

Synthesis of some New Tetra-aryl Porphyrins for Studies in Solar Energy Conversion. Part 2.* Asymmetric Porphyrins

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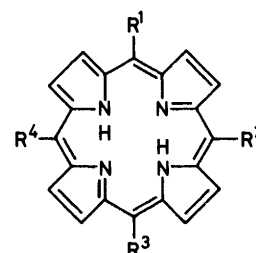
The synthesis and characterisation of some asymmetrical *meso*-substituted porphyrins, for studies in solar energy conversion, are described. Isomeric porphyrins (5) and (6) could be cleanly separated and distinguished by the number of ^{13}C n.m.r. resonances for the pyrrole α -carbon atoms. Similarly, ^{13}C and ^1H n.m.r. spectrometry was used to characterise a porphyrin with *n*-pentadecyl and benzoquinone *meso*-substituents, using the number of pyrrole α -carbon and β -hydrogen resonances. Thin films of porphyrin (11) coated onto glass slides fluoresced, indicating little or no concentration quenching in the coat.

The primary photophysical events in green-plant photosynthesis (*e.g.*, light harvesting and trapping by chlorophyll antennae) can be modelled using easily accessible *meso*-substituted porphyrins.¹⁻⁷ Porphyrins are also ideal photosensitisers in electron-transfer systems for the conversion of solar energy into stored chemical potential.^{8,9} Typically, these porphyrins contain only one kind of functional group. For example, porphyrin-quinones^{5,6} model photosynthetic charge-transfer;¹⁰ porphyrin-polyenes mimic the antenna action of the carotenoid photosynthetic accessory pigments;¹¹ a porphyrin with four *n*-pentadecyl *meso*-substituents³ models the inhibition of fluorescence concentration quenching as found in the chlorophyll antennae of chloroplasts.² Water-solubilising groups attached to the porphyrin^{8,9,12} allow sensitisation of photocatalytic water reduction,^{8,9} and photogalvanic effects.^{13,14} The porphyrin could be made more flexible in these systems if it contained more than one functional group. For example, a porphyrin with *n*-pentadecyl and quinone *meso*-substituents might conceivably model inhibition of concentration fluorescence quenching and photosynthetic charge-transfer. Such molecules could act as trapping sites of photonic energy in solar-energy devices based on the dispersal of pigments in thin films of polystyrene.^{3,15} Also, unsymmetrically functionalised porphyrin sensitisers could be covalently coated onto electrodes (for photoelectrochemical cells) and semiconductor particles (for microheterogeneous water photolysis) with greater control of the porphyrin's steric orientation to the coated surface. This paper, therefore, discusses the synthesis and characterisation of some asymmetrically bifunctionalised *meso*-substituted porphyrins.

Results and Discussion

Porphyrins (1)–(7) were obtained from the Rothmund reaction¹⁶ of two appropriately substituted benzaldehydes with pyrrole in refluxing propionic acid. For porphyrins (11)–(13), hexadecanal replaced one of the benzaldehydes (see Figure 1).

A mixture of six porphyrins is possible from this reaction † (see Figure 2). Anton and Loach¹⁷ separated similar porphyrin mixtures using preparative t.l.c. A better method is short-column or 'flash' chromatography¹⁸ which combines the separating power of t.l.c. with the convenience of column



