NMR (CF_3COOD) δ = 7.89 (s, 8H), 8.57 (s , 8H); UV-Vis (AcOEt) λ_{max} (log ε) = 423 nm (4.59); ^{19}F NMR (Et_2O-d_{10}) δ = -81.3 (br s, 3F), -111.1 (br s, 2F), -121.6 (m, 2F), -122.3 (m, 6F), -123.2. (br s, 2F), -126.4 (br s, 2F); Anal. Calcd for $(C_{76}H_{16}Cl_8F_{68}N_4)Zn$: C, 34.77; H, 0.61; F, 49.19; N, 2.13. Found: C, 34.48; H, 0.75; F, 48.91; N, 2.02.

Zn-**3** was dissolved in CF_3COOH (2 ml) and stirred at RT for 2 h. The acid was eliminated by evaporation in vacuum. The residue was dissolved in $CF_2ClCFCl_2$ (5 ml), washed with H_2O (5 ml), 10% aqueous $NaHCO_3$ (5 ml) and H_2O (5 ml) and dried over $MgSO_4$. Pentane was added dropwise to the solution until porphyrin **3** started to precipitate. 35 mg of purple solid was recovered by filtration of the suspension (yield based on **13** = 1.8 %). UV-Vis (AcOEt) λ_{max} (log ε) = 419 nm (5.54); MS (FAB$^+$): for $C_{76}H_{18}Cl_8F_{68}N_4$ m/z 2563 (100%).

*{Mn(III)-[5,10,15,20-tetrakis-(2,6-dichloro-4-perfluorooctylphenyl)porphyrin]} chloride (Mn-**3**).* Synthesized according to the general procedure described for Mn-**1**. Yield = 65 %. UV-Vis (AcOEt) λ_{max} (log ε) = 478 nm (4.71); MS (FAB$^+$): for $[C_{76}H_{16}Cl_8F_{68}N_4Mn]^+$ m/z 2613 (100%); Anal. Calcd for $[C_{76}H_{16}Cl_8F_{68}N_4Mn]^+Cl^-$: C, 34.44; H, 0.61; F = 48.73; N, 2.11. Found: C, 34.31; H, 0.68; F, 48.49; N = 2.06.

2,6-dichloro-3-nitrotoluene (25). A solution of 2,6-dichlorotoluene (6.44 g, 40 mmol) in CH_2Cl_2 (40 ml) was cooled at 5 °C and 96% H_2SO_4 (37 g, 225 mmol) was added. To the vigorously stirred mixture 95% HNO_3 (2.7 g, 40 mmol) was added at such a rate that the temperature remained below 5 °C. The temperature was allowed to rise to 20 °C. After 2 h stirring was stopped and the two layers were separated. The inorganic layer was extracted with CH_2Cl_2 (40 ml). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column-chromatography (silica-gel, light petroleum/Et_2O 95/5) affording **25** (7.82 g, yield = 95%) as colourless solid (mp = 53 °C). ^1H NMR ($CDCl_3$): δ = 2.55 (s, 3H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H); Anal. Calcd for $C_7H_5Cl_2NO_2$: C, 40.81; H, 2.45; N, 6.80. Found: C, 40.75; H, 2.49; N, 6.72.

2,4-dichloro-3-methylaniline (26). A mixture of **25** (2.06 g, 10 mmol) and $SnCl_2{\cdot}2H_2O$ (11.3 g, 50 mmol) in absolute ethanol (40 ml) was stirred under N_2. During the exothermic reduction temperature was kept below 25 °C. After 2 h the mixture was poured onto ice, the pH was raised to 8 by addition of 10% aqueous $NaHCO_3$ and the slurry was extracted with CH_2Cl_2 (4 x 50 ml). The organic layers were collected, washed with brine and dried over Na_2SO_4. Evaporation of the solvent afforded 3.25 g of pure **26** (mp = 50 °C, yield = 92%). ^1H NMR ($CDCl_3$): δ = 2.41 (s, 3H), 3.98 (br s, 2H), 6.52 (d, *J* = 8.6 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H); Anal. Calcd for $C_7H_7Cl_2N$: C, 47.76; H, 4.01; N, 7.96. Found: C, 47.88; H, 3.95; N, 7.83.

