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Synthesis of new sterically hindered porphyrins and their corresponding manganese(III) derivatives. Potential catalysts for oxidation reactions by ozone†

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Summary — The synthesis and characterization of new dodecaarylporphyrin derivatives as well as their manganese(III) complexes are described. A study of the catalytic ability of these sterically hindered porphyrins in oxidation reactions by ozone is reported and preliminary results on epoxidation reaction of stilbene are described.

hindered porphyrin / manganese / ozone / catalysis / oxidation reaction

Résumé — Synthèse de nouvelles porphyrines stériquement encombrées et de leurs complexes du manganèse(III). Catalyseurs potentiels de réactions d'oxydation par l'ozone. *La synthèse et la caractérisation de nouvelles dodécaarylporphyrines et de leurs complexes de manganèse sont décrites. L'intérêt de ces ligands porphyriniques stériquement encombrés dans des réactions d'oxydation par l'ozone est démontré. Des résultats préliminaires relatifs à l'époxydation du stilbène sont décrits.*

porphyrine encombrée / manganèse / ozone / catalyse / réaction d'oxydation

Introduction

Metalloporphyrins have been widely used as catalysts and several reports have focused on the epoxidation of olefins and hydroxylation of alkanes [1]. Numerous oxidation reactants have been used such as PhIO, NaOCl, O_2, H_2O_2 [1], peroxides as well as other oxygen atom donors [1].

The 'first generation' metalloporphyrin catalysts for oxidation reactions developed by JT Groves et al [2], ie, Fe(TPP)Cl and Mn(TPP)Cl (for definition of TPP see [3]), appeared to be unstable under the oxidizing conditions of the reaction. Later, Traylor and Dolphin [4] showed that the presence of electron-withdrawing or bulky substituents at the *ortho*, *ortho'* positions of the *meso* phenyl rings of tetraarylporphyrins increased the stability of the macrocycle towards oxidation reagents. Moreover, it has been observed that the catalytic activity of iron and manganese porphyrins of the type Mn(TDCPP)Cl, Fe(TDCPP)Cl, Mn(TMP)Cl and Fe(TMP)Cl (for definition of TDCPP and TMP see [3]) is strongly increased compared to the TPP complexes [5]. These 'second generation' catalysts are the precursors to more robust porphyrins. Traylor and Tsuchiya [6] reported the synthesis and reactivity of a 'third generation' metalloporphyrin catalyst bearing bromine atoms at the β-pyrrole positions. These compounds exhibit a higher stability towards oxidation and have been found to be better catalysts than the first and second generation complexes [7a-c]. However, recent studies have shown that a partial decomposition occurs under certain experimental conditions [8a,b]. The higher reactivity of these catalysts has been explained by their saddle-shaped structure which favors an alternative approach of the substrate to the metal-oxo site [7].

Our recent goal in this field is to find evidence for possible interactions between ozone and organometallic systems like metalloporphyrins. The high oxidation potential as well as the characteristic electrophilic attack of ozone on electron-rich double bonds generally leads to the destruction of regular porphyrins. This behavior of ozone incited us to synthesize metalloporphyrin catalysts possessing electron-deficient β-pyrrole double bonds.

To our knowledge, two reports have mentioned the use of metalloporphyrins catalysts in oxidation reactions by ozone. A few years ago DT Sawyer et al reported oxidation reactions with ozone at low temperature (−35 °C) using Fe(TDCPP)Cl as a

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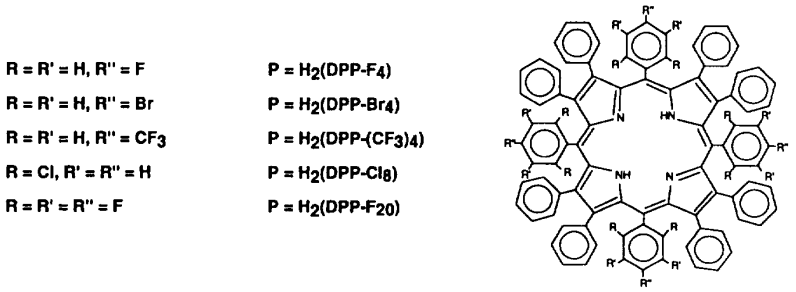

Fig 1. Synthesized dodecaphenylporphyrin derivatives.

catalyst. No degradation of the metalloporphyrin was observed by these authors [9]. More recently, Meunier et al [10] used ozone as an oxygen atom donor in olefin epoxidation reactions catalyzed by iron and manganese porphyrins; Mn(TMP)Cl and Mn(TDCPP)Cl catalysts were systematically destroyed by ozone while the β-octabrominated tetramesitylporphyrin, Mn(Br_8TMP)Cl is resistant.

