The synthesis and spectroscopic characterisation of chiral *meso*-tetraarylmetalloporphyrins bearing *meso*-pentafluorophenyl groups

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The successful synthesis of 5,10,15,20-tetrakis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin, with (*R*)-1-phenylbutoxy substituents on each of the eight *ortho*-positions, by a 2+2 approach *via meso*-[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]dipyrromethane rather than a one-pot condensation of (*R*,*R*)-2,6-bis(1-phenylbutoxy)benzaldehyde with pyrrole, is described. The synthesis has also been modified using *meso*-(pentafluorophenyl)dipyrromethane to prepare four further chiral porphyrins containing one, two (*cis* and *trans*) and three pentafluorophenyls in place of the bis(phenylbutoxy)phenyl groups. The cross-coupling of the two dipyrromethanes with pentafluorobenzaldehyde gave as one of the products the unexpected *cis*-disubstituted 5,10-bis(pentafluorophenyl)-15,20-bis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin. It seems likely that the formation of the latter compound involves the acid-catalysed reversion of the dipyrromethane synthesis. Both faces of each of the porphyrins are chiral and equivalent in this way the wasteful formation and time-consuming separation of atropisomers is avoided. Four iron(III) and one manganese(III) complex of these porphyrins have been prepared. The ^{1}H and ^{19}F NMR spectra of the series of porphyrin ligands reveal some interesting structure- and symmetry-dependent splitting patterns and trends which are used to confirm the identities of the compounds. In particular, the ^{1}H NMR couplings of the β-pyrrole hydrogens are very diagnostic of the substitution patterns of the *meso*-aryl groups on the porphyrin ring.

Introduction

In recent years, much effort has been put into the search for and development of catalysts for the enantioselective transformation of prochiral molecules into chiral products.[1] This synthetic methodology provides potential building blocks for the synthesis of biologically active molecules. One such process is epoxidation, since epoxides are key industrial intermediates and chiral epoxides are of particular importance for the synthesis of drugs, agrochemicals and natural products.[2]

Several generic systems for the asymmetric epoxidation of non-functionalised alkenes using metal-free and metal complex catalysts have been reported. Probably the most successful of the former, developed by Shi and co-workers,[3] are mediated by dioxiranes generated *in situ* from fructose-derived ketones and oxone. The two most thoroughly studied types of metal complex are chiral manganese(III) salens[4] and metalloporphyrins.[5] Manganese(III) salens are relatively simple to prepare (some are even commercially available) and can give high ee values for the epoxidation of (*Z*)-1,2-disubstituted alkenes and some tri- and tetra-substituted alkenes. Examples of their applications are in the syntheses of antihypertensive chromanol derivatives,[6] an HIV protease inhibitor (Indinavir)[7] and the chiral sidechain of the anticancer agent Taxol.[8] However, in general they give relatively low turnover numbers. By contrast, the metalloporphyrins can give very high turnover epoxidations but, with a few very recent exceptions,[9] the ee values of their reactions have been only moderate to good.

The design and synthesis of chiral porphyrins continues to be an active area of research, the aims of which are to devise simple preparations of oxidatively stable metalloporphyrins that show high enantioselectivity in their catalysis. Two general approaches are employed. The first involves making chiral picket fence porphyrins and, since the original paper by Groves and Myers,[10] this has been thoroughly studied by Halterman,[11] Kodadek,[12] Momenteau[13] and their co-workers. In the second method, the chirality is introduced using straps. The first chiral strapped porphyrin was reported by Mansuy and co-workers[14] and this approach has subsequently been extensively elaborated by the research groups of Collman,[15] Groves,[16] Naruta,[17] Gross[9a,18] and others.[19]

The synthesis of homochiral 5,10,15,20-tetraarylporphyrins with eight chiral pickets, four on each face of the porphyrin on the *meso*-phenyl groups, has been reported previously.[11,12b,20] However, our aim was to design a synthesis to make a series of related tetraarylporphyrins: (i) with two to eight chiral pickets, on the *ortho*-positions of the aryl groups; (ii) with both faces chiral and equivalent and (iii) avoiding the formation and hence the separation of atropisomeric mixtures.

In this paper we describe the preparation of a new family of porphyrins (**1**–**5**), with chiral aryl and pentafluorophenyl groups on the *meso*-positions. In subsequent papers we will describe the use of these compounds as epoxidation catalysts in homogeneous solution and when anchored to a solid support.

Results and discussion

Synthesis of 5,10,15,20-tetrakis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin (1) by the Lindsey method

The first porphyrin target was **1** with four identical *meso*-aryl groups each with two chiral *ortho*-substituents. This homochiral porphyrin has each face of the macrocycle substituted with four (*R*)-1-phenylbutoxy groups.

A widely used method for the synthesis of *meso*-tetraphenylporphyrins with bulky aryl groups is that of Lindsey and co-workers[21] and involves the acid-catalysed reaction of pyrrole and the appropriate aldehyde (Scheme 1, Route **A**). When applied to aldehyde **6**, the synthesis of which we have described previously,[22] the yield of **1** was very disappointing (<1%). The UV–Vis spectrum of the product mixture confirmed the formation of a porphyrin with a Soret band at

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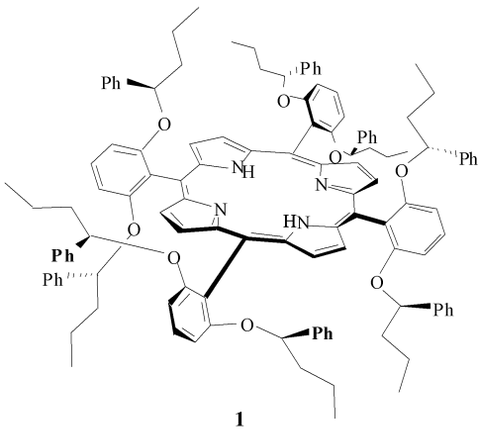

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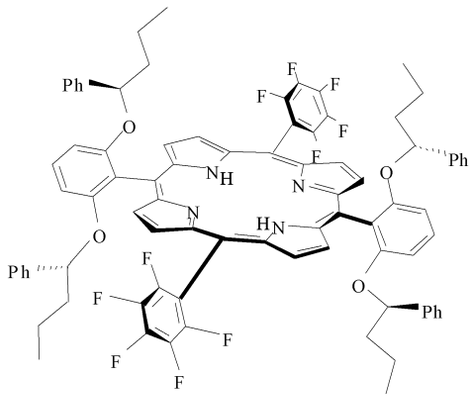

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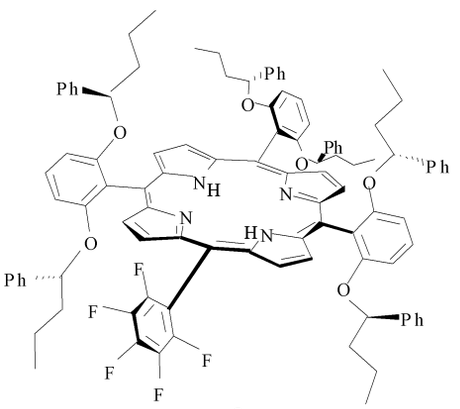

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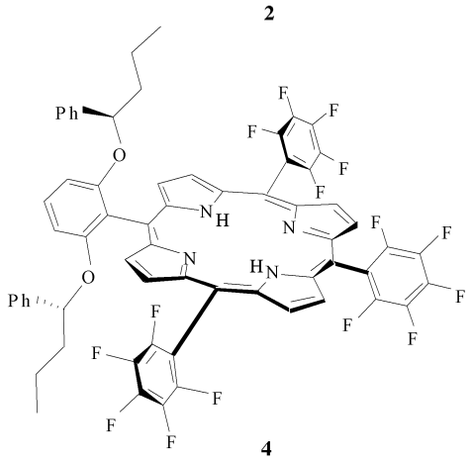

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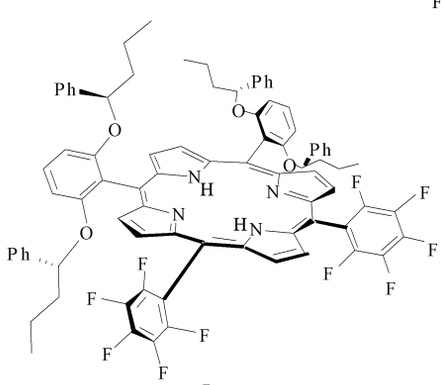

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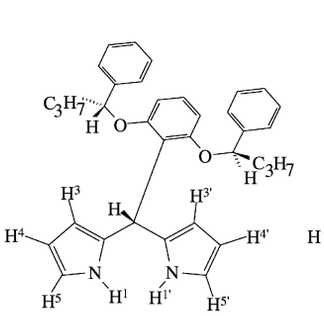
λ_{max} 420 nm and also of a chlorin by-product (λ_{max} 654 nm). The very low yields of **1** are likely to be due to the extreme bulkiness of the *ortho*-phenylbutoxy substituents in the aldehyde **6**, which make cyclisation to the porphyrinogen intermediate unfavourable compared to competing oligomerisation.