- (1) $\text{R}^1 = \text{R}^2 = \text{R}^3 = 4\text{-BrC}_6\text{H}_4$, $\text{R}^4 = 4\text{-MeOC}_6\text{H}_4$
- (2) $\text{R}^1 = \text{R}^2$ (or R^3) = $4\text{-BrC}_6\text{H}_4$, R^3 (or R^2) = $\text{R}^4 = 4\text{-MeOC}_6\text{H}_4$
- (3) $\text{R}^1 = 4\text{-BrC}_6\text{H}_4$, $\text{R}^2 = \text{R}_3 = \text{R}^4 = 4\text{-MeOC}_6\text{H}_4$
- (4) $\text{R}^1 = \text{R}^2 = \text{R}^3 = 4\text{-ClC}_6\text{H}_4$, $\text{R}^4 = 4\text{-MeO}_2\text{CC}_6\text{H}_4$
- (5) $\text{R}^1 = \text{R}^2 = 4\text{-ClC}_6\text{H}_4$, $\text{R}^3 = \text{R}^4 = 4\text{-MeO}_2\text{CC}_6\text{H}_4$
- (6) $\text{R}^1 = \text{R}^3 = 4\text{-ClC}_6\text{H}_4$, $\text{R}^2 = \text{R}^4 = 4\text{-MeO}_2\text{CC}_6\text{H}_4$
- (7) $\text{R}^1 = 4\text{-ClC}_6\text{H}_4$, $\text{R}^2 = \text{R}^3 = \text{R}^4 = 4\text{-MeO}_2\text{CC}_6\text{H}_4$
- (8) $\text{R}^1 = \text{R}^2 = \text{R}^3 = 4\text{-ClC}_6\text{H}_4$, $\text{R}^4 = 4\text{-HO}_2\text{CC}_6\text{H}_4$
- (9) $\text{R}^1 = \text{R}^2 = \text{R}^3 = 4\text{-ClC}_6\text{H}_4$, $\text{R}^4 = 4\text{-C}_{16}\text{H}_{33}\text{O}_2\text{CC}_6\text{H}_4$
- (10) $\text{R}^1 = \text{R}^2 = \text{R}^3 = 4\text{-ClC}_6\text{H}_4$, $\text{R}^4 = 4\text{-C}_{16}\text{H}_{33}\text{NH-CO-C}_6\text{H}_4$
- (11) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{C}_{15}\text{H}_{31}$
- (12) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{C}_{15}\text{H}_{31}$, $\text{R}^4 = 2,5\text{-(MeO)}_2\text{C}_6\text{H}_3$
- (13) $\text{R}^1 = \text{R}^2$ (or R^3) = $\text{C}_{15}\text{H}_{31}$, R^3 (or R^2) = $\text{R}^4 = 2,5\text{-(MeO)}_2\text{C}_6\text{H}_3$
- (14) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{C}_{15}\text{H}_{31}$, $\text{R}^4 = 2,5\text{-(HO)}_2\text{C}_6\text{H}_3$
- (15) $\text{R}^1 = \text{R}^2 = \text{C}_{15}\text{H}_{31}$, $\text{R}^3 = \text{R}^4 = 2,5\text{-(HO)}_2\text{C}_6\text{H}_3$
- (16) $\text{R}^1 = \text{R}^3 = \text{C}_{15}\text{H}_{31}$, $\text{R}^2 = \text{R}^4 = 2,5\text{-(HO)}_2\text{C}_6\text{H}_3$
- (17) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{C}_{15}\text{H}_{31}$, $\text{R}^4 = 1,4\text{-benzoquinonyl}$
- (18) $\text{R}^1 = \text{R}^2 = \text{C}_{15}\text{H}_{31}$, $\text{R}^3 = \text{R}^4 = 1,4\text{-benzoquinonyl}$
- (19) $\text{R}^1 = \text{R}^3 = 1,4\text{-benzoquinonyl}$, $\text{R}^2 = \text{R}^4 = \text{C}_{15}\text{H}_{31}$

Figure 1. Porphyrins synthesised during this work

chromatography. The procedure for porphyrin mixtures has been published.⁶

Initially, groups X and Y (Figure 2) were chosen to give the best separation on the column. For this reason, synthesis of porphyrin mixtures with X = 4-bromophenyl and Y = 4-methoxyphenyl (1)–(3) was undertaken. Porphyrin aryl methoxy groups can be readily demethylated to give the corresponding phenol,^{5-7,19} which will then undergo further functionalisation.⁷ However, halogenated tetra-arylporphyrins, while achieving good chromatographic separations, have poor singlet-state photophysical properties. This is an undesirable property in models of chlorophyll antenna action, and is due to intramolecular quenching of the singlet state by heavy-atom intersystem-crossing enhancement.²⁰ Halogenated aryl groups, perhaps further capable of functionalisation *via* Grignard-type reactions, were later discarded.⁶

Porphyrin (2) could not be resolved into '*cis*' and '*trans*' isomers (see Figure 2). However, the porphyrin mixture (4)–(7)

* Part 1 is ref. 7.

† Yields based on statistical proportions (1:4:6:4:1) of the mass of mixed porphyrins. These proportions are to some extent determined by the relative rates of reactivity of the starting benzaldehydes (see J. B. Kim, J. J. Leonard, and F. R. Longo, *J. Am. Chem. Soc.*, 1972, **94**, 3986).

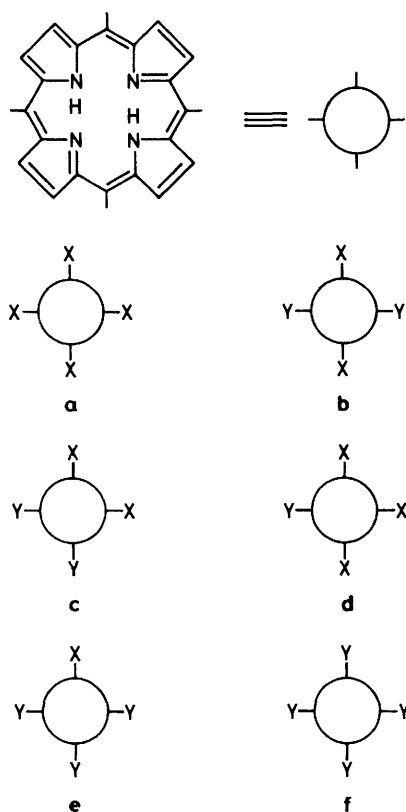


Figure 2. Possible six porphyrins from the Rothmund reaction of pyrrole with two different aldehydes. Porphyrins **a** and **f** are symmetrically substituted. Porphyrins **c** and **d** are the 'cis' and 'trans' asymmetrically disubstituted porphyrins respectively

