

**FACILE AERIAL OXIDATION OF UNSYMMETRICAL MESO-TETRAARYL
PORPHYRINS WITH 3,5-DI-t-BUTYL-4-HYDROXYPHENYL (DtB4HP) AND
4-NITROPHENYL (4-NP) SUBSTITUENTS.**

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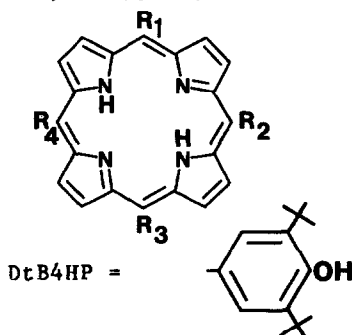
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Abstract - Porphyrins unsymmetrically substituted with 3,5-di-t-butyl-4-hydroxyphenyl (DtB4HP) and 4-nitrophenyl (4-NP) groups, have been synthesised and characterised. Their aerial oxidation in basified dichloromethane solutions has been studied, using u.v.-visible spectroscopy, and compared with their half-wave potentials (E^0) obtained from cyclic voltammetry.

Introduction

In previous papers,^{1,2} we examined the aerial oxidation, in basified (1M n-Bu₄N⁺OH⁻ or KOH in MeOH) dichloromethane solutions, of unsymmetrical porphyrins meso-substituted with redox-active (DtB4HP) and functionalisable 4-hydroxyphenyl (4-HP)¹ and 3-hydroxyphenyl (3-HP)² groups.



- (1). R₁=R₂=R₃=R₄=DtB4HP
- (2). R₁=R₂=R₃=P; R₄=DtB4HP
- (3). R₁=R₂=P; R₃=R₄=DtB4HP
- (4). R₁=R₃=P; R₂=R₄=DtB4HP
- (5). R₁=P; R₂=R₃=R₄=DtB4HP
- (6). R₁=R₂=R₃=R₄=P

P = 4-HP in (2a-5a)
P = 3-HP in (2b-5b)
P = 4-NP in (2c-5c)

Scheme 1

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We found that these porphyrins oxidised much less than (1) under similar conditions,³ but that (2a-5a) were more reactive to oxygen than (2b-5b). We rationalised this in terms of the relative deprotonating power of the two bases used⁴, decreased acidity of phenols with bulky substituents ortho to the hydroxy group⁵, and competition between the different electron-releasing powers of the phenoxide anions.⁶

We also found no correlation between the E° values (obtained by cyclic voltammetry) and reactivity to oxygen for the two sets of porphyrins. We argued that the key to this behaviour could be the availability of electron density on DtB4HP substituents to oxygen.²

The functional groups in these two sets of porphyrins donate electrons onto the macrocycle. We wished to see the effect electron-withdrawing groups, such as meso-4-nitrophenyl (4-NP), would have on the ease of aerial oxidation.

Results and Discussion

Porphyrins (2c-5c) were prepared using the mixed Rothmund reaction, as described in previous papers.^{1,2,7} The mixture of unsymmetrical porphyrins was purified by column chromatography on alumina, and then separated by column chromatography on silica gel, eluting with solvent mixtures of dichloromethane and n-hexane.

The porphyrins (2c-5c) were characterised using FABS, mass spectroscopy, microanalysis, ^1H -n.m.r., u.v.-visible and infra-red spectroscopy. The ^1H -n.m.r. spectra of 4c and 5c indicated an AB spin system ($J_{AB}=4.9$ Hz) for the pyrrole β -protons of the porphyrin macrocycle, in line with previous n.m.r. observations of unsymmetrical porphyrins 'trans'-di-meso-substituted with electron donating and electron withdrawing moieties.⁷