Owing to the high stability of octabrominated derivatives, similar porphyrins, bearing chlorine, fluorine or sulfonate groups as β-pyrrole protective groups, were synthesized and used as catalysts for oxidation reactions using various oxygen atom donors [11].

Furthermore, porphyrins substituted at β-pyrrole positions and *meso* positions by phenyl groups (generic name: dodecaphenylporphyrins) have been recently reported and fully characterized [12]. They present the same saddle-shaped conformation of the macrocycle as the β-halogenated porphyrins. The electroattractive character of the phenyl groups at β-pyrrole positions should prevent the electrophilic attack of ozone and therefore these derivatives are a priori good candidates for catalysis of oxidation reactions by ozone. We have synthesized various dodecaarylporphyrins bearing differently substituted *meso* phenyl groups and their corresponding Mn(III) complexes. Only the base complex Mn(DPP)Cl (for definition of DPP see ref 3) is fully destroyed by ozone. We report here the synthesis and characterization of this series of free bases as well as their chloromanganese(III) derivatives. Preliminary results on the epoxidation reaction of stilbene with ozone catalyzed by Mn(DPP-F_{20})Cl [3] are also reported.

Results and discussion

Synthesis of porphyrins

The synthesis of 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrin, H_2(DPP), was performed according to a previously described procedure [13]. More sterically hindered dodecaarylporphyrins, H_2(DPP-Cl_8) and H_2(DPP-F_{20}) were also synthesized according to the literature [14]. The new free base H_2(DPP-$(CF_3)_4$) was prepared according a similar procedure by condensation of 3,4-diphenylpyrrole [15] with an equivalent of the corresponding aldehyde in refluxing acetic acid for 1 day followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The yield of the reaction is close to 12% (see *Experimental section*). The bases H_2(DPP-F_4) and H_2(DPP-Br_4) were synthesized by condensation of 3,4-diphenylpyrrole with an equivalent of the corresponding aldehyde in dichloromethane followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in refluxing toluene [13]. The yield of the reaction is close to 50% (see *Experimental section*).

All these free base porphyrins were metallated with manganese(II) chloride tetrahydrate in refluxing DMF or benzonitrile. Manganese complexes, Mn(DPP)Cl, Mn(DPP-F_4)Cl, Mn(DPP-Br_4)Cl, Mn(DPP-$(CF_3)_4$)Cl, Mn(DPP-Cl_8)Cl and Mn(DPP-F_{20})Cl, were obtained after purification on an alumina column with a good yield (ca 65%, see *Experimental section*).

Mass spectrometry

All the compounds were characterized by mass spectrometry. The molecular ion is the parent peak for the free bases whereas the loss of the chlorine ion is observed for the manganese complexes. Indeed for all the chloro manganese complexes the parent peak is the $M(P)^+$ ion. The loss of the anionic axial ligand is often observed in mass spectra of metalloporphyrins in LSIMS mode using 3-nitrobenzyl alcohol as a matrix [16]. Mass spectral data are reported in the *Experimental section.*

UV-visible

As previously stated, dodecaphenylporphyrins with electron-withdrawing and bulky phenyl groups at β-pyrrole positions present a saddle-shaped conformation similar to that of the β-pyrrole perhalogenated porphyrins.