(X = 4-chlorophenyl and Y = 4-methoxycarbonylphenyl) was separated and the porphyrins (**5**) and (**6**) resolved into 'cis' and 'trans' isomers. These were identified and characterised using ^{13}C n.m.r. spectroscopy. The ^{13}C -assignments were achieved by comparison with similar values for symmetrical tetrapyrroles, obtained by Abraham *et al.*²¹ In particular, they reported the pyrrole α -carbon ^{13}C -resonance as a broad, weak signal at δ 145.8 p.p.m. (in CDCl_3) for the porphyrin in its free-base form. This resonance becomes a sharp, well defined singlet at δ 145.2 p.p.m. [in CDCl_3 -trifluoroacetic acid (TFA)]. The same behaviour was observed here with the asymmetrically substituted porphyrins (**5**) and (**6**). However, more than one pyrrole α -carbon resonance was observed, the number depending on the *meso*-substitution pattern of the porphyrin (see Table).

Figure 3 shows the two isomers (**5**) and (**6**) and their planes of symmetry. The 'cis' isomer's α -carbon atoms have four different chemical environments and gave four sharp ^{13}C n.m.r. resonances with TFA at δ ca. 145 p.p.m. The 'trans' isomer has only two different α -carbon chemical environments and gave two sharp ^{13}C n.m.r. resonances in TFA at δ ca. 145 p.p.m. Compounds (**4**)–(**7**) were originally prepared as precursor porphyrins to analogues of surfactant ruthenium trisbipyridyl complexes, used in earlier experiments on the photochemical cleavage of water.²² The subsequent photolability of the ruthenium complexes²³ precluded further work on their porphyrin analogues. Nevertheless, the hexadecyl ester (**9**) and the hexadecyl amide (**10**) were prepared *via* the acid chloride of the carboxylic acid (**8**).

The symmetrical porphyrin (**11**) was obtained as part of the mixture (**11**)–(**13**). A thin film of this porphyrin could be coated onto glass slides from light petroleum solutions. The film

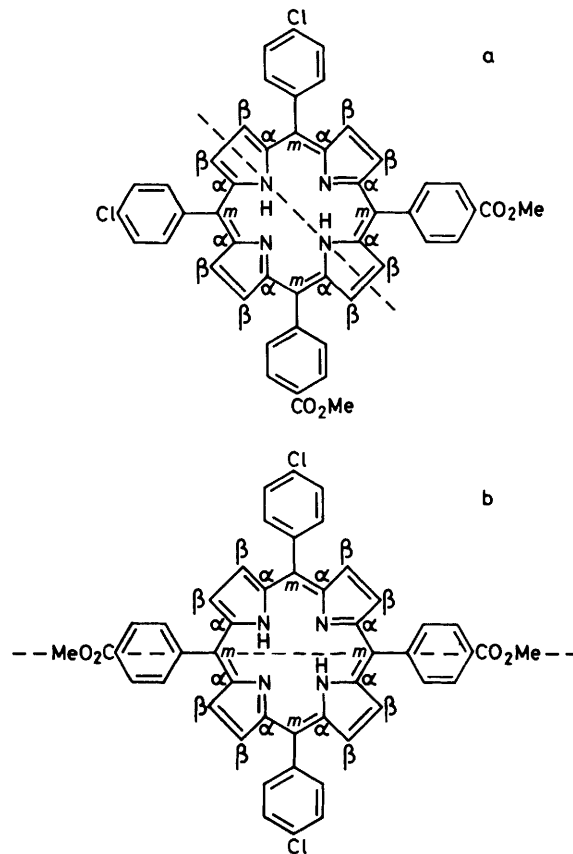


Figure 3. (a) 'cis' isomer porphyrin (**5**). (b) 'trans' isomer porphyrin (**6**). α , pyrrole α -carbons; β , pyrrole β -carbons; *m*, porphyrin *meso*-carbons

fluoresces red in u.v. light, indicating that the n-pentadecyl substituents are sterically hindering the intermolecular proximity of the porphyrin molecules that normally leads to concentration quenching of fluorescence. This confirms an earlier prediction by Porter² that porphyrins with bulky substituents could be used to model the inhibition of chlorophyll fluorescence concentration quenching in chloroplasts.

Porphyrins (**17**)–(**19**) were synthesised by boron tribromide demethylation^{6,7} of compounds (**14**)–(**16**) followed by oxidation of the hydroquinones with DDQ (2,3-dichloro-5,6-diazano-1,4-benzoquinone).^{5,6} Again, using ^{13}C n.m.r. spectroscopy, it was possible to assign a 'trans' configuration to porphyrin (**18**) by identification of the two pyrrole α -carbon resonances at δ ca. 148 p.p.m. The two resonances do not need to be resolved with TFA. The two chemical environments of the pyrrole β -carbon atoms are also sufficiently dissimilar to show as two resonances at δ ca. 129 p.p.m. without the need for TFA. Final confirmation of the *trans* configuration of (**18**) was provided by the ^1H n.m.r. spectrum. This showed an AB-type spin-system in the region of the porphyrin β -hydrogens (δ_{H} 9.22; J_{AB} 4.9 Hz). This is indicative of two different β -hydrogen environments, only possible with a *trans* configuration of *meso* substituents (see Table).