Synthesis of 5,10,15,20-tetrakis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)-phenyl]porphyrin (1) by the 2+2 approach

The possibility of obtaining porphyrin **1** through a "2+2" approach (Scheme 1, Route **B**) was investigated. Although this second strategy involves two reactions, it was argued that the overall procedure might give cleaner results since the formation of oligomer chains and tars should be much reduced by the absence of pyrrole in the second step. A further advantage of this method is that it allows the introduction of different substituents on the porphyrin *meso*-positions by using different aromatic aldehydes in the two steps.

The synthesis of the dipyrromethane, **7**, was achieved by dissolving aldehyde **6** in pyrrole and using TFA as the catalyst following the procedure of Lindsey and Lee.[23] Preparing the dipyrromethane in high purity was considered essential for its application in porphyrin synthesis. However, 5,5′-unsubstituted dipyrromethanes are known to be relatively unstable compounds and consequently the work-up was carried out as rapidly as possible. The final distillation to remove the pyrrole was carried out at room temperature; increasing the temperature leads unavoidably to the decomposition of the dipyrromethane. After chromatography and crystallisation **7** was obtained in good yield (65%) as white needles. It was found to be stable if stored in the dark at <0 °C. Solutions of dipyrromethane **7**, however, are less stable and decompose relatively quickly at room temperature.



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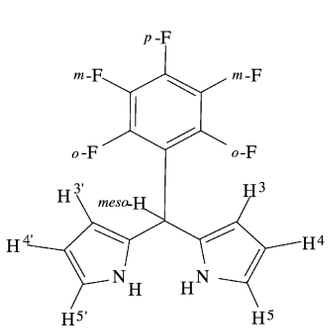

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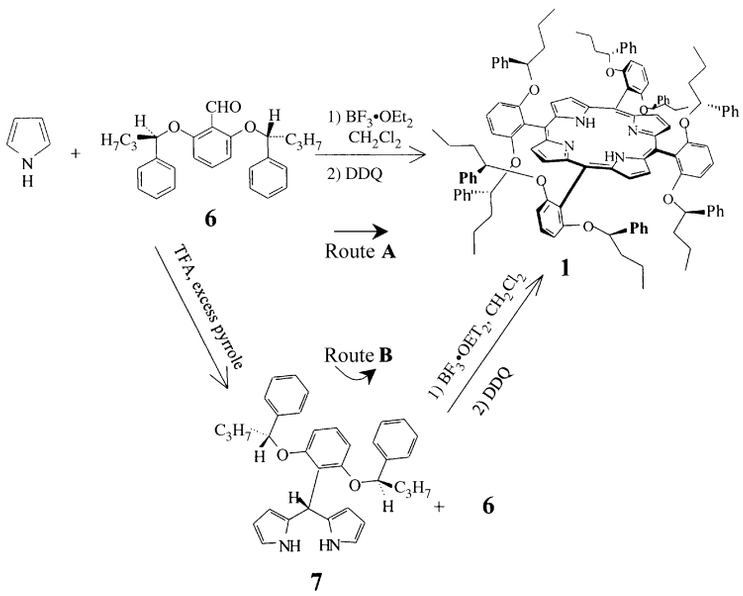


Scheme 1

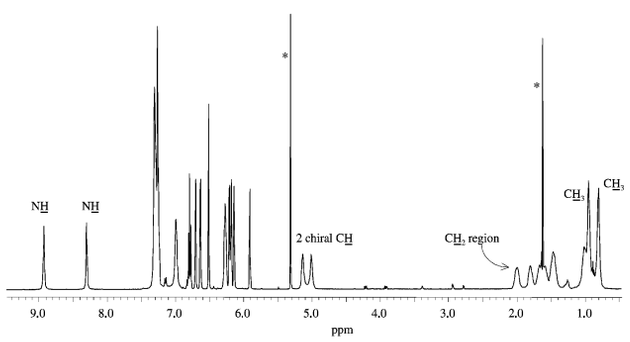


Fig. 1 ^{1}H NMR (500 MHz) spectrum of **7** (in CD_2Cl_2) at $T = -10$ °C.

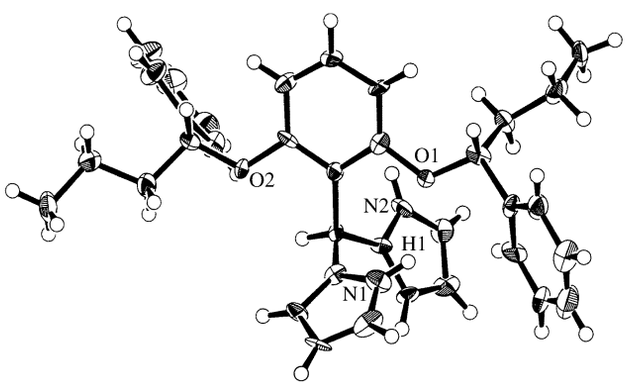


Fig. 2 ORTEP representation (30% probability ellipsoids) of $C_{35}H_{38}N_2O_2$, **7**. Distance H(1)···O(1): 2.219(11) Å.

The dipyrromethane **7** was characterised by NMR spectroscopy, mass spectrometry and single crystal X-ray crystallography. The ^{1}H NMR spectrum at −10 °C (Fig. 1) shows that the bulky *ortho*-phenylbutoxy groups effectively prevent rotation of the 2,6-disubstituted aryl about the methylene bridge carbon of **7**. As a result the two phenylbutoxy substituents on each of the *meso*-aryl groups are diastereotopic: the hydrogens and the methyls on each of the chiral carbon atoms have different chemical shifts (CHC_3H_7, 5.13 and 5.01 ppm and CH_2CH_3, 0.95 and 0.80 ppm, respectively). At room temperature these become superimposed at ~5.1 and ~1.0 ppm, respectively.

Further interesting information on the preferred conformation of **7** was obtained by analysing its room temperature ^{1}H–^{1}H COSY NMR spectrum. The two scalar coupling pathways of the protons show the non-equivalence of the two diastereotopic pyrrole units: the N–H protons of each pyrrole unit couple with all the other hydrogens on the same ring. The coupling patterns and the multiplicity of each peak in the aromatic region of the ^{1}H–^{1}H COSY spectrum of **7** allowed the unambiguous assignment of the peaks of all the pyrrole hydrogens. Proton H^5, α to the nitrogen, resonates downfield from H^3 and H^4 and is coupled to H^3 and H^4. Proton H^4 is likewise coupled to H^3 and H^5. The hydrogens on the second pyrrole ring show a similar pattern with the $H^{4'}$ and $H^{5'}$ signals each being doublets of doublets. A closer examination of the peaks corresponding to H^3 and $H^{3'}$ reveals that the H^3 resonance is composed of seven lines whilst $H^{3'}$ gives four lines. The extra splitting observed with H^3 must arise from long range coupling with the hydrogen on the methylene bridge, suggesting that the methylene-bridge C–H bond lies in the plane of the pyrrole with H^3 but not that with $H^{3'}$. This conclusion is supported by the crystal structure obtained by single crystal X-ray diffraction (see below).