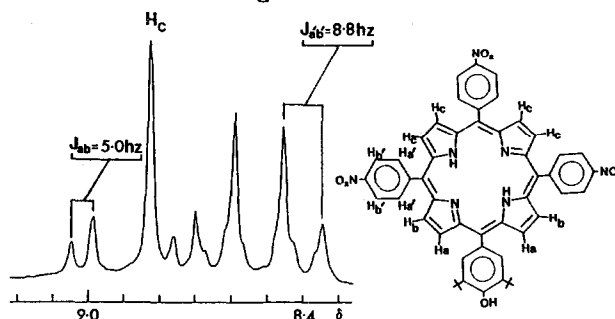
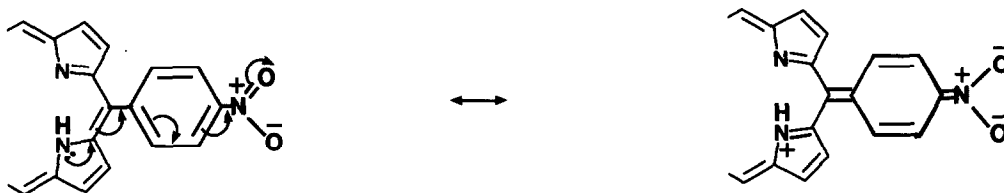


Figure 1. Detail of ^1H -n.m.r. spectrum of 5c showing AB spin-systems for 4-NP and pyrrole β -protons.

The u.v.-visible spectra of porphyrins (**2c-5c**) (Figure 2) are typical⁸ of *meso*-tetraarylporphyrin free-bases, with intense B bands (around 425 nm) and four much less intense Q bands (480 - 650 nm) in neutral dichloromethane, and less intense B bands (450-460 nm) with a broad Q band (670-700 nm) of increased intensity, in acidified (TFA) dichloromethane.

The dication B band spectra of (**3c-5c**) have pronounced shoulders to shorter wavelength of the main B band, indicating small amounts of neutral non-protonated porphyrins probably remaining in equilibrium with the dicationic forms.

Comparison of N-O antisymmetric IR stretching frequencies⁸ in *meso*-tetra(4-nitrophenyl)porphyrin (1518 cm^{-1}) and 4-nitrobenzaldehyde (1535 cm^{-1}) support this view: the shift to a lower frequency in the former is most likely due to increased conjugation of the 4-NP group to the porphyrin macrocycle (scheme 2), making it harder to protonate the central nitrogens.



Scheme 2

We find similar shifts in the N-O antisymmetric stretching frequencies for porphyrins (**2c-5c**).

Addition of base (1M solutions of either $n\text{-Bu}_4\text{N}^+\text{OH}^-$ or KOH in MeOH; 10 drops) to dichloromethane solutions of porphyrins (**2c-5c**) led to colour and spectroscopic changes (see Figure 2) similar to the previous two series of unsymmetrical porphyrins.^{1,2} In particular, B band absorption was reduced; for **2c** it disappeared completely. There were also differences in the amount of serial oxidation produced in these two bases. This was measured by acidifying aliquots of the basified porphyrin solutions at different time intervals, and measuring the intensity of the dicationic B band compared to that produced by acidifying the neutral porphyrin solution^{1,2}.