Experimental

Pyrrole (Aldrich), substituted benzaldehydes (Aldrich), and propionic acid (Aldrich) were used as supplied. Neutral alumina (Merck) was made up to Brockmann grade III by shaking it (500 g) with water (21 g; hence 4.3% of water w/w) until cool. Silica gel (Merck) for short-column chromatography was t.l.c.-grade Kieselgel 60G. Boron tribromide (BDH) and 2,3-

Table. Comparison of ^{13}C and ^1H n.m.r. shifts for some symmetric and asymmetrically *meso*-substituted porphyrins

	$\delta_{\text{C}}/\text{p.p.m. base}$			δ_{H}
	C_{α}	C_{β}	C_{meso}	
TPP ^a	145.8	130.6	119.6	8.75 ^b
TPPH ₂ ²⁺ ^a	145.2	127.7	122.1	
Porphyrin (5)	146.5	131.0	119.1	8.84 ^c
Porphyrin (5) + TFA	145.0, 145.2, 145.5, 145.7	131.0	123.1, 123.7	
Porphyrin (6)	146.6	131.1	118.9, 119.1	8.94 ^c
Porphyrin (6) + TFA	144.9, 145.7	131.5	122.0, 123.0	
Porphyrin (9)	146.0	130.5	118.3	8.81
Porphyrin (11)		128.0	118.3	9.46
Porphyrin (19)	147.2, 148.7	128.8		8.95, ^d
		129.8		9.03,
				9.41,
				9.45

^a TPP = Tetraphenylporphin, TPPH₂²⁺ = tetraphenylporphin dication. Data given in ref. 21. ^b See H. Scheer and J. J. Katz in 'Porphyrins and Metalloporphyrins,' ed. K. M. Smith, Elsevier, New York, 1974, p. 413. ^c See ref. 3. ^d AB-spin system, centred on δ 9.22, τ_{AB} 4.9 Hz.

dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Aldrich) were used as supplied. Chloroform, methylene dichloride, and methanol were reagent grade (Fisons). Methylene dichloride for demethylation reactions was dried and distilled from phosphorus pentoxide. Samples of porphyrins for micro-analysis and spectroscopic analysis were sublimed under high vacuum at 250–300 °C. N.m.r. spectra were performed on a Jeol FX60 machine in CDCl₃-TFA. I.r. data were obtained using a Perkin-Elmer 1570 grating spectrophotometer. U.v.-visible spectra were obtained using a Pye-Unicam SP 1800 spectrophotometer, fitted with a Unicam AR25 Linear Recorder.

Synthesis of Compounds (1)–(3).—4-Methoxybenzaldehyde (1.4 ml, 12.5 mmol) and 4-bromobenzaldehyde (2.3 gm, 12.5 mmol) were added to propionic acid (250 ml) and the mixture brought to reflux. Pyrrole (1.75 ml, 25 mmol) was then added and the mixture was refluxed for a further 2 h and allowed to cool overnight. The purple plates of mixed porphyrins were filtered off and washed with methanol. The dark propionic acid residues were concentrated to yield a second crop of crystals. The total crude material was taken into the minimum amount of chloroform, chromatographed on alumina, and eluted with chloroform. The red band of mixed porphyrins was collected, concentrated, and crystallised from methanol (1.1 g, 21.4%*). The porphyrin mixture by t.l.c. on silica, on development with methylene dichloride-cyclohexane (1:1), showed five spots. The first was shown to be *meso*-tetrakis-(4-bromophenyl)porphyrin and the last was *meso*-tetrakis-(4-methoxyphenyl)porphyrin. The mixture was separated on a larger scale by short-column chromatography on t.l.c.-grade silica. The method is described elsewhere.⁶ The porphyrins were eluted with methylene dichloride-cyclohexane (2:3). Fraction 1 was identified by t.l.c. as the *meso*-tetrakis-(4-bromophenyl)porphyrin and was discarded. Fraction 2, eluted with the same solvent mixture, was evaporated to dryness, taken into methylene dichloride, and crystallised from methanol to give *porphyrin* (1) (75 mg) as purple plates (Found: C, 61.1; H, 3.4; N, 6.3. C₄₅H₂₉Br₃N₄O requires C, 61.29; H, 3.29; N, 6.36%); λ_{max} (benzene) ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$) 423 (504), 518 (20.7), 552 (10.0), 595 (6.0), and 652 nm

(6.6); λ_{max} (benzene plus two drops of TFA) 447 (360) and 677 nm (59.3).

Fraction 3, eluted from the column with methylene dichloride-cyclohexane (3:2), was evaporated to dryness, taken into methylene dichloride, and crystallised from methanol to give *porphyrin* (2) (60 mg) as purple microcrystals (Found: C, 66.3; H, 3.9; N, 6.6. C₄₆H₃₂Br₂N₄O requires C, 66.35; H, 3.85; N, 6.73%); λ_{max} (benzene) ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$) 421 (458), 517 (18.2), 552 (10.0), 594 (5.0), and 652 nm (6.6); λ_{max} (benzene plus two drops TFA) 449 (320) and 675 nm (60.0).