The crystal structure of **7** was determined by X-ray diffraction at 150 K (Fig. 2). The structure reveals that the methylene-bridge C–H bond lies in the same plane as only one of the pyrrole rings. This conformation is favoured by an H-bond between H^1 and O^1. It seems likely, based on the ^{1}H NMR data above, that the H-bond results in this conformation also being preferred in solution.

5,10,15,20-Tetrakis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]-porphyrin, **1**, was obtained by condensing dipyrromethane, **7**, with aldehyde, **6**, in dichloromethane, using $BF_3{\cdot}OEt_2$ as catalyst (Scheme 1, Route **B**) to give the porphyrinogen. This was then oxidised and purified by chromatography to give compound **1** in 6.7% yield.

Preparation of 5,15-bis(pentafluorophenyl)-10,20-bis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin (2)

The "2+2" synthesis readily allows the preparation of porphyrins with two different *meso*-substituents in a *trans* configuration. Thus, when equimolar amounts of pentafluorobenzaldehyde and dipyrromethane, **7**, were condensed, using the same procedure as described for porphyrin **1**, porphyrin **2** was obtained, in 18% yield. The greater electrophilicity and the reduced bulk of pentafluorobenzaldehyde relative to aldehyde **6** probably accounts for the improved yields obtained for this reaction over that for the synthesis of **1**.

Preparation of 5-pentafluorophenyl-10,15,20-tris[(*R*,*R*)-2,6-bis-(1-phenylbutoxy)phenyl]porphyrin (3)

To obtain a porphyrin with one pentafluorophenyl group and three chiral *meso*-substituents required co-condensation of pentafluorobenzaldehyde and **6** with dipyrromethane **7**, following the general procedure described above. Using the molar ratios 1 : 1 : 2, respectively, gave the three expected porphyrins (**1**–**3**). Their separation was achieved by column chromatography with **2** (7.1% yield) eluting first, followed by **3** (8.0%) and lastly porphyrin **1** (1.6%). Although the separation of the three porphyrins by TLC was very good, the resolution of **2** and **3** by column chromatography was incomplete and iterative column chromatography was necessary to obtain each in a pure state.

Products **1** and **2** were identified by comparison of their R_f values with those of authentic samples prepared as described above, whilst porphyrin **3** was identified by ^{1}H and ^{19}F NMR and UV–Vis spectroscopy and mass spectrometry.

Preparation of 5,10,15-tris(pentafluorophenyl)-20-[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin (4)

The preparation of a porphyrin bearing a single chiral *meso*-aryl unit and three pentafluorophenyl rings can be achieved by a co-condensation of *meso*-(pentafluorophenyl)dipyrromethane **8** with dipyrromethane **7** and pentafluorobenzaldehyde. This route should give three porphyrins and by tuning the proportions of the three reactants, it is possible to optimise the yields of the desired product.

meso-(Pentafluorophenyl)dipyrromethane, **8**, was prepared in 31% yield from pentafluorobenzaldehyde, using the procedure described for compound **7**. The ^{1}H NMR spectrum of **8** shows a very broad peak at 8.09 ppm corresponding to the two N*H* protons and the *meso*-proton appears as a broad singlet at 5.89 ppm. The other signals were assigned by analysis of the 2D-COSY spectrum. As for dipyrromethane **7**, the N–H protons are coupled with the three hydrogens on their respective pyrrole groups, a doublet of triplets at 6.71 ppm (J = 2.7 and 1.7 Hz) has been assigned to protons H^5 and H$^{5'}$ and the doublet of doublets at 6.15 ppm (J = 6.0 and 2.7 Hz) corresponds to H^4 and H$^{4'}$. Protons H^3 and H$^{3'}$ give a broad singlet integrating for two protons at 6.01 ppm. Since, however, both of these are coupled with the *meso*-H, dipyrromethane **8** does not have the same preferred conformation of the pyrrole groups about the methylene bridge as dipyrromethane **7**. This is not surprising because the structure-controlling H-bond in **7** is absent in **8**.

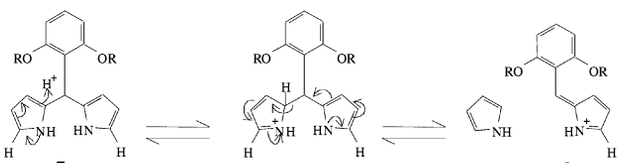
The ^{13}C NMR spectrum gives five peaks for the carbon atoms of the dipyrromethane skeleton, a signal for C^1 of the *meso*-aryl ring at 115.8 ppm and three doublets (all with coupling constants ~250 Hz) at low field from the non-equivalent phenyl carbon atoms bearing the fluorine atoms.

The ^{19}F NMR spectrum confirms the structure of **8** with a signal assigned to fluorine atoms attached to each of the different positions on the phenyl rings: the *ortho*-fluorines at −142.0 ppm give a doublet (J = 16.6 Hz), a triplet at −156.2 ppm from the *para*-fluorine with a coupling constant of 21 Hz and the *meta*-fluorines give a doublet of triplets at −161.7 ppm (J = 21.0 and 8.2 Hz). The last signal also shows an additional small splitting (J = 2.2 Hz) due to the coupling of fluorines positioned *meta* to one another.[24]

5,10,15-Tris(pentafluorophenyl)-20-[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin, **4**, was obtained from the acid-catalysed reaction of **7**, **8** and pentafluorobenzaldehyde. TLC analysis of the crude product mixture revealed the presence of three different porphyrins with R_f values of 0.42, 0.35, 0.27 (eluent hexane–dichloromethane, 30 : 70). The product with R_f 0.35 was identified as the expected porphyrin **2** (8.8% yield) by comparison with the R_f value of an authentic sample. This structural assignment was confirmed by column chromatographic separation followed by ^{1}H and ^{19}F NMR spectroscopy and mass spectrometry.

The first chromatographic fraction contained porphyrin **4** (8.1% yield), but interestingly the third porphyrin was not the expected tetrakis(pentafluorophenyl)porphyrin, which was not detected in the reaction mixture. Spectroscopic analysis showed it to be 5,10-bis(pentafluorophenyl)-15,20-bis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin, **5** (2.2% yield), the *cis*-structural isomer of the *trans*-compound **2**, bearing two pentafluorophenyl groups and two chiral aryl substituents.

The formation of porphyrin **5** can be explained in terms of the reversibility of the porphyrinogen formation. Exchange experiments carried out by Lindsey and co-workers[21a] have demonstrated that a thermodynamic equilibrium takes place when pyrrole and benzaldehyde are reacted under acidic conditions. A possible mechanism[25] leading to **5** in which the formation of the dipyrromethanes is reversed by the acid catalyst to give the stabilised 2-substituted monopyrrole cation **9** is shown in Scheme 2.[25] This can then be involved in forward



Scheme 2

reactions to give porphyrin **5**. The comparable reaction of dipyrromethane **8** would be less favoured due to the strongly electron-withdrawing pentafluorophenyl group destabilising the cation equivalent to **9**.

In conclusion, the cross-coupling between dipyrromethanes **7** and **8** with pentafluorobenzaldehyde, in a molar ratio of 1 : 1 : 1.3, gives three porphyrins which are readily separated by column chromatography. The spectroscopic analysis carried out on each fraction identified the first as the expected porphyrin **4**, the second as porphyrin **2** and the last as the unexpected porphyrin **5** from the equilibration pathway of the dipyrromethane **7**.

Preparation of the metal derivatives of porphyrins 1–4

Metallation of porphyrins **1**–**4** was achieved by the metal carbonyl method with $Fe(CO)_5$ or $Mn_2(CO)_{10}$ in refluxing toluene.[26] This was used to prepare chloroiron(III) porphyrins, **Fe1**–**Fe4**, and chloromanganese(III) porphyrin, **Mn2**, respectively. Partial dealkylation of the *ortho*-phenyl substituents occurred in some reactions, especially after prolonged refluxing. These products, which were easily detected from the tailing brown bands observed during column chromatography, were discarded.