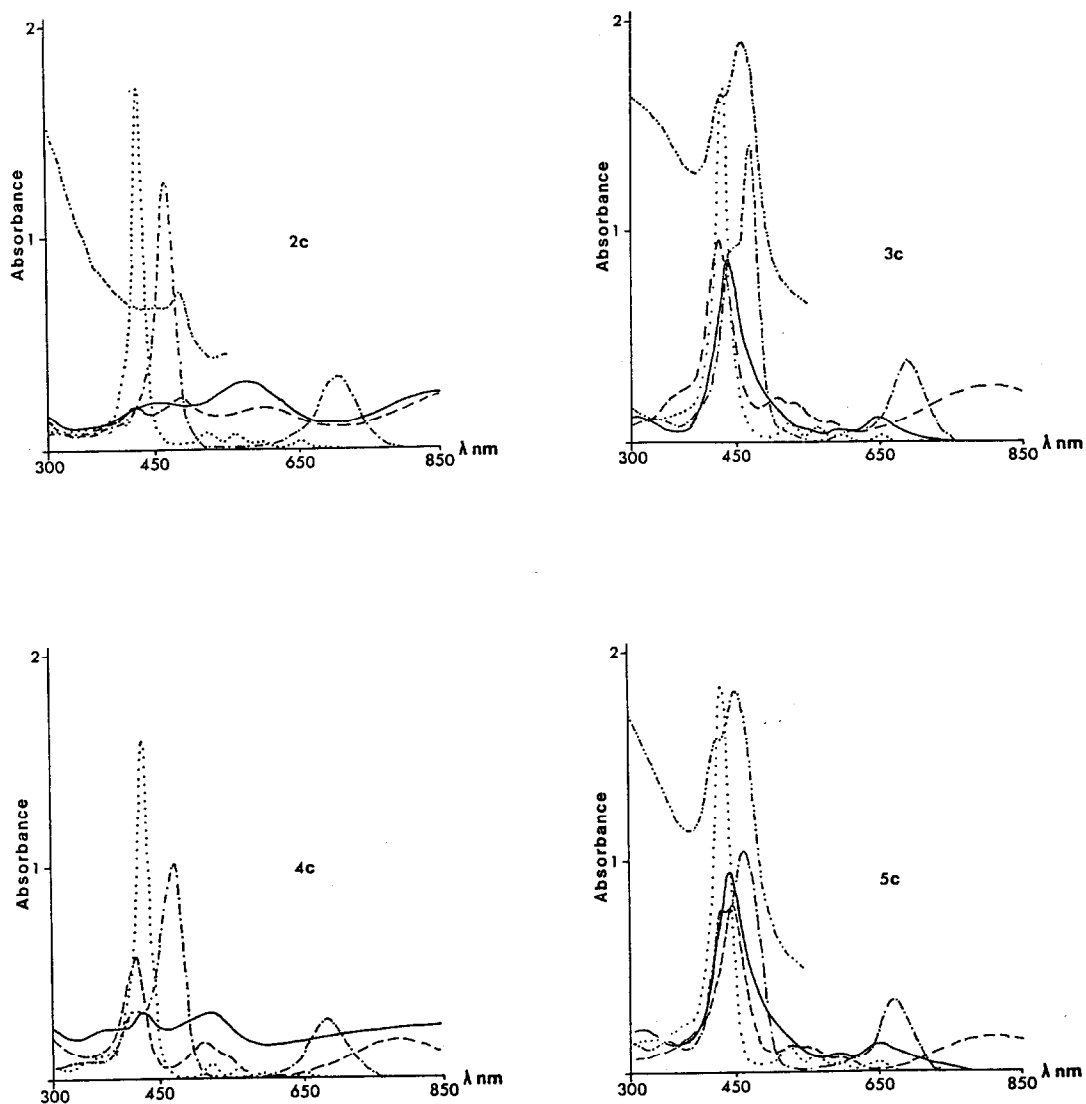


Figure 2. U.v.-visible spectra of porphyrins (2c-5c) in neutral (....), acidified (with TFA, -.-.-), basified (with 1M $n\text{-Bu}_4\text{N}^+\text{OH}^-/\text{MeOH}$, _____), basified, then reacidified (-.-.-) DCM.

Thus, with the exception of **2c**, $n\text{-Bu}_4\text{N}^+\text{OH}^-$ produces very little aerial oxidation. The base 1M KOH/MeOH, however, causes porphyrins **2c** and **4c** to undergo very extensive aerial oxidation (Table 1).

Basification of porphyrins **3c** and **5c** with methanolic KOH leads to spectral changes very similar to *meso*-tetrakis(4-hydroxyphenyl)porphyrin under similar conditions⁹, i.e., a change in colour of the solutions to olive green, accompanied by reduction in B band intensity and red shift (427 nm to 438 nm), and collapse of the Q bands from four to two. Similar changes were observed with methanolic $n\text{-Bu}_4\text{N}^+\text{OH}^-$ except both porphyrins also gave broad peaks centred around 800 nm.

Acidification of these basified porphyrin solutions showed that very little aerial oxidation of **3c** and **5c** had taken place: that only weak e.s.r. spectra were obtained for these porphyrins tends to confirm this.

In neutral solutions, cyclic voltammograms of porphyrins **3c** and **4c** (see Table 2) show a steady increase in E^0 , compared to previously studied series of unsymmetrically *meso*-substituted porphyrins, such that:-



This is expected as the non-oxidisable substituent in each case changes from the mesomerically donating 4-HP group, through inductively donating 3-HP, to electron-withdrawing 4-NP.