Recent theoretical calculations have shown how the electronic and steric properties of the β-pyrrole substituents modify the orbital energy diagrams [17]. On the one hand, the distortion of the macrocycle induces a red shift of the absorptions resulting from HOMO and LUMO energy changes: HOMO and LUMO energies increase but HOMO orbitals are more destabilized than the LUMOs. On the other hand, these calculations have shown that the increase of the electronegativity of the β-pyrrole groups induces the same stabilization for the HOMOs and LUMOs and therefore no further modification of the electronic spectra results. The UV-visible spectra of dodecaphenylporphyrins exhibit the same characteristics (see fig 2) which can be explained in the same way. UV-visible data of free bases and manganese(III) derivatives are set forth in table I.

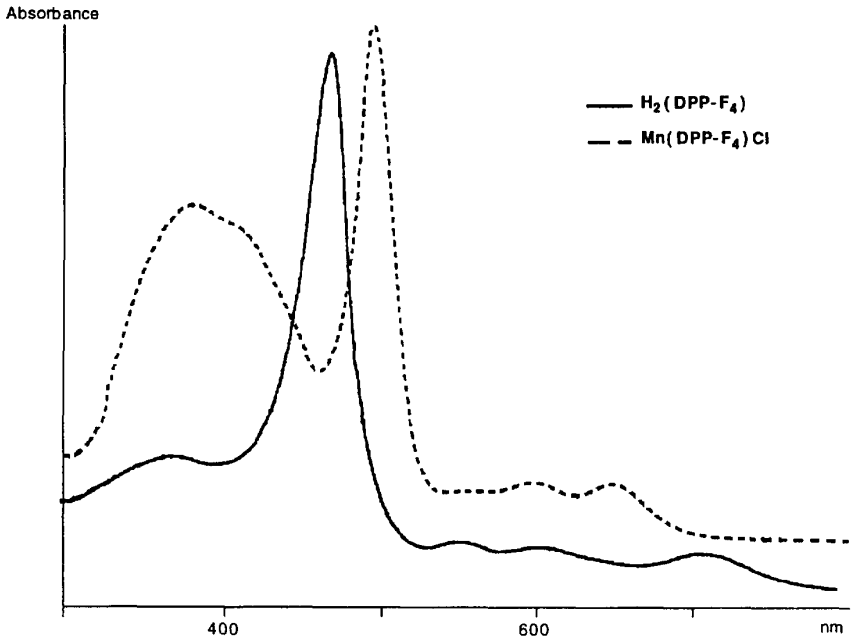

Fig 2. UV-visible spectra of H_2(DPP-F_4) and Mn(DPP-F_4)Cl.

Table I. UV-visible data for the synthesized derivatives.

Compound	λ *nm* (ε, $L \times mol^{-1} \times cm^{-1} \times 10^{-3}$)
H_2(DPP-Br_4)	465 (228), 559 (14.7), 612 (13.9), 716 (8.1)
H_2(DPP-F_4)	464 (165), 560 (10.2), 612 (9.4), 716 (5.9)
H_2(DPP-$(CF_3)_4$)	462 (141), 556 (9.1), 606 (7.7), 709 (10.3)
Mn(DPP)Cl	389 (49.4), 502 (81.2), 603 (8.8), 653 (9)
Mn(DPP-Br_4)Cl	385 (62.5), 501 (111), 602 (11.1), 653 (12)
Mn(DPP-F_4)Cl	385 (56), 500 (93), 601 (10), 651 (10.4)
Mn(DPP-$(CF_3)_4$)Cl	386 (55), 498 (84.6), 599 (10), 651 (9.5)
Mn(DPP-Cl_8)Cl	379 (51.6), 504 (70.1), 604 (12)
Mn(DPP-F_{20})Cl	375 (59.4), 482 (61.3), 586 (13.2), 632 (9.4)

Electronic spectra of the studied free bases present the expected red-shifted Soret and Q bands which range from 462 to 465 nm and from 606 to 716 nm, respectively. The spectra of the chloromanganese complexes exhibit a hyperporphyrin pattern as observed for Mn(III) porphyrins [18]. However, a red shift of all the absorption bands was observed in comparison with regular Mn(III) tetraarylporphyrins. Moreover, the absorption bands of the Mn(DPP-F_{20})Cl complex are slightly blue shifted with respect to the Mn(DPP)Cl derivative (see table I). Such a shift has previously been noticed for Zn(DPP-F_{20}) [14]; this was explained either by reduced intramolecular interactions between *meso* phenyl groups and the other phenyl substituents of the macrocycle leading to less ring distortion or by a greater stabilization of the HOMOs compared to the LUMOs.