Some conclusions on the ^{1}H NMR spectra of porphyrins 1–5

This research describes the systematic substitution of chiral 2,6-disubstituted phenyl groups, on the *meso*-positions of the porphyrin macrocycle, by pentafluorophenyl groups. Five porphyrins have been prepared; two of which, with two pentafluorophenyl groups, are structural isomers. The ^{1}H and ^{19}F NMR data from compounds **1**–**5** reveal some general features, trends and interesting distinguishing characteristics that can be used to identify the substitution patterns of the porphyrins.[27]

The above syntheses all have a common chiral building block, (*R*,*R*)-2,6-bis(1-phenylbutoxy)benzaldehyde, **6**. Using a single aldehyde enantiomer leads to a major simplification of the NMR spectra of the products. This became very apparent since all the syntheses and work-up procedures were first delineated with racemic **6** and the NMR spectra of the resulting

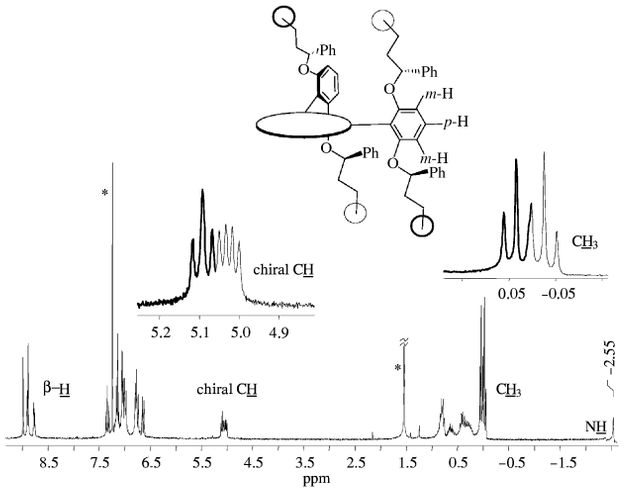


Fig. 3 ^{1}H NMR (270 MHz) spectrum of **5**.

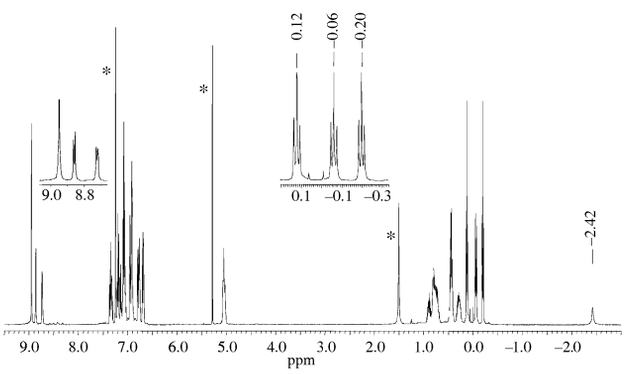


Fig. 4 ^{1}H NMR (500 MHz) spectrum of **3**.

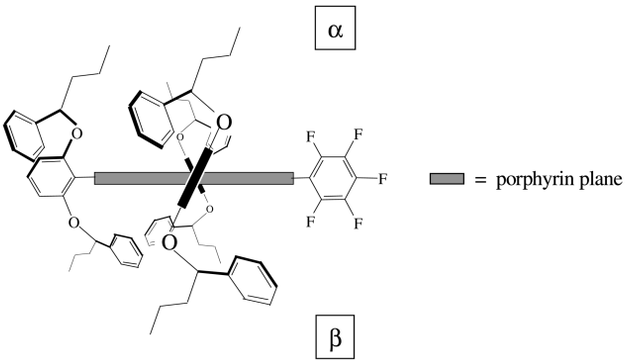


Fig. 5 Schematic representation of porphyrin **3** showing the diastereotopic relationship of the methyls on the phenylbutoxy groups on carbon C^{10} and C^{20}.

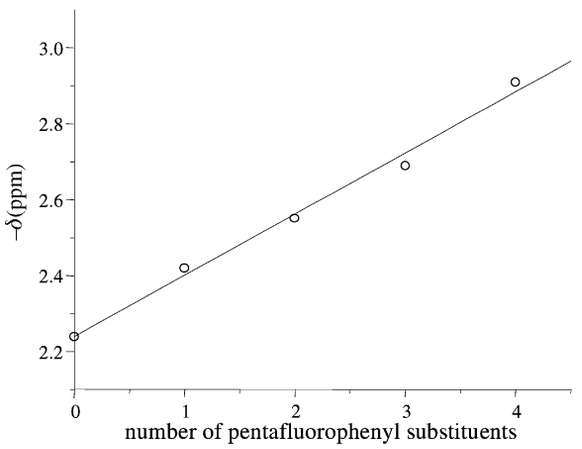


Fig. 6 Linear plot (correlation coefficient 0.996) of the ^{1}H NMR chemical shifts of the N–H protons *vs.* the number of C_6F_5 substituents on the porphyrin ring.

diastereoisomeric mixtures were distinctly more complicated. In particular, the β-pyrrole protons are sensitive to this change and can be used to provide a good measure of the stereochemical purity of the porphyrin.

The peaks in the ^{1}H NMR spectrum from the methyls on each of the chiral carbons all showed distinct upfield shifts (chemical shifts, 0.3 to −0.2 ppm) from typical values of a methyl on a saturated alkyl chain. This indicates that the methyl groups in these porphyrins lie above and below the plane of the macrocycle and experience a shielding effect from its aromatic ring current. Each of the porphyrins, except **5**, give a single signal in their ^{1}H NMR spectra from their chiral C–H groups with very similar chemical shifts (5.05 ± 0.04 ppm). Compound **5** interestingly gives two signals, a triplet at 5.09 ppm and a doublet of doublets at 5.02 ppm. The four methyls on the butoxy groups of **5** also give two sets of signals (two overlapping triplets centred at 0.04 and −0.02 ppm) (Fig. 3) as do the *meta*-hydrogens of **5** (centred at 6.78 and 6.64 ppm). Nevertheless, the two *para*-hydrogens give only one triplet at 7.33 ppm confirming the overall symmetry of the macrocycle. A similar effect is seen in the ^{19}F NMR of spectrum **5** (*vide infra*).

A relatively complex ^{1}H NMR resonance pattern is found for both the aromatic and the aliphatic protons of porphyrin **3**. The six methyl groups give rise to three triplets in the region between 0.12 and −0.20 ppm, each of which integrates to six protons (Fig. 4). Such a pattern is expected since the two chiral phenylbutoxy substituents on the *meso*-aryl rings on C^{10} and C^{20} are diastereotopic. Consequently, the methyl groups on the α-side are equivalent to those diametrically opposite on the β-side of the macrocyclic ring (Fig. 5).

The chemical shifts of the N–H protons show a clear linear upfield trend as the number of pentafluorophenyl groups attached to the porphyrin is increased (Fig. 6). This suggests that the shielding effect of the macrocyclic ring current on the N–H protons increases proportionately with the number of pentafluorophenyl substituents. The identical values for the structural isomers **2** and **5** show that the chemical shifts are *independent* of the relative positions of the aryl groups.

The chemical shifts of the aromatic fluorines in the ^{19}F NMR spectra of the fluorinated porphyrins **2**–**5** are all remarkably consistent. Furthermore, they can readily be assigned by comparison with the data and assignments for tetrakis-(pentafluorophenyl)porphyrin (H_2TF_5PP) reported by Gray and co-workers.[24] Thus, the *ortho*-fluorines are observed at −137.34 ± 0.25, the *meta*-fluorines at −162.89 ± 0.5 and the *para*-fluorines at −153.10 ± 1.2 ppm. The comparable values for H_2TF_5PP are −136.9, −161.8 and −151.7, respectively. Compounds **4** and **5** give more than one signal for some of the aromatic fluorines. In porphyrin **4** one set arises from the two equivalent pentafluorophenyl groups on *meso*-carbons C^5 and C^{15} and the second from the C_6F_5 group on C^{10}. The *ortho*-fluorines give two sets of doublets of doublets centred at −137.1 and −137.5 ppm, the *para*-fluorines give triplets at −152.5 and −152.7 ppm and the six *meta*-fluorines give a multiplet centred at −162.4 ppm. With porphyrin **5** the phenomenon, described above, that gives rise to two sets of signals in the ^{1}H NMR spectrum also leads to two sets of doublets of doublets for the *ortho*-fluorines in the ^{19}F NMR spectrum, demonstrating the non-equivalence of F^1 and F^5; the *meta*-fluorines give a multiplet of overlapping signals (−162.8 ppm) rather than the doublet of triplets that is observed with porphyrins **2** and **3**, since F^2 and F^4 are inequivalent, and the *para*-fluorines give a simple triplet at −153.5 ppm (Fig. 7).