On basification, the E^0 values for **3c** and **4c** decrease markedly. This is in line with similar behaviour observed in porphyrins **3a**, **3b**, **4a**, and **4b**. However, with the exception of **4c**, the differences in E^0 between neutral and basified solutions of these porphyrins shows a steady increase in going from 4-HP, to 3-HP, to 4-NP substituents. Again, this probably reflects 4-NP groups pulling more electron density onto the macrocycle from deprotonated DtB4HP groups, so making the molecule harder to oxidise.

We indicated previously^{1,2} that as DtB4HP groups are replaced, respectively, with 4-HP and 3-HP *meso*-substituents, the amount of aerial oxidation (in 1M KOH/MeOH) decreases compared to (1). This is because there is less resistance to electron donation onto the macrocycle, by deprotonated DtB4HP groups. We expected, therefore, that replacing DtB4HP groups with electron-withdrawing 4-NP groups (**2c-5c**) should enhance this effect.

Table 1 shows that this expectation is fulfilled for porphyrins **3c** and **5c**. However, porphyrins **2c** and **4c** undergo much more extensive aerial oxidation than **2a** or **2b**, and **4a** or **4b**, respectively.

Table 1. Maximum reduction in returned dicationic B band absorption^a after acidifying^b aliquots of the basified porphyrin solutions.

PORPHYRIN ^d	BASE ^c	
	1M tNBAl/MeOH	1M KOH/MeOH
2a	<10%	70%
2b	<10%	45%
<u>2c</u>	40%	virtually complete
3a	<10%	75%
3b	Nil	12%
<u>3c</u>	<10%	<10%
4a	<10%	47%
4b	<10%	46%
<u>4c</u>	10%	>75%
5a	<10%	65%
5b	---	---
<u>5c</u>	<10%	<10%

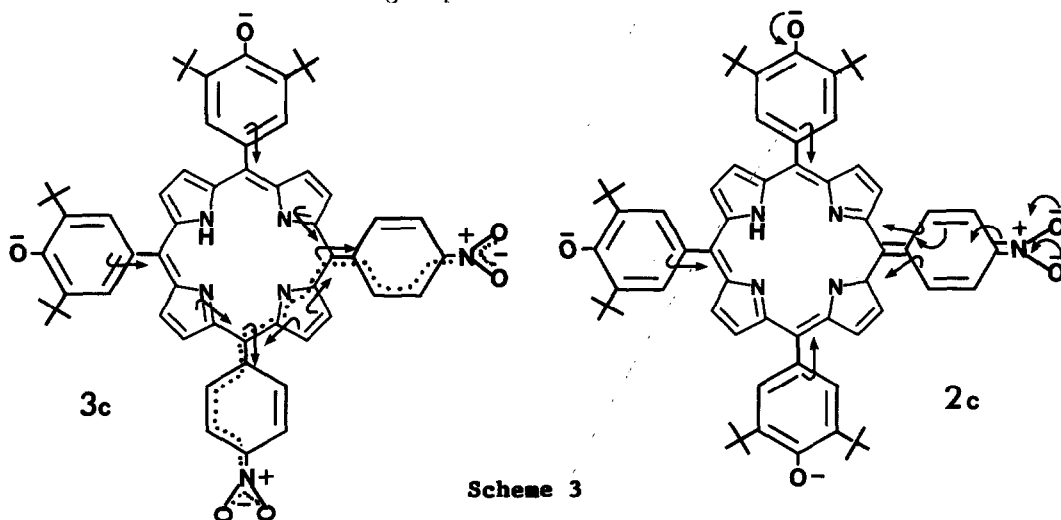
^aThis is a direct indication of the amount of aerial oxidation that has taken place. ^bTFA. ^c10 drops added to a neutral stock solution of the porphyrin in dichloromethane. ^dData for the a- and b-series porphyrins taken from refs. 1 and 2.

Table 2. First half-wave potentials (V vs. s.c.e.^a) of 'cis' (3) and 'trans' (4) di-substituted porphyrins in neutral and basified^b dichloromethane.