2,6-dichloro-3-iodotoluene (27). Aniline **26** (3.52 g, 20 mmol) was suspended in 36% HCl (5.7 ml) and H_2O (5.8 ml) and cooled at 0 °C. A solution of $NaNO_2$ (1.43 g, 21 mmol) was added dropwise while stirring, keeping the temperature of the mixture below 5 °C. After 10 min a solution of KI (3.48 g, 21 mmol) in H_2O (3.7 ml) was slowly added to the suspension. When N_2 evolution settled the mixture was warmed at 50 °C for 15 min, then cooled to RT and made alkaline with saturated $NaHCO_3$. The dark brown slurry was extracted with CH_2Cl_2 (4 x 20 ml). The combined organic phases were washed with 5% aqueous $NaHSO_3$, brine and dried over $MgSO_4$. Evaporation of the solvent afforded a dark paste that was purified by column chromatography (silica-gel, light petroleum) to give 4.02 g of pure **27** (colourless oil, yield = 70 %). ^1H NMR ($CDCl_3$): δ = 2.54 (s, 3H), 6.97 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H); $^{13}C\{H\}$ NMR ($CDCl_3$) δ = 19.8, 96.6, 128.7, 135.5, 135.9, 137.6, 139.4.

2,6-dichloro-3-perfluorooctyltoluene (28). Synthesized starting from **27** according to the procedure described for ester **17**. Yield = 50 %. Colourless solid (mp = 42 °C). ^1H NMR ($CDCl_3$): δ = 2.55 (s, 3H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1H); $^{13}C\{H\}$ NMR ($CDCl_3$) δ = 18, 106-120 (m, C_8F_{17}), 125.6 (t, $J_{C\text{-}F}$ = 23 Hz), 127.5, 127.7 (t, $J_{C\text{-}F}$ = 9 Hz), 134.9, 137.4, 139.6; ^{19}F NMR ($CDCl_3$) δ = -81.3 (t, *J* = 10 Hz, 3F), -106.8 (t, *J* = 14 Hz, 2F), -120.3 (br s, 2F), -122.2 (m, 6F), -123.2 (br s, 2F), -126.6 (br s, 2F); Anal. Calcd for $C_{15}H_5Cl_2F_{17}$: C, 31.12; H, 0.87; F, 55.77. Found: C, 31.03; H, 0.94; F, 55.58.

2,6-dichloro-3-(perfluorooctyl)benzyl acetate (29). A suspension of **28** (3.62 g, 6.2 mmol), *N*-bromosuccinimide (1.21 g, 6.8 mmol), dibenzoyl peroxide (10 mg) in CCl_4 (30 ml) was stirred under irradiation with a 100 W lamp for 7 h. After cooling to RT the solid succinimide was filtered off and washed with CCl_4 (2 x 20 ml). The combined liquid phases were evaporated under reduced pressure. The colourless solid containing mostly 2,6-dichloro-3-(perfluorooctyl)benzyl bromide was dissolved in CH_3CN (100 ml) and treated with

CH_3COOK (2.64 g, 26.4 mmol) in the presence of $Bu_4N^+HSO_4^-$ (0.15 g, 0.4 mmol). The suspension was stirred at RT for 4 h. The solid was filtered off, washed with Et_2O (30 ml) and the filtrate evaporated in vacuum to give pure **29** (3.80 g, yield = 96%) as colourless solid (mp = 73-75 °C). ^1H NMR ($CDCl_3$): δ = 2.13 (s, 3H), 5.48 (s, 2H), 7.52 (d, J = 8.7 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H); $^{13}C\{H\}$ NMR ($CDCl_3$) δ = 20.6, 61.2, 105-117 (m, C_8F_{17}), 126.7, 128.3, 131.2, 134.2, 136.8, 141.3, 170.6; ^{19}F NMR ($CDCl_3$) δ = -81.3 (t, J = 10 Hz, 3F), -106.9 (t, J = 15 Hz, 2F), -120.2 (br s, 2F), -122.1 (m, 6F), -123.2 (br s, 2F), -126.6 (br s, 2F); Anal. Calcd for $C_{17}H_7Cl_2F_{17}O_2$: Anal. Calcd for $C_{17}H_7Cl_2F_{17}O_2$: C, 32.05; H, 1.11; F, 50.69. Found: C, 31.85; H, 1.19; F, 50.39.

*(2,6-dichloro-3-perfluorooctylphenyl)methanol (**30**).* Synthesized starting from **29** according to the procedure described for alcohol **24**. Yield = 90 %. Colourless solid (mp = 82 °C). ^1H NMR ($CDCl_3$): δ = 2.13 (t, J = 7 Hz, 1H), 5.04 (d, J = 7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 1H), 7.52 (d, J = 8.7 Hz, 1H); $^{13}C\{H\}$ NMR ($CDCl_3$) δ = 60.3, 108-120 (m, C_8F_{17}), 126.4 (t, $J_{C\text{-}F}$ = 24 Hz), 128.1, 130.3 (t, $J_{C\text{-}F}$ = 8 Hz), 135.6, 138.3, 140.3; ^{19}F NMR ($CDCl_3$) δ = -81.2 (t, J = 10 Hz, 3F), -106.8 (t, J = 15 Hz, 2F), -120.3 (br s, 2F), -122.1 (m, 6F), -123.2 (br s, 2F), -126.6 (m, 2F); Anal. Calcd for $C_{15}H_5Cl_2F_{17}O$: C, 30.28; H, 0.85; F, 54.27. Found: C, 30.14; H, 0.93; F, 54.02.