The ^{1}H NMR spectral pattern of the β-pyrrole hydrogens of a tetraarylporphyrin is characteristic of the symmetry elements possessed by the molecule and can consequently be used

to identify the symmetry of the porphyrin.[28] The five chiral tetraarylporphyrins synthesised in this study present a range of symmetry types (Fig. 8). The homochiral porphyrin **1** is D_4 and the β-pyrrole protons, being equivalent, give a singlet (8.92 ppm). Porphyrin **2** belongs to the D_2 point group and, as expected, because the hydrogens on each pyrrole unit are non-equivalent the signals appear as two doublets (8.94 and 8.78 ppm). Porphyrins **3**, **4** and **5** have a C_2 symmetry and the different positions of the symmetry axis of each is responsible for the different NMR patterns (Fig. 7). With porphyrin **3** the C_2 axis is located in the porphyrin plane and through the pentafluorophenyl ring and the opposite chiral *meso*-phenyl unit. This leads to the β-pyrrole protons H^7 and H^8 giving two doublets at $\delta = 8.86$ and 8.73 ppm, in the ^{1}H NMR spectrum, with coupling constants of 4.5 Hz (each equivalent to two protons), however, since the chemical environments of H^{12} and H^{13} are very similar [each is flanked by a 2,6-bis(1-phenylbutoxy)phenyl group] these hydrogens give a singlet at 8.95 ppm (equivalent to four protons) rather than two doublets. The C_2 symmetry axis in porphyrin **4** passes through the chiral *meso*-aryl and the opposite pentafluorophenyl groups (Fig. 8). The β-pyrrole protons H^2 and H^3 give the two doublets at 8.96 and 8.76 ppm ($J = 4.3$ Hz), whereas protons H^7 and H^8 give two doublets with very similar chemical shifts at 8.90 and 8.88 ppm. This pattern relates to the pentafluorophenyl rings at the C^5 and C^{15} not being perpendicular relative to the macrocycle plane due to the steric constraints of the bulky chiral aryl group on C^{20}. This geometry is different to the one possessed by the pentafluorophenyl substituent on C^{10}. The ^{1}H NMR spectrum of porphyrin **5** shows two β-pyrrolic singlets (8.98 and 8.88 ppm) and two doublets (8.89 and 8.76 ppm, $J = 4.9$ Hz). This pattern is in agreement with the C_2 symmetry axis of **5** bisecting pyrroles A and C (Fig. 8). Thus, protons H^8 and H^{18} are expected to give singlets whilst protons H^{12} and H^{13} will each give a doublet.

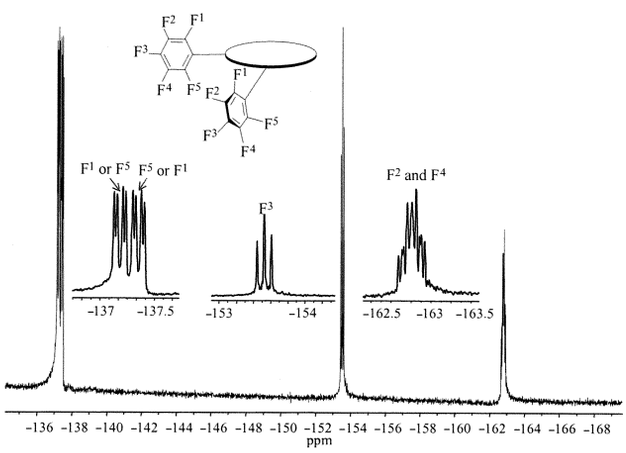


Fig. 7 ^{19}F NMR (254 MHz) spectrum of **5**.

UV–Vis spectra of porphyrins 1–5

All the porphyrins prepared in this study, as expected, have phyllo-type UV–Vis spectra with Q-band intensities IV > II > III > I. Peripheral substitution affects the electronic structure of the porphyrin ring which in turn affects the energies of the Q and B transitions. For porphyrins **1**–**5** the Soret band undergoes a small blue shift (4 nm) with the increasing number of pentafluorophenyl rings on the porphyrin macrocycle (λ_{max} 419, 418, 417 and 415 nm for **1**, **3**, **2** and **5**, and **4** respectively), whereas the Q bands are slightly red-shifted (2–5 nm). The Soret bands of the iron complexes, like those of the free base porphyrins also undergo a blue shift with increasing numbers of pentafluorophenyl groups on the macrocyclic ligand.

Conclusions

1) A "2 + 2" synthesis provides a route to the highly sterically crowded porphyrin **1** with (*R*)-1-phenylbutoxy substituents in all eight of the *ortho*-positions on the *meso*-aryl groups.

2) The "2 + 2" procedure with pentafluorobenzaldehyde gives porphyrin **2** with two pentafluorophenyl and two (*R*,*R*)-bis(1-phenylbutoxy)phenyl groups in a *trans*-configuration.

3) A mixed condensation using two different dipyrromethanes can be used to make porphyrins **3**, **5** and **4** with one, two (in a *cis*-configuration) and three pentafluorophenyl groups.

4) ^{1}H and ^{19}F NMR spectra of the five porphyrins provide structural information and reveal trends and diagnostic structure-dependent splitting patterns.

5) Four iron(III) and one manganese(III) complexes of these porphyrins have been prepared.

Experimental

Instrumentation and methods

UV–Visible spectra were recorded on a Hewlett Packard diode array spectrophotometer, model HP8453 and analysed using a Viglen Pentium PC running Hewlett Packard's A.02.05 UV–Vis

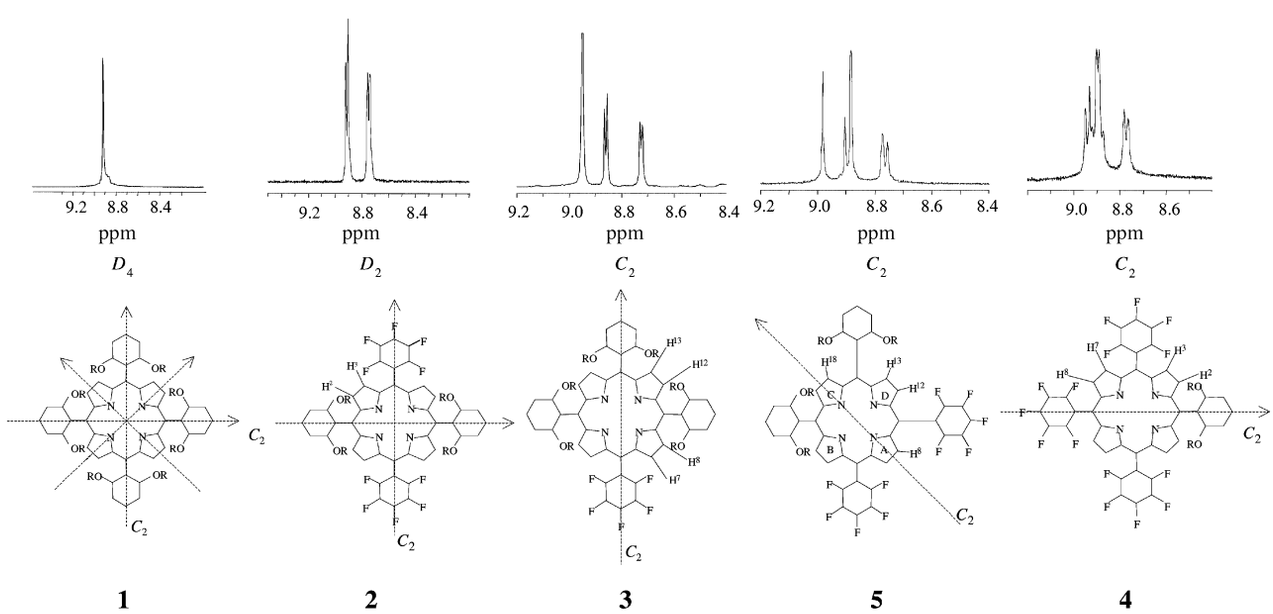


Fig. 8 The regions of the ^{1}H NMR spectra of the β-pyrrole hydrogens of porphyrins **1**–**5**.