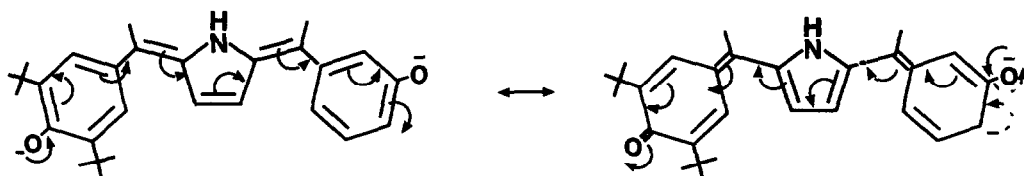
PORPHYRIN ^c	E ^o (V)		
	Neutral	Basic	Difference
3a	0.75	0.42	0.33
3b	0.87	0.51	0.36
<u>3c</u>	0.96	0.50	0.46
4a	0.78	0.46	0.32
4b	0.89	0.34	0.55
<u>4c</u>	1.03	0.48	0.55

^aSaturated calomel electrode. ^bBy addition of NaOEt. ^cData for the a- and b-series porphyrins taken from ref. 1 and 2.

In the previous paper² we argued that ease of aerial oxidation could depend on the availability to oxygen of electron density around deprotonated DtB4HP groups. Further, E° values obtained by cyclic voltammetry reflect the ease of one-electron oxidation of a whole porphyrin molecule, i.e., macrocycle and substituents, and are therefore not necessarily correlated with the ease of aerial oxidation (which would be site-specific to DtB4HP groups). Scheme 3 illustrates how changes in the availability of electron density on deprotonated DtB4HP groups could be modulated by their relative positions to one another on the macrocycle (i.e., 'cis' or 'trans') and the the different actions of 4NP groups in **3c** and **2c**.



In the case of porphyrin **4b**, although DtB4HP groups are opposing each other's electron donation onto the macrocycle, their electron density could conceivably find its way onto the 3-HP meso-substituents (as the latter's phenoxide groups cannot oppose them - see Scheme 4).



The overall effect would be to deplete electron density around the DtB4HP groups so that compared to **4c**, **4b** would be likely to undergo less aerial oxidation. Some preliminary evidence for this point of view comes from the complexity of the e.s.r. spectrum of porphyrin **4b** in basified dichloromethane (see Figure 3), which suggests that unpaired electron density is no longer localised on a DtB4HP group (as is the case for porphyrin **1** which gives a simple 1:2:1 triplet in its e.s.r. spectrum in basified dichloromethane).^{1,3c}

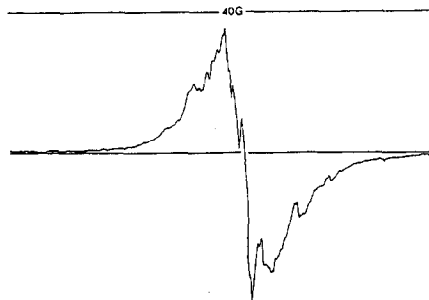
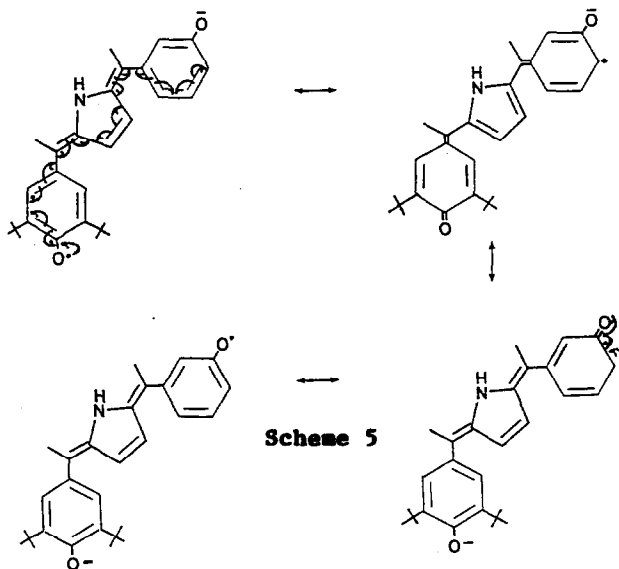


Figure 3. E.s.r. spectrum of **4b**, $g = 2.0048 \pm 0.0003$

The low E^0 value for **4b** from cyclic voltammetry, could be due to stabilisation of unpaired electron density onto a 3-HP group (Scheme 5).



An e.s.r. spectrum for porphyrin **5c** has been obtained and, although weak, shows features which suggest that the 4-NP groups are withdrawing unpaired electron density away from the lone DtB4HP group onto the rest of the molecule (Figure 4).