This stabilization is due to the presence of the fluorine atoms on the *meso*-phenyl groups. It is interesting to note that the *para* withdrawing group of the *meso*-phenyl Mn(DPP-F_4)Cl, Mn(DPP-Br_4)Cl, Mn(DPP-$(CF_3)_4$)Cl derivatives does not lead to a significant blue shift of the absorption bands when compared to Mn(DPP)Cl (see table I).

^1H *NMR*

The ^{1}H NMR spectra of the three newly synthesized free-bases exhibit classical features [14]. The signals of the *meso* phenyl protons are well defined and the *ortho* protons are the more deshielded. The deshielding of the *ortho* protons increases as expected with the electron-withdrawing effect of the *para* substituent along the sequence *p*-CF_3 > *p*-F > *p*-Br. The *meta* protons are located at 6.96, 6.82 and 6.39 ppm for *p*-F, *p*-Br and *p*-CF_3 derivatives, respectively. These shifts are in agreement with the resonance effect normally induced on the *meso* phenyl rings by the F and Br atoms. A further coupling between *o*-H, *m*-H and the fluorine atom is noted as expected for *p*-fluoro derivative. The β-phenyl protons cannot be unambiguously assigned since the signal appears in a narrow range (6.7–6.9 ppm).

The spectra of the manganese(III) derivatives are difficult to interpret since the paramagnetism of the metal ion induces a large broadening of all the resonance signals. Nevertheless signals appear in the range 5–9 ppm, which is in accordance with previous data reported for chloromanganese tetraarylporphyrin derivatives [19]. These signals can be attributed to *meso* phenyl protons resonance. No supposition can be made about the β-phenyl protons, which can appear in the same region or as broad signals which overlap with the noise.

Epoxidation reactions

All the manganese(III) complexes were exposed to ozone in methylene chloride solution. No significant degradation of the complex was observed, except for Mn(DPP)Cl which was fully destroyed. For the resistant compounds, the removal of ozone from the solution led

to the starting Mn(III) derivative. Preliminary epoxidation reactions were achieved with Mn(DPP-F_{20})Cl. The catalytic epoxidation of stilbene was carried out following a procedure similar to that reported by Meunier et al [10].

The results are given in table II and compared to those of Meunier et al, who reported the catalytic formation of epoxide with a 14% yield (turnover 5) for *trans*-stilbene and a 34% yield (turnover 39) for the *cis*-stilbene. In the presence of our catalyst and pyridine, and under an O_3/O_2 atmosphere (35 g/m^3), the reaction epoxidation of *trans*-stilbene gave only *trans*-stilbene oxide (7% yield and turnover 7) whereas *cis*-stilbene epoxidation reaction led to *cis* and *trans*-stilbene oxide (20% overall yield and turnover 18). This result requires a *cis/trans* inversion involving radical intermediates [21]. Another experiment under the same ozone/dioxygen mixture without catalyst led to the formation of aldehydes and carboxylic acids as the sole reaction products. In the same experimental conditions but only under dioxygen the blank showed that no epoxidation occurs. It is interesting to note that in the absence of pyridine as sixth ligand on the manganese atom, aldehydes and carboxylic acids are formed rather than epoxide. This work and previous reports [20] indicate that whatever the oxidizing species is, the presence of a sixth axial ligand such as pyridine or imidazole favors epoxidation reactions when manganese porphyrins are used as catalysts.

Table II. Stilbene epoxidation by O_3 catalyzed by Mn(DPP-F_{20})Cl in the presence of pyridine[a].

Olefin	*Catalyst versus olefin*[b]	*Molar ratio pyridine/ catalyst*	*Epoxide yield*[c] *(%)*	*Turnover*[d]
trans-Stilbene	1	16.5	7	7
cis-Stilbene	1.1	30	18 (*cis*) + 2 (*trans*)	18

[a] Reaction time: 20 min; [b] in moles for 100 moles of olefin; [c] based on olefin; [d] molar ratio epoxide/catalyst.