*2,6-dichloro-3-perfluorooctylbenzaldehyde (**14**).* Synthesized starting from **29** according to the procedure described for aldehyde **11**. Yield = 81 %. Colourless solid (mp = 72-73 °C). ^1H NMR ($CDCl_3$): δ = 7.51 (d, J = 8.7 Hz, 1H), 7.69 (d, J = 8.7 Hz, 1H), 10.42 (s, 1H); $^{13}C\{H\}$ NMR ($CDCl_3$) δ = 106-120 (m, C_8F_{17}), 126.8 (t, $J_{C\text{-}F}$ = 23 Hz), 129.6, 133.1 (t, $J_{C\text{-}F}$ = 8 Hz), 134.2, 135.7, 139.2, 188.2; ^{19}F NMR ($CDCl_3$) δ = -81.3 (t, J = 10 Hz, 3F), -106.8 (t, J = 14 Hz, 2F), -120.3 (br s, 2F), -121.9 (m, 6F), -123.8 (br s, 2F), -126.6 (br s, 2F); Anal. Calcd for $C_{15}H_3Cl_2F_{17}O$: C, 30.38; H, 0.51; F, 54.45. Found: C, 30.41; H, 0.58; F, 54.23.

*5,10,15,20-tetrakis-(2,6-dichloro-3-perfluorooctylphenyl)porphyrin (**4**).* Synthesized starting from aldehyde **14** and pyrrole, according to the procedure described for porphyrin **1**. Yield = 15 %. ^1H NMR ($CDCl_3$) δ = -2.52 (br s, 2H), 7.94 (d, J = 8.7 Hz , 4H), 8.05 (d, J = 8.7 Hz , 4H), 8.59 (s, 8H); ^{19}F NMR ($CDCl_3$) δ = -81.2 (t, J = 10 Hz, 3F), -106.7 (t, J = 14 Hz, 2F), -120.8 (m, 2F), -122.0 (m, 6F), -123.1 (br s, 2F), -126.5 (m, 2F); UV-Vis (CH_2Cl_2) λ_{max} (log ε) = 418 nm (5.55); MS (FAB^+): for $C_{76}H_{18}Cl_8F_{68}N_4$ m/z 2563 (100%); Anal. Calcd for $C_{76}H_{18}Cl_8F_{68}N_4$: C, 35.63; H, 0.71; F, 50,41; N, 2.08. Found: C, 35.30; H, 0.79; F, 50,16; N, 2.23.

*{Mn(III)-[5,10,15,20-tetrakis-(2,6-dichloro-3-perfluorooctylphenyl)porphyrin]} chloride (Mn-**4**).* Synthesized according to the general procedure described for Mn-**1**. Yield = 62 %. UV-Vis (CH_2Cl_2) λ_{max} (log ε) = 478 nm (4.95); MS (FAB^+): for $[C_{76}H_{16}Cl_8F_{68}N_4Mn]^+$ m/z 2613 (100%); Anal. Calcd for $[C_{76}H_{16}Cl_8F_{68}N_4Mn]^+Cl^-$: C, 34.44; H, 0.61; F = 48.73; N, 2.11. Found: C, 34.25; H, 0.71; F, 48.52; N = 2.15.

General procedure for the epoxidation of alkenes.

Reactions were carried out in a 20 ml flask equipped with a teflon lined screw cap and magnetic stirrer, maintained at 0 ± 0.2 °C with circulating ethanol by means of a Haake F3 Cryostat. Stirring was maintained at the

maximal rate achievable (1300 ± 50 rpm) in order to ensure the best contact between the organic and the aqueous phase. The flask was charged with: (i) 1 ml of a 2.0 x 10^{-4} M solution of Mn(III)-porphyrin in the proper organic solvent; (ii) 1 ml of a 0.2 M solution of alkene in the same solvent, containing either tetradecane or 1,2-dichlorobenzene (0.025 M) as internal standard for gas-chromatography; (iii) 15 µl of a 4.0 x 10^{-2} M solution of N-hexylimidazole in CH_2Cl_2. The solution was stirred 5 min, then 0.57 ml of NaOCl 0.7 M (or 40 µl of 30% H_2O_2) was added to the flask. The pH of NaOCl was previously adjusted to 10.0 with solid $NaHCO_3$ (the pH of 30% H_2O_2 was previously adjusted to 4.5 with NaOH and benzoic acid). The mixture was stirred and samples were taken at different times and analysed by G.C..

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