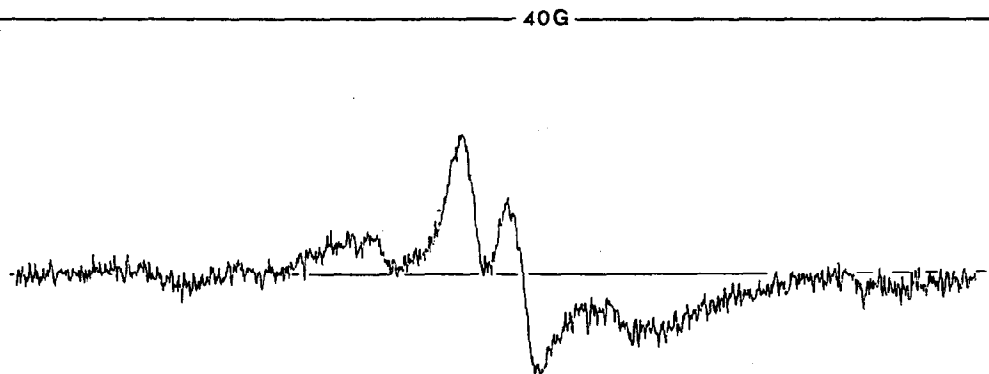


Figure 4. E.s.r. spectrum of **5c**, $g = 2.0048 \pm 0.0003$

The effect of electron donating and withdrawing groups, *meso*-substituted into the same porphyrin macrocycle could be to so increase the polarisability of the molecule that it may demonstrate non-linear optical (NLO) effects, such as second-harmonic generation (SHG).^{11,12} We have measured the molecular hyperpolarisability constant, for the neutral species **3c**, using the SHG powder method¹³ but found that the value was small (1.3×10^{-3} compared to urea [with an assigned value of unity] at an excitation wavelength of 1.906

m.). However, this measurement was performed on the neutral form of **3c**, in which the full electron-donating effect of deprotonated DtB4HP groups has not been developed. Consequently, the polarisability of the molecule is expected to be small. We expect substantially higher values for **3c**, and similar unsymmetrically substituted porphyrins, when their anionic forms (as counterions to Group 1 metal cations or quaternary ammonium cations) can be obtained in the solid state. Experiments along these lines are currently in progress.

Experimental

Chromatographic separations of the porphyrins were performed on columns made from slurries of neutral alumina (Brockmann activity grade III, B.D.H.)

or silica gel (Kieselgel 60, 230-400 mesh, Merck). Thin-layer chromatography plates (alumina and silica, Merck) were obtained ready-made. Pyrrole, substituted benzaldehydes, propionic acid, 1M n-Bu₄N⁺OH⁻ in MeOH, and TFA were purchased from Aldrich, and used as supplied. Chloroform, dichloromethane, MeOH, and n-hexane were reagent grade (B.D.H.). N.m.r. spectra were run on a Bruker WP80SY instrument using deuterated dichloromethane as solvent and TMS as internal reference. E.s.r. spectra were run on a Varian E/109 spectrometer, using approximately 10⁻²M porphyrin solutions in basified dichloromethane. Cyclic voltammograms were performed in neutral and basified dried, nitrogen-purged dichloromethane, with tetra-n-butylammonium fluoroborate (0.1M) as supporting electrolyte. For the basic solutions, sodium ethoxide in ethanol (10⁻²M) was added, after purging with nitrogen. All u.v.-visible spectra were recorded on a Shimadzu UV-260 spectrophotometer. Stock solutions of the porphyrins were prepared in dichloromethane (4-6*10⁻⁶M; 100 cm³) and their spectra recorded. A solution of 1M n-Bu₄N⁺OH⁻/MeOH or 1M KOH/MeOH (10 drops) was then added to each stock solution at room temperature and their spectra recorded again. Acidification (to test the amount of aerial oxidation) was performed by withdrawing aliquots of these basic solutions, at different time intervals, placing them in a cuvette, and adding TFA (2-3 drops). The u.v.-visible were then rerecorded and the change in the intensity of the dicationic B band measured.