Further experiments will be run to improve reaction conditions and catalyst efficiency. Other substrates will be used to confirm the ability of O_3 to epoxidize olefins.

This paper reports the possible use of manganese(III)-substituted dodecaarylporphyrins as oxidation reaction catalysts in presence of ozone. Morever, this work shows that these derivatives are easily synthesized compared to β-halogenated porphyrins. These highly stable complexes should be also remarkable models to elucidate the key oxidized intermediate species of the catalytic cycle. As a further development of this work, we propose the use of this new series of complexes in the hydroxylation reaction of alkanes by ozone.

Experimental section

Instrumentation

UV-visible spectra were obtained with a Varian Cary I spectrophotometer. Infrared spectra of solid samples were obtained as a 1% dispersion in CsI using a Bruker IFS 66 V FTIR spectrophotometer.

^{1}H NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer of the Centre de Spectrométrie Moléculaire at the Université de Bourgogne. Spectra were recorded in 0.5 mL of $CDCl_3$ using tetramethylsilane as an internal reference.

Mass spectra were obtained using a Kratos Concept 32 S of the Centre de Spectrométrie Moléculaire at the Université de Bourgogne in the LSIMS mode (liquid secondary ion mass spectrometry).

GC/MS analyses were performed with a Hewlett Packard 5972A equipped with a HP-FFAP (Crosslinked FFAP) 50 m × 0.2 mm × 0.3 μm capillary column. Ozone was generated by an ozonizer Labo/LO2 Trailigaz (oxygen stream: 25 mL/min; current intensity 0.4 A; ozone concentration 35 g/m^3 or 0.73 mM).

Catalytic experiments were carried out in a Schlenk tube at room temperature: 750 μmol of *trans*-stilbene, 7.5 μmol of Mn(DPP-F_{20})Cl and 125 μmol of pyridine were stirred in 5 mL dichloromethane and 310 μmol ozone was bubbled through the solution; 750 μmol *cis*-stilbene, 8.5 μmol Mn(DPP-F_{20})Cl and 250 μmol pyridine were stirred in 5 mL dichloromethane and 625 μmol ozone was bubbled through the solution.

Materials

Chemicals were from Acros Chemica. Acetic acid, DMF, dichloromethane, toluene, pyridine and benzonitrile were purchased from SDS, 13124 Peypin, France and used as received.

meso-*Tetrakis(4-fluorophenyl)octaphenylporphyrin*

A solution of 3,4-diphenylpyrrole (4.56 mmol, 1 g) and 4-fluorobenzaldehyde (4.56 mmol, 0.49 mL) in 500 mL of dichloromethane was purged with N_2 for 10 min and boron trifluoride etherate (1.67 mmol, 0.21 mL) was added. The condensation reaction was performed at room temperature for 24 h until the solution turned dark purple. After evaporation of the solvent, the mixture was refluxed 2 h with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (3.7 mmol, 840 mg) in 250 mL toluene. Triethylamine (3.6 mmol, 0.5 mL) was added at room temperature to reduce the protonated porphyrin. After evaporation of the solvent, the crude product was purified by two successive columns on basic alumina. Elution with a dichloromethane/heptane 50:50 mixture gave the desired porphyrin. The partial evaporation of the solvent and then addition of pentane led to the precipitation of the porphyrin. After filtration 710 mg (48% yield) of H_2(DPP-F_4) was obtained.

^{1}H NMR ($CDCl_3$): δ (ppm) : 7.48 (8H, dd, J_{HH}: 8.5 Hz, J_{HF}: 6.5 Hz, *meso*-Ph H_o), 6.79–6.73 (40H, m, β-Ph $H_{o,m,p}$), 6.39 (8H, m, J_{HH}: 8.5 Hz, J_{HF}: 8.5 Hz, *meso*-Ph H_m), −0.99 (2H, br s, NH).

MS (LSIMS): 1 295 ($[M]^{+\cdot}$, 100%).

Anal calc for $C_{92}H_{58}N_4F_4$: C 85.30 H 4.51 N 4.32 F 5.87. Found: C 84.87 H 4.49 N 4.51 F 5.78.