ChemStation software. Electron impact, FAB^+ (matrix: 4-nitrobenzyl alcohol) and high resolution mass spectra were obtained on a Fisons Analytical (VG) Autospec mass spectrometer; electrospray mass spectra were recorded on a Finnigan LCQ mass spectrometer equipped with an electrospray interface. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a JEOL EX-270 (270 MHz) instrument using an internal deuterium lock or on a Bruker AMX500 (500 MHz) spectrometer. Optical rotations were recorded on a JASCO DIP-370 polarimeter using the sodium D line and $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}.

Crystals suitable for X-ray diffraction were mounted on a glass capillary. Data were collected at 150(2) K on a Rigaku AFC6S diffractometer and Mo-Kα radiation ($\lambda = 0.71069$ Å). Unit cell parameters and their esd values were determined from a least-squares fitting of the setting angles of 20 automatically centred reflections. Three standard reflections, monitored every 150 reflections, showed no significant variation of intensity during data collection. Intensities were corrected for Lorentz and polarization effects. Empirical absorption corrections were based on azimuthal scans of 10 reflections. Structures were solved by direct methods with SHELXS-86[29] and refined by full-matrix least-squares on F^2 with SHELXL-97.[30] No restraints or constraints were used. All non-hydrogen atoms were refined anisotropically. A riding model was applied to H atoms, which were placed at calculated positions, with the equivalent isotropic thermal parameters of their parent C or N atoms. Goodness of fit was calculated using the formula: $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{\frac{1}{2}}$ where p = number of parameters, n = number of data. R-factors were calculated as: $R1 = \Sigma 2F_o* - *F_c 2/\Sigma *F_o*$ and $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

Unless stated otherwise, purification of products by column chromatography used silica gel 60 supplied by ICN Biomedicals GmbH. Thin layer chromatography was carried out on commercially available Merck 5554 aluminium-backed silica plates (Kieselgel 60 F_{254}, 0.2 mm).

Materials

All reagents and solvents were used as purchased unless otherwise stated. Dichloromethane and chloroform were distilled over calcium hydride, and pyrrole was distilled under reduced pressure prior their use.

meso-[(*R*,*R*)-2,6-Bis(1-phenylbutoxy)phenyl]dipyrromethane (7)

Trifluoroacetic acid (0.060 cm^3, 0.78 mmol) was added slowly to a solution of the aldehyde **6**[11] (3.11 g, 7.73 mmol) in pyrrole (25.85 g, 385 mmol) under nitrogen at room temperature. The progress of the reaction was checked by TLC and when the aldehyde had been consumed the reaction mixture was neutralised with 0.1 M NaOH, washed with water and brine and dried ($MgSO_4$). After removal of the pyrrole under vacuum at room temperature, the crude oil was purified by column chromatography on silica gel (dichloromethane–hexane, 10 : 90 v/v) to give 2.60 g of **7** as a pale yellow oil (65%), which was crystallised from hexane to give white crystals. Mp 94–95 °C; $[\alpha]_D^{28} = -104.6$ (c 0.965 in $CHCl_3$); δ_H (500 MHz; $CDCl_3$, see the structure of **7** for the numbering of the pyrrole hydrogens) 8.84 (1 H, s, N$H^{1'}$), 8.19 (1 H, s, NH^1), 7.3–7.2 (10 H, m, PhH), 6.79 (1 H, t, *p*-ArH), 6.66 (1 H, dd, J 4.6 and 2.5 Hz, CH^5), 6.58 (1 H, dd, J 4.6 and 2.5 Hz, C$H^{5'}$), 6.48 (1 H, s, *meso*-H), 6.29, (2 H, d, *m*-ArH), 6.18 (1 H, dd, J 5.9 and 2.9 Hz, CH^4), 6.16 (1 H, dd, J 5.7 and 2.9 Hz, C$H^{4'}$), 6.14 (1 H, m, C$H^{3'}$), 5.89 (1 H, m, CH^3), 5.07 (2 H, br s, CH), 2.0–0.7 (14 H, m, aliphatic protons); δ_C (125 MHz; $CDCl_3$) 156.4, 133.5, 132.6, 128.5, 127.6, 127.5, 126.2, 119.4, 117.6, 116.2, 115.3, 108.3, 107.6, 106.9, 106.7, 105.5, 80.2, 32.8, 31.6, 22.6, 18.6, 13.9; EI-MS m/z 518 (55%, M^+), 385 (60, $M - PhCHC_3H_7$), 253 (35); HREI-MS m/z M^+, 518.2947, $C_{35}H_{38}N_2O_2$ requires m/z 518.2933.

Crystal data. $C_{35}H_{38}N_2O_2$, $M = 518.67$, orthorhombic, $a = 14.101(6)$, $b = 23.237(5)$, $c = 8.945(3)$ Å, $U = 2931.0(16)$ Å^3, $T = 150$ K, space group $P2_12_12_1$, $Z = 4$, μ(Mo-K$_\alpha$) = 0.072 mm^{-1}, 2933 independent reflections. The final R_1 was 0.0545 ($F4\sigma F$, 935 reflections) and $wR(F^2)$ was 0.2722 (all data). CCDC reference number 156612. See http://www.rsc.org/suppdata/p2/b1/b100478f/ for crystallographic files in .cif or other electronic format.

meso-Pentafluorophenyldipyrromethane (8)

Using the same experimental procedure outlined for compound **7** above, **8** was obtained as grey crystals from cyclohexane (31%). Mp 116–118 °C; δ_H (500 MHz; $CDCl_3$) 8.09 (2 H, br s, NH), 6.71 (2 H, dt, J 2.7 and 1.7 Hz, CH), 6.15 (2 H, dd, J 6.0 and 2.7 Hz, CH), 6.01 (2 H, br s, CH), 5.89 (1 H, br s, *meso*-H); δ_F (254 MHz; $CDCl_3$, $CFCl_3$) −142.00 (d, J 16.61 Hz, *ortho*-F), −156.22 (t, J 20.90 Hz, *para*-F), −161.69 (dt, J 20.90 and 8.2 Hz, *meta*-F); δ_C (125 MHz; $CDCl_3$) 33.1, 107.7, 108.7, 118.1, 115.8, 128.1, 136.8, 138.83, 141.4, 144.0, 146.0; EI-MS m/z 312 (100%, M^+), 246 (40), 145 (65); HREI-MS m/z M^+, 312.0694; $C_{14}H_9F_5N_2$ requires m/z 312.0686.

5,10,15,20-Tetrakis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]-porphyrin (1) from pyrrole and aldehyde 6

A solution of pyrrole (0.138 cm^3, 1.99 mmol) and **6** (800 mg, 1.99 mmol) in chloroform (200 cm^3) was purged with N_2 for 15 min before the slow addition $BF_3{\cdot}OEt_2$ (0.084 cm^3, 0.663 mmol) at room temperature reaction in the dark. The progress of the reaction was monitored by periodically removing aliquots, oxidising with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and analysing them by UV–Vis spectroscopy. After two hours, DDQ (242 mg, 1.28 mmol) was added to the mixture which was left stirring at room temperature. After 1 h the reaction mixture was evaporated to dryness with a rotary evaporator and the residue was purified by chromatography on a dry silica gel column with dichloromethane–cyclohexane (50 : 50, v/v). The product, which contained some tar, was rechromatographed on silica gel with dichloromethane–hexane (50 : 50) to give 30 mg of an impure, oily sample of **1**.