Synthesis of porphyrins (2c-5c)---4-Nitrobenzaldehyde (7.55 g; 50 mmol) and 3,5-di-t-butyl-4-hydroxybenzaldehyde (11.75 g; 50 mmol) were brought to reflux in propionic acid (500 cm³). Pyrrole (7.0 cm³; 100 mmol) was added and reflux continued for a further 3 h. The mixture was concentrated to 20% of its original volume, and then cooled overnight. The purple slurry of mixed porphyrins was then filtered and washed with methanol. The crude material was dissolved in the minimum dichloromethane, applied to a column of neutral alumina, and the brown-red band of mixed porphyrins eluted with DCM. The eluant was collected and precipitated with hexane fraction, to give a mixture off *αααα* *ββββ* (1.0 g). Half of this was divided into batches of 50 mg, which were then taken into the minimum of DCM, applied to a column of silica gel, and eluted with a solvent mixture consisting of 60:40 DCM/hexane fraction. The separated porphyrin fractions were collected and tested for purity via thin layer chromatography on silica and alumina. All separated fractions gave one spot. M.p.'s exceeded 300°C.

The **first fraction** to leave the column was porphyrin 1, which was discarded. The **second fraction** off the column was concentrated and precipitated with hexane fraction to give a purple amorphous powder of porphyrin 2c (100 mg) (Found: C, 79.46; H, 9.38; N, 5.22; C₆₈H₇₈N₄O₅ requires C, 79.3; H, 9.4; N, 5.1). (EARS: found M_r, m/z=1045; requires m/z=1045). (Mass spectrum(CI), m/z [344 (M⁺), [329 ([M+1]-CH₃, 22%), 998 ([M+1]-NO₂, 8%): max(CDCl₃) 3640 (OH), 3310 (pyrrole

NH), 2960 - 2850 (t-butyl-H), 1600 (benzene ring), 1520 (N-O antisymmetric stretch), 1430 (CH deformation), 1350 cm^{-1} (N-O symmetric stretch). $\max(\text{CH}_2\text{Cl}_2)$ ($/1 \text{ mol}^{-1} \text{ cm}^{-1}$) 426(188), 521(8.2), 561(7.3), 595(2.8), 653(3.5); $\max(\text{CH}_2\text{Cl}_2 + \text{two drops TFA})$ 463(137), 702 nm(37): ^1H (80 MHz; CDCl_3 , TMS) - 2.75 (broad s, -NH, 2H), 1.63 (m, t-butyl-H, 54H), 5.52 (s, -OH, 3H), 8.04 (s, aromatic-H [DtB4HP], 6H), 8.34, 8.45, 8.57, 8.68 (q, aromatic-H[4-NP], 4H; AB spin system centred on 8.51 ppm, $J_{AB}=8.7 \text{ Hz}$), 8.94 (s, pyrrole -H, 4H), 8.68, 8.73, 8.94, 8.98 (q, pyrrole -H, 4H; AB spin system, overlapping with 4-NP, centred on 8.83 ppm, $J_{AB}=4.0 \text{ Hz}$).

The **third fraction** off the column was concentrated and precipitated with hexane fraction, to give a purple amorphous powder of porphyrin **4c** (50 mg) (Found: C, 71.7; H, 6.0; N, 8.5: $\text{C}_{60}\text{H}_{60}\text{N}_6\text{O}_6 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ requires C, 71.87; H, 6.05; N, 8.30.). (FABS: found M+1, $m/z=961$): (Mass spectrum(CI), m/z 961 (M^++1 , 100%), 946 ([M+1]- CH_3 , 33%), 915 ([M+1]- NO_2 , 17%): $\max(\text{CDCl}_3)$ 3640 (OH), 2960 - 2850 (t-butyl-H), 1600 (benzene ring), 1520 (N-O antisymmetric stretch), 1350 cm^{-1} (N-O symmetric stretch): $\max(\text{CH}_2\text{Cl}_2)$ ($/1 \text{ mol}^{-1} \text{ cm}^{-1}$) 427(338.5), 521(19), 560(14.7), 595(6.7), 653(8.7); $\max(\text{CH}_2\text{Cl}_2 + \text{two drops TFA})$ 413(71), 469(225.3), 680(58.5) nm; ^1H (d_2 -DCM, TMS) -2.73 (broad s, -NH, 2H), 1.63(m, t-butyl-H, 36H), 5.62(s, -OH, 2H), 8.04(s, aromatic-H[DtB4HP], 4H), 8.35, 8.46, 8.59, 8.70 (q, aromatic-H[4-NP], 8H, AB spin system centred on 8.52 ppm, $J_{AB}=8.8\text{Hz}$), 8.73, 8.79, 8.96, 9.02 ppm(q, pyrrole-H, 8H, AB spin system centred on 8.88 ppm, $J_{AB}=4.9 \text{ Hz}$).