*Chloro(*meso-*tetrakis(4-fluorophenyl)octaphenylporphyrin)manganese(III)*

H_2(DPP-F_4) (0.077 mmol, 100 mg) was dissolved in 50 mL DMF and manganese(II) chloride tetrahydrate (0.38 mmol, 75 mg) was then added. The mixture was refluxed for 2 h. After evaporation of the solvent, the product was dissolved in 300 mL dichloromethane and washed with water. The solution was dried on magnesium sulfate and evaporated

to dryness. The crude product was purified by column chromatography on alumina eluted with 5% methanol in dichloromethane. The partial evaporation of the solvent and then addition of pentane led to the precipitation of the porphyrin. After filtration 59 mg (55% yield) of Mn(DPP-F_4)Cl were obtained.

IR (CsI) : υ (cm^{-1}): 286 (υ_{Mn-Cl})

^1H NMR ($CDCl_3$): δ (ppm): 8.57, 6.89, 6.38, 5.32.

MS (LSIMS): 1 348 ($[M-Cl]^+$, 100%).

Anal calc for $C_{92}H_{56}N_4F_4MnCl$: C 79.85 H 4.08 N 4.05 F 5.49 Cl 2.56. Found: C 74.66 H 3.52 N 4.43 F 5.41 Cl 2.50.

meso-*Tetrakis(4-bromophenyl)octaphenylporphyrin*

The synthesis was performed using the same method as described above starting from 3,4-diphenylpyrrole (12.6 mmol, 2.7 g), 4-bromobenzaldehyde (12.6 mmol, 2.3 g) and boron trifluoride etherate (4.5 mmol, 0.7 mL) in 1.3 L of dichloromethane; 2.70 g (55.7% yield) of H_2(DPP-Br_4) was obtained.

^1H NMR ($CDCl_3$): δ (ppm) : 7.35 (8H, d, *meso*-Ph H_o), 6.87 (8H, m, β-Ph H_o), 6.82 (8H, d, *meso*-Ph H_m), 6.76–6.70 (32H, m, β-Ph $H_{o',m,p}$), −1.00 (2H, br s, NH).

MS (LSIMS): 1 538 ($[M + H]^+$, 100%).

Anal calc for $C_{92}H_{58}N_4Br_4$: C 71.80 H 3.80 N 3.64 Br 20.77. Found: C 71.90 H 3.84 N 3.62 Br 20.63.

*Chloro(*meso-*tetrakis(4-bromophenyl)octaphenylporphyrin)manganese(III)*

The synthesis was performed using the same method as described above starting from H_2(DPP-Br_4) (0.065 mmol, 100 mg) and manganese(II) chloride tetrahydrate (0.38 mmol, 75 mg) in 50 mL benzonitrile; 64 mg (60% yield) of Mn(DPP-Br_4)Cl was obtained.

^1H NMR ($CDCl_3$): δ (ppm): 8.62, 8.09, 7.28, 6.55.

MS (LSIMS): 1 591 ($[M-Cl]^+$, 100%).

Anal calc for $C_{92}H_{56}N_4Br_4MnCl$: C 67.90 H 3.47 N 3.44 Br 19.64 Cl 2.18. Found: C 68.03 H 3.49 N 3.40 Br 19.14 Cl 1.98.

meso-*Tetrakis[4-(trifluoromethyl)phenyl]octaphenylporphyrin*

A solution of 3,4-diphenylpyrrole (3.65 mmol, 800 mg) in 50 mL acetic acid was added to a refluxing solution of 4-(trifluoromethyl)benzaldehyde (3.65 mmol, 0.5 mL) in 50 mL acetic acid. The mixture was further refluxed for 24 h until the solution turned from purple to brown. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (2.7 mmol, 613 mg) was then added and the solution was refluxed for another hour. After evaporation of solvent the crude product was purified by two successive columns on basic alumina. Elution with a dichloromethane/heptane 50:50 mixture gave the desired porphyrin. The partial evaporation of the solvent and then addition of pentane led to the precipitation of the porphyrin. After filtration 164 mg (12% yield) of H_2(DPP-$(CF_3)_4$) was obtained.