Fraction 4 was eluted with methylene dichloride-cyclohexane (3:1) and crystallised as before to give *porphyrin* (3) (20 mg) as purple microcrystals (Found: C, 71.9; H, 4.6. C₄₇H₃₅BrN₄O₃ requires C, 72.03; H, 4.47%); λ_{max} (benzene) ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$) 422 (268), 518 (11.7), 553 (7.1), 595 (3.1), and 650 nm (3.8); λ_{max} (benzene plus two drops of TFA) 450 (186) and 680 nm (46.1).

Porphyrin (2) could not be resolved into *cis* and *trans* isomeric forms. Only a small part of the mixed porphyrin yield was chromatographed.

Synthesis of Compounds (4)–(7).—4-Chlorobenzaldehyde (3.51 g, 25 mmol) and 4-carboxybenzaldehyde (4-formylbenzoic acid) (3.75 g, 25 mmol) were added to propionic acid (500 ml) and the mixture was brought to reflux. Pyrrole (3.5 ml, 50 mmol) was then added and the mixture was refluxed for a further 1 h. The propionic acid was then distilled off and the purple residues refluxed in a solution (500 ml) of tetrahydrofuran-methanol (2:3) containing 5% conc. sulphuric acid for 48 h. The dark green solution was cooled, neutralised with triethylamine, evaporated to dryness, taken into methylene dichloride, and chromatographed three times on alumina with methylene dichloride as eluant. The eluate was concentrated and crystallised from methanol to give purple microcrystals (1.92 g, 19.2%*) of a porphyrin mixture, t.l.c. of which gave six spots on alumina on development with methylene dichloride-benzene (1:9). The porphyrin mixture (1.46 g) was subjected to short-column chromatography as before on t.l.c.-grade silica with methylene dichloride as eluant. Fraction 1 was shown by t.l.c. to be *meso*-tetrakis-(4-chlorophenyl)porphyrin and discarded. Fraction 2 was eluted from the column, concentrated, and crystallised from methanol as purple microcrystals (439 mg) of *porphyrin* (4) (Found: C, 70.6; H, 4.0; N, 7.2. C₄₆H₂₉Cl₃N₄O₂· $\frac{1}{2}$ H₂O requires C, 70.36; H, 3.82; N, 7.14%); λ_{max} (benzene) ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$) 420 (355), 514 (16.7), 549

* Yields based on statistical proportions (1:4:6:4:1) of the mass of mixed porphyrins. These proportions are to some extent determined by the relative rates of reactivity of the starting benzaldehydes (see J. B. Kim, J. J. Leonard, and F. R. Longo, *J. Am. Chem. Soc.*, 1972, **94**, 3986).

(7.2), 591 (4.6), and 650 nm (3.7); λ_{\max} (benzene plus two drops of TFA) 442 (347), and 656 nm (39.8); ν_{\max} (Nujol) 1720 cm^{-1} [CO (aryl ester) stretch].

Fractions 3 and 4 were combined, concentrated, and crystallised from methanol to give purple microcrystals of isomeric porphyrins (5) and (6) (597 mg) (Found: C, 71.8; H, 4.2; N, 7.2. $\text{C}_{48}\text{H}_{32}\text{Cl}_2\text{N}_4\text{O}_4$ for both isomers requires C, 72.09; H, 4.01; N, 7.01%). The isomer mixture was then subjected to further short-column chromatography which cleanly separated the 'cis' and 'trans' isomers. Fraction 3b was eluted, concentrated, and crystallised from methanol to give porphyrin (5) as purple microcrystals (331 mg) (Found: C, 72.3; H, 4.1; N, 7.1%); λ_{\max} (benzene) ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$) 420 (431), 515 (20.6), 549 (9.0), 592 (5.6), and 651 nm (5.0); λ_{\max} (benzene plus two drops of TFA) 442 (407) and 655 nm (47.1); ν_{\max} (Nujol) 1720 cm^{-1} [CO (aryl ester) stretch]; $\delta_{\text{C}}(\text{CDCl}_3; \text{SiMe}_4)$ 52.3 (s, CO_2CH_3), 119.1 (s, porphyrin meso-carbons), 126.9 and 127.8 (s, aryl C-3 carbons), 129.5 (s, aryl C-4 carbons), 131.0 (br, pyrrole β -carbons), 134.2 and 134.3 (s, aryl C-4 carbons), 135.3 (s, aryl C-2 carbons), 140.1 (s, aryl C-1 carbons), 146.5 (s, pyrrole α -carbons), and 167.1 p.p.m. (s, CO_2CH_3); $\delta_{\text{C}}(\text{CDCl}_3 + \text{TFA})$ 53.4 (s, CO_2CH_3), 123.1 and 123.7 (s, porphyrin meso-carbons), 129.1, 129.4, and 129.7 (br m, aryl C-3 carbons and aryl C-4 carbons), 131.0 (s, pyrrole β -carbons), 137.3 and 138.4 (s, aryl C-4 carbons), 137.9 and 139.1 (br, aryl C-2 carbons), 143.0 (s, aryl C-1 carbons), 145.0, 145.2, 145.5, and 145.7 (s, pyrrole α -carbons), and 168.6 p.p.m. (s, CO_2CH_3).