The **fourth fraction** off the column was concentrated and precipitated to give an amorphous purple powder of porphyrin **3c** (60 mg) (Found: C, 72.0; H, 5.8; N, 8.3: $\text{C}_{60}\text{H}_{60}\text{N}_6\text{O}_6 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ requires, C, 71.87; H, 6.05; N, 8.38.). (FABS: found M+1, $m/z=961$; requires $m/z=961$); (Mass spectrum(CI), m/z 961 (M^++1 , 100%), 946 ([M+1]- CH_3 , 31%), 915 ([M+1]- NO_2 , 15%): $\max(\text{CDCl}_3)$ 3640 (OH), 2960 - 2850 (t-butyl-H), 1600 (benzene ring), 1520 (N-O antisymmetric stretch), 1350 cm^{-1} (N-O symmetric stretch): $\max(\text{CH}_2\text{Cl}_2)$ ($/1 \text{ mol}^{-1} \text{ cm}^{-1}$) 427(279.5), 521(16.2), 561(12.8), 594(6.2); $\max(\text{CH}_2\text{Cl}_2 + \text{two drops TFA})$ 464(235.7), 688(64.5) nm; ^1H (d_2 -DCM, TMS) -2.74 (broad, s, -NH, 2H), 1.63 (m, t-butyl-H, 36H), 5.63 (s, -OH, 2H), 8.03 (s, aromatic-H[DtB4HP], 4H), 8.35, 8.46, 8.59, 8.70 (q, aromatic-H[4-NP], 8H, AB spin system centred on 8.52 ppm, $J_{AB}=8.8\text{Hz}$), 8.83, 8.87, 8.91, 8.94 ppm(pyrrole -H, 8H).

The **fifth fraction** off the column, which required eluting with 80:20 DCM/hexane fraction, was concentrated and precipitated with hexane fraction as an amorphous purple solid of porphyrin **5c** (140 mg) (Found: C, 69.8; H, 5.1; N, 10.9: $\text{C}_{52}\text{H}_{43}\text{N}_7\text{O}_7 \cdot \text{H}_2\text{O}$ requires, C, 69.72; H, 5.02; N, 10.95.). (FABS: found M+1, $m/z=878$, requires $m/z=878$): (Mass spectrum(CI), m/z 878 (M^++1 , 100%), 862 (M- CH_3 , 25%), 832 ([M+1]- NO_2 , 15%): $\max(\text{CDCl}_3)$ 3640 (OH), 3310 (NH), 2960 - 2850 (t-butyl-H), 1600 (benzene ring), 1520 (N-O antisymmetric stretch), 1350 cm^{-1} (N-O symmetric stretch): $\max(\text{CH}_2\text{Cl}_2)$ ($/1 \text{ mol}^{-1} \text{ cm}^{-1}$) 426.5(285.7), 520(18.3), 556(10.8), 594(7.7), 651(8.0); $\max(\text{CH}_2\text{Cl}_2 + \text{two drops TFA})$ 427.6(116), 456(161), 668.5(52); ^1H (d_2 -DCM, TMS) -2.78 (broad s, -NH, 2H), 1.63(m, t-butyl-H, 18H), 5.65(s, -OH, 1H), 8.05(s, aromatic-H[DtB4HP], 2H), 8.35, 8.46, 8.59, 8.70(q, aromatic-H[4-NP], 12H, AB spin system centred on 8.52 ppm, $J_{AB}=8.8 \text{ Hz}$), 8.83(s, pyrrole-H, 4H), 8.76, 8.83, 8.99, 9.05(q, pyrrole-H, 4H, AB spin system centred on 8.91, $J_{AB}=5.0 \text{ Hz}$).

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