^1H NMR ($CDCl_3$): δ (ppm) : 7.62 (8H, d, *meso*-Ph H_o), 6.96 (8H, d, *meso*-Ph H_m), 6.79 (8H, m, β-Ph H_o), 6.71 (32H, m, β-Ph $H_{o',m,p}$), −0.98 (2H, br s, NH).

MS (LSIMS): 1 495 ($[M]^{+\bullet}$, 100%).

Anal calc for $C_{96}H_{58}N_4F_{12}$: C 77.10 H 3.91 N 3.75 F 15.24. Found: 75.51 H 3.96 N 3.45 F 14.78.

*Chloro(*meso-*tetrakis(4-trifluoromethylphenyl)octaphenylporphyrin)manganese(III)*

The synthesis was performed using the same method as described above starting from H_2(DPP-$(CF_3)_4$) (0.08 mmol, 120 mg) and manganese(II) chloride tetrahydrate (0.38 mmol, 75 mg) in 50 mL benzonitrile; 100 mg (79% yield) of Mn(DPP-$(CF_3)_4$)Cl was obtained.

IR (CsI): υ (cm^{-1}): 288 (υ_{MnCl}).

^1H NMR ($CDCl_3$): δ (ppm): 8.56, 7.03, 6.51.

MS (LSIMS): 1 548, ($[M-Cl]^+$, 100%).

Anal cal for $C_{96}H_{56}N_4F_{12}MnCl$: C 72.80 H 3.56 N 3.54 F 14.39 Cl 2.24. Found: C 72.45 H 3.67 N 3.86 F 12.93 Cl 2.04.

*Chloro(*meso-*tetrakis(2,6-dichlorophenyl)octaphenylporphyrin)manganese(III)*

The synthesis was performed using the same method as described above starting from H_2(DPP-Cl_8) (0.067 mmol, 100 mg) and manganese(II) chloride tetrahydrate (0.38 mmol, 75 mg) in 40 mL benzonitrile; 75 mg (71% yield) of Mn(DPP-Cl_8)Cl was obtained.

^1H NMR ($CDCl_3$): δ (ppm): 8.75, 7.29, 6.94, 6.49, 4.90.

MS (LSIMS): 1 551 ($[M-Cl]^+$, 100%).

Anal calc for $C_{92}H_{52}N_4Cl_9Mn$: C 69.61 H 3.30 N 3.53 Cl 20.10. Found: C 70.21 H 3.21 N 3.46 Cl 19.23.

*Chloro(*meso-*tetrakis(pentafluorophenyl)octaphenylporphyrin)manganese(III)*

The synthesis was performed using the same method as described above starting from H_2(DPP-F_{20}) (0.095 mmol, 150 mg) and manganese(II) chloride tetrahydrate (0.51 mmol, 100 mg) in 50 mL benzonitrile; 140 mg (88% yield) of Mn(DPP-(F_{20})Cl was obtained.

IR (CsI): υ (cm^{-1}): 307 (υ_{MnCl}).

^1H NMR ($CDCl_3$): δ (ppm): 8.78, 7.30, 6.95.

MS (LSIMS): 1 636 ($[M-Cl]^+$, 100).

Anal calc for $C_{92}H_{40}N_4F_{20}MnCl$: C 66.10 H 2.41 N 3.35 Cl 2.12 F 22.73. Found: C 65.89 H 2.51 N 3.43 Cl 2.17 F 22.75.

Chloro(dodecaphenylporphyrin)manganese(III)

The synthesis was performed using the same method as described above starting from H_2(DPP) (0.082 mmol, 100 mg) and manganese(II) chloride tetrahydrate (0.4 mmol, 80 mg) in 50 mL benzonitrile; 65 mg (60% yield) of Mn(DPP)Cl was obtained.

IR (CsI): υ (cm^{-1}): 291 (υ_{MnCl}).

^1H NMR ($CDCl_3$): δ (ppm): 8.99, 8.00, 6.16, 5.00.

MS (LSIMS): 1 276 ($[M-Cl]^+$, 100)%.

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