Fraction 4b was eluted, concentrated, and crystallised from methanol to give porphyrin (6) as purple microcrystals (133 mg) (Found: C, 72.1; H, 4.0; N, 6.7%); λ_{\max} (benzene) ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$) 420 (423), 515 (20.0), 549 (8.7), 592 (5.5), and 651 nm (5.5); λ_{\max} (benzene plus two drops of TFA) 442 (401) and 655 nm (44.3); ν_{\max} (Nujol) 1720 cm^{-1} [CO (aryl ester) stretch]; $\delta_{\text{C}}(\text{CDCl}_3; \text{SiMe}_4)$ 52.3 (s, CO_2CH_3), 118.9 and 119.1 (s, porphyrin meso-carbons), 126.9 and 127.9 (s, aryl C-3 carbons), 129.6 (s, aryl C-4 carbons), 131.1 (br, pyrrole β -carbons), 134.2 and 134.4 (s, aryl C-4 carbons), 135.3 (s, aryl C-2 carbons), 140.1 (s, aryl C-1 carbons), 146.6 (s, pyrrole α -carbons), and 167.1 p.p.m. (s, CO_2CH_3); $\delta_{\text{C}}(\text{CDCl}_3 + \text{TFA})$ 52.6 (s, CO_2CH_3), 122.0 and 123.0 (s, porphyrin meso-carbons), 128.6 and 129.3 (br, m, aryl C-3 and aryl C-4 carbons), 131.5 (s, pyrrole β -carbons), 137.6 (s, aryl C-4 carbons), 137.9 and 139.0 (br, aryl C-2 carbons), 142.8 (s, aryl C-1 carbons), 144.9 and 145.7 (s, pyrrole α -carbons), 166.6 p.p.m. (s, CO_2CH_3).

Fraction 5 was eluted, concentrated, and crystallised with methanol to give porphyrin (7) as purple microcrystals (200 mg) (Found: C, 73.2; H, 4.35; N, 6.9. $\text{C}_{50}\text{H}_{35}\text{ClN}_4\text{O}_3$ requires C, 72.95; H, 4.26; N, 6.81%); λ_{\max} (benzene) ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$) 421 (408), 515 (19.7), 550 (8.8), 592 (5.5), 652 (5.8); λ_{\max} (benzene plus two drops of TFA) 442 (382) and 653 nm (43.0); ν_{\max} (Nujol) 1720 cm^{-1} [CO (aryl ester) stretch].

Synthesis of Compound (8).²⁴—Porphyrin (4) (400 mg, 0.52 mmol) was dissolved in pyridine (2 ml) and THF (10 ml). To the stirred solution was added a mixture of KOH (10 g) in methanol (100 ml), and the solution was refluxed for 54 h. After it had cooled, the solution was acidified with an excess of saturated aqueous citric acid and the resulting porphyrin was extracted into chloroform. The extract was washed several times with water, dried (MgSO_4), filtered, and evaporated to dryness. The solid porphyrin was taken into the minimum of THF and precipitated (cyclohexane) as a purple amorphous powder to yield the impure porphyrin (8) (374 mg, 95%). Identified by t.l.c. (silica; benzene): porphyrin (4) one spot, R_F 0.9; porphyrin (8), one spot, R_F 0; ν_{\max} (Nujol) 1685 cm^{-1} [CO (aryl carboxylic acid) stretch]. The compound was used without further purification.

Synthesis of Compound (9).—A solution of the foregoing porphyrin (8) (30 mg, 0.04 mmol) in sodium-dried benzene (10 ml) was treated with excess of thionyl chloride (0.3 ml) and refluxed for 1 h. The green solution was then evaporated to dryness and excess of thionyl chloride was removed by repeated addition and evaporation of sodium-dried benzene. The green porphyrin dication acid chloride was then converted into its red free-base form with excess of triethylamine (1 ml). This was followed by addition of a sodium-dried benzene solution (10 ml) containing n-hexadecanol (50 mg, 0.2 mmol) in five-fold excess. The mixture was refluxed (2 h) and then stirred at room temperature (12 h). After evaporation to dryness, the residue was taken into methylene dichloride, and chromatographed on silica gel and then on alumina, with elution with methylene dichloride on both occasions. The eluted porphyrin band was collected, filtered, concentrated, and precipitated as a dark red powder from methanol, to yield porphyrin (9) (33 mg, 85%), m.p. 212–213 °C (Found: C, 73.5; H, 6.2; N, 6.05. $\text{C}_{61}\text{H}_{59}\text{Cl}_3\text{N}_4\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires C, 73.60; H, 6.03; N, 5.63%); λ_{\max} (benzene) ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$) 420 (408), 514 (14.7), 548 (6.3), 590 (4.0), and 646 nm (2.69); λ_{\max} (benzene plus two drops of TFA) 442 (395), 606 (5.8, sh), and 655 nm (34.6); ν_{\max} (Nujol) 1720 [CO (aryl ester) stretch]; $\delta_{\text{C}}(\text{CDCl}_3; \text{SiMe}_4)$ 26.5 and 29.0 (two main peaks, alkyl carbons), 118.3 (porphyrin meso-carbons), 126.3 and 127.4 (aryl C-3 carbons), 129.7 (aryl C-4 carbons), 130.5 (pyrrole β -carbons), 133.9 and 135 (aryl C-2 carbons), and 146 p.p.m. (pyrrole α -carbons).