5,10,15,20-Tetrakis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]-porphyrin (1) from aldehyde 6 and dipyrromethane (7)

A solution of **6** (388 mg, 0.97 mmol) and **7** (507 mg, 0.97 mmol) in chloroform (100 cm^3) was purged with N_2 for 15 min before the addition of $BF_3{\cdot}OEt_2$ (0.040 cm^3, 0.013 mmol) in the dark. The progress of the reaction was periodically checked by UV–Vis analysis as described above and after 1 h DDQ (280 mg, 1.23 mmol) was added and the mixture was left stirring a further hour. After removal of the solvent with a rotary evaporator, the crude residue was chromatographed on a silica gel column with dichloromethane–hexane (60 : 40, v/v) affording 58 mg of **1** (6.7%). Compound **1**: δ_H (270 MHz; $CDCl_3$) 8.92 (8 H, br s, β-H), 7.33–6.68 (52 H, m, ArH), 5.02 (8 H, br s, PhCHC$_3$H$_7$), 0.72–0.35 (56 H, m, aliphatic protons), −2.25 (2 H, br s, NH); δ_C [68 MHz; $(CD_3)_2CO$] 160.12, 143.74, 130.24, 129.20, 128.09, 127.14, 121.82, 113.02, 107.22, 80.04, 41.10, 19.17, 13.32; λ_{max} (CH_2Cl_2)/nm 419 (ε/m^2 mol^{-1}, 3.98×10^4), 512 (2.15×10^3), 544 (476), 589 (660), 644 (158); ESI-MS m/z 1801 (M+1, 100%); HRMS-FAB$^+$ m/z M^+, 1798.9588, $C_{124}H_{126}N_4O_8$ requires m/z 1798.9576.

5-Pentafluorophenyl-10,15,20-tris[(*R*,*R*)-2,6-bis(1-phenylbutoxy)-phenyl] porphyrin (3)

A solution of compound **7** (1 g, 1.93 mmol), **6** (388 mg, 0.96 mmol) and pentafluorobenzaldehyde (189 mg, 0.96 mmol) in chloroform (195 cm^3) was reacted with $BF_3{\cdot}OEt_2$ and the product worked up and purified as described above for **1**. The

porphyrin products obtained were eluted from the column in the following order: **2** (47 mg, 7.1%), **3** (121 mg, 8.0%) and **1** (17 mg, 1.6%). Compound **3**: δ_H (500 MHz; $CDCl_3$) 8.95 (4 H, s, β-H), 8.86 (2 H, d, *J* 4.5 Hz, β-H), 8.73 (2 H, d, *J* 4.5 Hz, β-H), 7.38–6.65 (39 H, m, Ar*H*), 5.06 (6 H, m, PhC*H*C_3H_7), 1.00–0.16 (24 H, m, CH_2CH_2), 0.12 (6 H, t, *J* 7.4, CH_3), −0.06 (6 H, t, *J* 7.4, CH_3), −0.20 (6 H, t, *J* 7.4, CH_3), −2.42 (2 H, s, N*H*); δ_C (68 MHz; $CDCl_3$) 159.25, 159.11, 142.69, 142.61, 142.29, 129.44, 129.32, 128.23, 128.11, 127.93, 127.02, 126.92, 125.83, 125.71, 120.96, 113.16, 106.61, 106.29, 106.15, 79.84, 79.70, 79.52, 40.18, 40.08, 39.87, 18.32, 18.12, 18.02, 12.88, 12.82; δ_F (254 MHz; $CDCl_3$–$CFCl_3$) −137.37 (2 F, dd, *J* 24.25 and 8.43 Hz, *ortho*-F), −154.59 (1 F, t, *J* 21.28 Hz, *para*-F), −163.39 (2 F, dt, *J* 23.02, 21.53 and 8.43 Hz, *meta*-F); λ_{max} (CH_2Cl_2)/nm 418 (ε/m² mol^{-1} 3.72×10^4), 512 (2.04×10^3), 544 (402), 587 (664), 641 (155); ESMS *m*/*z* 1593.4 ($M^{+\bullet}$, 100%); HRMS-FAB$^+$ *m*/*z* M^+, 1592.7325, $C_{104}H_{95}F_5N_4O_6$ requires *m*/*z* 1592.7328.

5,15-Bis(pentafluorophenyl)-10,20-bis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin (2)

A solution of compound **6** (785 mg, 1.51 mmol) and pentafluorobenzaldehyde (296 mg, 1.51 mmol) in chloroform (150 cm^3) was reacted with $BF_3{\cdot}OEt_2$ and the products were worked up as described for porphyrin **1** to give porphyrin **2** (184 mg, 18%); δ_H (270 MHz; $CDCl_3$) 8.94 (4 H, d, *J* 4.5 Hz, β-H), 8.78 (4 H, d, *J* 4.5 Hz, β-H), 7.38 (2 H, t, *J* 8.5 Hz, Ar*H*), 7.97 (12 H, m, Ar*H*), 6.76 (12 H, m, Ar*H*), 5.09 (4 H, dd, *J* 4.8 and 6.0 Hz, PhC*H*C_3H_7), 0.97–0.82 (8 H, m, PhCHC*H*$_2C_2H_5$), 0.56 (8 H, m, $PhC_2H_3CH_2CH_3$), 0.26 (12 H, t, *J* 7.2 Hz, C*H*$_3$), −2.55 (2 H, s, N*H*); δ_C (68 MHz; $CDCl_3$) 159.03, 142.31, 129.96, 128.05, 126.96, 125.51, 120.15, 114.55, 106.43, 80.02, 40.20, 18.38, 12.98; δ_F (254 MHz; $CDCl_3$–$CFCl_3$) −137.42 (4 F, dd, *J* 24.26 and 8.91 Hz, *ortho*-F), −153.71 (2 F, t, *J* 20.80 Hz, *para*-F), −162.97 (4 F, dt, *J* 8.93 Hz, *meta*-F); λ_{max} (CH_2Cl_2)/nm 417 (ε/m² mol^{-1} 2.75×10^4), 511 (1.67×10^3), 543 (381), 588 (538), 642 (262); ESI-MS *m*/*z* 1387.4 ($M^{+\bullet}$, 100%); HRMS-FAB$^+$ *m*/*z* M^+, 1386.5083, $C_{84}H_{68}F_{10}N_4O_4$ requires *m*/*z* 1386.5081.

5,10,15-Tris(pentafluorophenyl)-20-[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin (4) and 5,10-bis(pentafluorophenyl)-15,20-bis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin (5)

Compounds **7** (660 mg, 1.28 mmol) and **8** (400 mg, 1.27 mmol) were reacted in chloroform (256 cm^3) with pentafluorobenzaldehyde (308 mg, 3.16 mmol) as described above for porphyrin **1**. The products were eluted from a silica gel column using dichloromethane–hexane (60 : 40, v/v) in the following order: porphyrin **4** (75 mg, 8.1%), **2** (96 mg, 8.8%) and **5** (24 mg, 2.2%).

Porphyrin 4. δ_H (500 MHz; $CDCl_3$) 8.96 (2 H, d, *J* 4.3 Hz, β-*H*), 8.90 (2 H, d, β-*H*), 8.88 (2 H, d, β-*H*), 8.76 (2 H, d, *J* 4.3 Hz, β-*H*), 7.39 (1 H, t, *J* 8.6 Hz, Ar*H*), 7.07 (2 H, t, *J* 7.1 Hz, Ar*H*), 7.03 (4 H, t, *J* 7.4 Hz, Ar*H*), 6.77 (4 H, d, *J* 7.1 Hz, Ar*H*), 6.74 (2 H, d, *J* 8.6 Hz, Ar*H*), 5.08 (2 H, dd, *J* 8.6 and 4.8 Hz, PhC*H*C_3H_7), 0.95–0.88 (2 H, m, PhCHC*H*$_2CH_2CH_3$), 0.79–0.72 (2 H, m, PhCHC*H*$_2CH_2CH_3$), 0.49–0.39 (4 H, m, PhCH-$CH_2CH_2CH_3$), 0.14 (6 H, t, *J* 7.3 Hz, CH_3); δ_C (68 MHz; $CDCl_3$) 158.83, 142.15, 128.17, 127.14, 125.53, 106.29, 79.96, 40.12, 18.22, 12.90; δ_F (254 MHz; $CDCl_3$–$CFCl_3$) −137.10 (dd, *J* 7.87 and 23.6 Hz, *ortho*-F), −137.46 (dd, *J* 7.87 and 23.58 Hz, *ortho*-F), −152.47 (t, *J* 22.00 Hz, *para*-F), −152.68 (t, *J* 22.00 Hz, *para*-F), −162.37 (m, *meta*-F); λ_{max} (CH_2Cl_2)/nm 415 (ε/m² mol^{-1} 2.50×10^4), 510 (1.62×10^3), 539 (252), 585 (561), 639 (100); FAB$^+$-MS *m*/*z* 1181 ($M^{+\bullet}$, 90%); HRMS-FAB$^+$ *m*/*z* M^+, 1180.2841, $C_{64}H_{39}F_{15}N_4O_2$ requires *m*/*z* 1180.2834.