Synthesis of Compound (10).—The procedure and molar ratios were the same as for porphyrin (9) except n-hexadecylamine was used in place of n-hexadecanol. Porphyrin (10) was obtained as a dark red powder from methanol (15 mg, 39%), m.p. 248–251 °C (Found: C, 73.5; H, 6.4; N, 7.1. $\text{C}_{61}\text{H}_{60}\text{Cl}_3\text{N}_5\text{O} \cdot \frac{1}{2}\text{H}_2\text{O}$ requires C, 73.68; H, 6.14; N, 7.05%); λ_{\max} (benzene) ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$) 419 (330), 514 (9.9), 548 (3.9), 592 (2.3), and 650 nm (2.3); λ_{\max} (benzene plus two drops of TFA) 441 (310), 608 (4.4, sh), and 655 nm (24.1).

Synthesis of n-Hexadecanal.—The procedure followed is the Glaros modification²⁵ of the pyridinium chlorochromate oxidation of alcohols by Corey and Suggs.²⁶ Thus, a solution of n-hexadecanol (12.1 gm, 0.05 mol) in methylene dichloride (100 ml) was added dropwise to a stirred solution of pyridinium chlorochromate (Aldrich; 161.5 g, 0.075 mol) in methylene dichloride (75 ml) at room temperature. After addition of all the n-hexadecanol solution, the dark brown mixture was stirred for a further 1.5 h. Sodium-dried diethyl ether (200 ml) was then added and the brown precipitate was filtered on a bed of grade 0 neutral active alumina. The alumina bed and the brown residue were washed with several aliquots of diethyl ether. The combined filtrate was evaporated to dryness and the clear liquid cooled to yield a white powder of n-hexadecanal that was used without further purification (10.6 g, 88%), m.p. 35–37 °C (lit.,²⁷ 34 °C); ν_{\max} (Nujol) 1715 cm^{-1} [CO (aldehyde) stretch].

Synthesis of Compounds (11)–(13).—To a refluxing mixture of n-hexadecanal (3 g, 12.5 mmol) and 2,5-dimethoxybenzaldehyde (2.07 g, 12.5 mmol) in propionic acid (125 ml) was added pyrrole (1.75 ml, 25 mmol) and the mixture was refluxed for a further 2 h. The propionic acid was then distilled off and the remaining solid chromatographed on alumina and then silica, with elution with methylene dichloride in both cases. The eluant was collected, evaporated to dryness, taken into the minimum of methylene dichloride, and subjected to short-column chromatography, as previously described, with benzene as eluant. Only the first three fractions were collected and individually evaporated to dryness. Fraction 1 was taken into

light petroleum (b.p. 40–60 °C) and precipitated with acetone as red microcrystals of *porphyrin* (**11**) (20 mg), m.p. 82–85 °C (Found: C, 83.8; H, 11.8; N, 4.7. $C_{80}H_{134}N_4$ requires C, 83.48; H, 11.65; N, 4.87%) λ_{max} (benzene) ($\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1}$) 418 (591), 520 (16.4), 554 (12.9), 600 (3.7), and 652 nm (5.6); λ_{max} (benzene plus two drops of TFA) 423 (631), 554 (2.5), 586 (9.5), and 634 nm (30.8); δ_H (CDCl₃; SiMe₄) 0.88 (s, CH₃), 1.25 and 2.16 (each s, main peaks, CH₂), and 9.46 (pyrrole β -protons); δ_C (CDCl₃; SiMe₄) 14.0, 22.6, 25.5, 29.6, 31.8, 33.9, 35.3, and 38.6 (main strong peaks, alkyl carbons), 118.3 (s, porphyrin *meso*-carbons), and 128.0 p.p.m. (pyrrole β -carbons).

Fraction 2 was obtained as a thick oil after evaporation to dryness to give *porphyrin* (**12**) (Found: C, 80.5; H, 10.6. $C_{73}H_{112}N_4O_2 \cdot \frac{1}{2}H_2O$ requires C, 80.73; H, 10.41%).

Fraction 3 was also obtained as a thick oil after evaporation to dryness to give *porphyrin* (**13**) (Found: C, 79.35; H, 8.6; N, 5.8. $C_{66}H_{90}N_4O_4$ requires C, 79.04; H, 8.98; N, 5.59%). Porphyrins (**12**) and (**13**) were used without further characterisation. Fractions 4 and 5 were left on the column and discarded.

Synthesis of Compounds (14)–(16).—The thick oily porphyrin (**12**) was taken into methylene dichloride (10 ml) and the solution was slowly added to a stirred solution of boron tribromide (0.5 ml) in methylene dichloride cooled to –80 °C in a bath of ϵ -ketone and solid carbon dioxide. The apparatus was fitted with a calcium chloride drying tube to exclude moisture. When all the porphyrin had been added, the stirred green solution was maintained at –80 °C (1 h) and then slowly allowed to come to room temperature overnight. The solution was then cooled in an ice-bath and water was added to destroy excess of boron tribromide. The lower (methylene dichloride) layer was separated and washed with water until the colour changed from green to red, indicating conversion of the dicationic porphyrin into its free-base form. The methylene dichloride layer was separated, dried (anhydrous MgSO₄), filtered, and chromatographed on silica, with chloroform as eluant. The eluted porphyrin band was concentrated and crystallised from methanol to yield dark red microcrystals of the *porphyrin* (**14**) (230 mg), m.p. 139–141 °C (Found: C, 81.0; H, 10.6; N, 5.5. $C_{71}H_{108}N_4O_2$ requires C, 81.30; H, 10.31; N, 5.34%); λ_{max} (benzene) ($\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1}$) 417 (486), 518 (17.0), 551 (9.0), 596 (4.3), and 625 nm (5.4); λ_{max} (benzene plus two drops of TFA) 425 (390), 554 (3.1), 586 (8.5), and 638 nm (24.2).

Porphyrin (**13**) is, in fact, a mixture of two isomers. The thick oily porphyrin (**13**) was demethylated with boron tribromide in the same way as porphyrin (**12**). Chromatography of the resulting methylene dichloride solution on silica gel gave two clear bands. Band 1 was eluted with chloroform, concentrated, and crystallised from light petroleum (b.p. 60–80 °C) to yield the *porphyrin* (**15**) (41 mg), m.p. 145–148 °C (Found: C, 79.1; H, 8.6; N, 5.6. $C_{62}H_{82}N_4O_4 \cdot \frac{1}{2}C_6H_6$ requires C, 79.19; H, 8.63; N, 5.69%). Band 2 was eluted with chloroform–acetone (9:1), concentrated, and crystallised from light petroleum to yield the *porphyrin* (**16**) (59 mg), m.p. 118–121 °C (Found: C, 79.1; H, 8.4; N, 5.5. $C_{62}H_{82}N_4O_4 \cdot \frac{1}{2}C_6H_6$ requires C, 79.19; H, 8.63; N, 5.69%). Porphyrins (**14**)–(**16**) were used without further characterisation.

Synthesis of Compounds (17)–(19).—Porphyrin (**14**) (20 mg, 0.02 mmol) was taken into acetone (10 ml) and the solution was brought to reflux. A solution of DDQ (10 mg, 0.05 mmol) in acetone (5 ml) was added and the mixture was refluxed for a further 45 min. After evaporation to dryness, the mixture was chromatographed on alumina, and eluted with chloroform. The eluted red band was crystallised from methanol to yield the *porphyrin* (**17**) (15 mg, 75%) (Found: C, 81.5; H, 10.6; N, 5.4. $C_{71}H_{106}N_4O_2$ requires C, 81.45; H, 10.13; N, 5.35%); λ_{max} (benzene) ($\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1}$) 418 (591), 516 (17.2), 548 (6.3), 600

(3.9), and 660 nm (3.1); λ_{max} (benzene plus two drops of TFA) 425 (445), 587 (8.9), and 645 (23.1); δ_H (CDCl₃; SiMe₄) 0.88 (CH₃), 1.26 and 2.16 (two main strong peaks, CH₂), 8.87 (pyrrole β -protons next to *meso*-carbons bearing a benzoquinone moiety), and 9.48 (pyrrole β -protons next to *meso*-carbons bearing n-pentadecyl moieties).

Both bands 1 and 2 were oxidised with DDQ in the manner of porphyrin (**17**) to give porphyrins (**18**) and (**19**) but only porphyrin (**19**) (from band 2) was identified: δ_C (CDCl₃; SiMe₄) 13.9, 22.5, 29.5, 30.4, 31.7, 35.1, and 38.6 (main strong peaks, alkyl carbons), 128.8 and 129.8 (pyrrole β -carbons), 136.8, 137.1, and 138.5 (quinone carbons bearing protons), 143.5 (quaternary quinone carbons), 147.2 and 148.7 (pyrrole α -carbons), and 187.5 p.p.m. (quinone carbonyl carbons); δ_H (CDCl₃; SiMe₄) –2.72 (br, NH), 0.86 (CH₃), 1.24 and 2.17 (two main strong peaks, CH₂), 7.58 (quinone protons), and 8.95, 9.03, 9.41, and 9.49 (AB spin system centred on δ 9.22, J_{AB} 4.9 Hz pyrrole β -protons).

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