Porphyrin 5. δ_H (270 MHz; $CDCl_3$) 8.98 (2 H, s, β-H), 8.89 (2 H, d, *J* 5.83 Hz, β-H), 8.88 (2 H, s, β-H), 8.76 (2 H, d, *J* 4.86 Hz, β-H), 7.31–6.55 (26 H, m, Ar*H*), 5.09 (2 H, t, *J* 6.53 Hz, PhC*H*C_3H_7), 5.02 (2 H, dd, *J* 8.98 and 4.62 Hz, PhC*H*C_3H_7), 0.79–0.22 (16 H, m, PhCHC*H*$_2CH_2CH_3$), 0.04 (6 H, t, *J* 7.05 Hz, $PhCHCH_2CH_2CH_3$), −0.02 (6 H, t, *J* 7.26, $PhCHCH_2$-CH_2CH_3), −2.55 (2 H, s, N*H*); δ_C (68 MHz; $CDCl_3$) 159.11, 158.79, 142.57, 142.23, 129.80, 128.25, 128.11, 127.10, 125.81, 125.59, 120.05, 115.68, 106.07, 106.03, 79.72, 79.40, 40.26, 39.83, 18.22, 18.04, 12.94, 12.82; δ_F (254 MHz; $CDCl_3$, $CFCl_3$) −137.22 (dd, *J* 24.21 and 8.46 Hz, *ortho*-F), −137.42 (dd, *J* 24.21 and 8.46 Hz, *ortho*-F), −153.52 (t, *J* 20.55 Hz, *para*-F), −162.81 (m, *meta*-F); λ_{max} (CH_2Cl_2)/nm 417 (ε/m² mol^{-1} 3.42×10^4), 512 (2.04×10^3), 543 (329), 585 (730), 640 (74); ESI-MS *m*/*z* 1387 ($M^{+\bullet}$, 100%); HRMS-FAB$^+$: found M^+, 1386.5084, $C_{84}H_{68}F_{10}N_4O_4$ requires *m*/*z* 1386.5081.

Chloroiron 5,10,15,20-tetrakis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)-phenyl]porphyrin (Fe1)

Iodine (33 mg, 0.130 mmol) and $Fe(CO)_5$ (0.1 cm^3, 0.760 mmol) were added to a solution of porphyrin **1** (56 mg, 0.031 mmol) in toluene (150 cm^3) under nitrogen. The mixture was stirred under reflux until no more free-base could be detected by UV–Vis analysis (2.5 h) and the solution was cooled to room temperature and left stirring overnight under aerobic conditions. Removal of the solvent with a rotary evaporator gave a brownish residue which was dissolved in dichloromethane, washed with water and dried ($MgSO_4$). Column chromatography of the crude product mixture on silica gel using dichloromethane as eluant gave two main bands, the first was bright red and was identified by UV–Vis spectroscopy to be a hydroxo-iron porphyrin by comparison with literature spectra for the hydroxoiron(III) *meso*-tetrakis(pentafluorophenyl)-porphyrin.[31] The second is believed to have iodide as the axial ligand on the iron porphyrin arising from the iodine used in the metallation process. The two fractions were converted with 10% hydrochloric acid solution to the same metalloporphyrin with an axial chloride. The solution was dried over NaCl and solvent removal gave the iron(III) porphyrin **Fe1** (50 mg, 85%); λ_{max} (CH_2Cl_2/nm) 376 (ε/m² mol^{-1}, 5.20×10^3), 421 (1.02×10^4), 510 (1.49×10^3), 584 (461); ESI-MS *m*/*z* 1853.7 [(M + 1) − Cl, 100%].

Chloroiron 5,15-bis(pentafluorophenyl)-10,20-bis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin (Fe2)

Porphyrin **2** (44 mg, 0.032 mmol), $Fe(CO)_5$ (0.1 cm^3, 0.760 mmol) and iodine (33 mg, 0.130 mmol) were reacted in toluene (15 cm^3) using the same procedure as for **Fe1** to give **Fe2** (38 mg, 8%); λ_{max} (CH_2Cl_2/nm) 373 (ε/m² mol^{-1} 4.33×10^3), 417 (8.36×10^3), 508 (973), 605 (445); ESI-MS *m*/*z* 1440.2 (M − Cl, 100%); HRMS-FAB$^+$ *m*/*z* M^+, 1440.4281, $C_{84}H_{68}F_{10}FeN_4O_4$ requires *m*/*z* 1440.4274.

Chloroiron 5-pentafluorophenyl-10,15,20-tris[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin (Fe3)

Porphyrin **3** (50 mg, 0.031 mmol) and $Fe(CO)_5$ (0.1 cm^3, 0.760 mmol) were dissolved in toluene (15 cm^3) and reacted with iodine (27 mg, 0.106 mmol) using the same procedure as for **Fe1** to give **Fe3** (45 mg, 85%); λ_{max} (CH_2Cl_2/nm) 373 (ε/m² mol^{-1} 4.79×10^3), 420 (8.79×10^3), 508 (1.25×10^3), 577 (475), 647 (377); ESI-MS *m*/*z* 1647.8 (M − Cl, 100%); HRMS-FAB$^+$ *m*/*z* M^+, 1646.6528, $C_{104}H_{95}F_5FeN_4O_6$ requires *m*/*z* 1646.6521.

Chloroiron 5,10,15-tris(pentafluorophenyl)-20-[(*R*,*R*)-2,6-bis-(1-phenylbutoxy)phenyl]porphyrin (Fe4)

Porphyrin **4** (20 mg, 0.017 mmol) and $Fe(CO)_5$ (0.1 cm^3, 0.760 mmol) were reacted with iodine (12 mg, 0.048 mmol) in toluene (10 cm^3) using the method for **Fe1** to give **Fe4** (16 mg, 74%); λ_{max} (CH_2Cl_2/nm) 354 (ε/m² mol^{-1}, 5.83×10^3), 413 (1.12×10^4), 505

(1.35×10^3), 634 (581); ESI-MS *m*/*z* 1234 (M − Cl, 100%); HRMS-FAB$^+$ *m*/*z* M^+, 1234.2035, $C_{64}H_{37}F_{15}FeN_4O_2$ requires *m*/*z* 1234.2026.

Chloromanganese 5,15-bis(pentafluorophenyl)-10,20-bis[(*R*,*R*)-2,6-bis(1-phenylbutoxy)phenyl]porphyrin (Mn2)

Porphyrin **2** (40 mg, 0.029 mmol), $Mn_2(CO)_{10}$ (202 mg, 0.518 mmol) and iodine (18 mg, 0.071 mmol) were reacted in toluene (15 cm^3) using the same procedure as for **Fe1** to give **Mn2** (25 mg, 58%); λ_{max} (CH_2Cl_2/nm) 371 (ε/m^2 mol^{-1} 6.60×10^3), 477 (1.28×10^4), 577 (1.24×10^3), 610 (618); ESI-MS *m*/*z* 1439.3 (M − Cl, 100%); HRMS-FAB$^+$ *m*/*z* M^+, 1439.4302, $C_{84}H_{68}F_{10}MnN_4O_4$ requires *m*/*z* 1439.4305.

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