

Synthesis of some New Tetra-arylporphyrins for Studies in Solar Energy Conversion

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The synthesis of tetra-arylporphyrins, for studies in solar energy conversion, is described. They are derived from 5,10,15,20-*meso*-tetrakis(4-hydroxyphenyl)porphyrin (4) which, in basic media, forms a green intermediate that is probably the tetraphenoxide (6). The porphyrins (10) and (13), were synthesised as prospective sensitisers for catalysed microheterogeneous water photo-oxidation. U.v./visible spectroscopy demonstrates that the porphyrin (10) aggregates in aqueous solution. Cyclic voltammetry shows that the porphyrin (13) behaves as a typical viologen with bulky substituents. A pentameric porphyrin (15) was synthesised and characterised in order to model energy transfer in photosynthetic chlorophyll antennae. There is some evidence that weak singlet-energy transfer occurs between the porphyrin sub-units of the pentamer.

Porphyrins are currently receiving attention as photosensitisers in prospective photochemical electron-transfer systems for solar energy conversion. Water-soluble porphyrins, for example, can sensitise photocatalytic water reduction,¹ oxidation,² and are of potential use in photogalvanic cells.³ Typically, such porphyrins are derived from *meso*-tetra-4-pyridylporphyrin (1), which is water solubilised by quaternisation of the pyridine nitrogens, to give positively charged or zwitterionic⁴ moieties, such as (2) or (3). A more versatile synthetic strategy, based on *meso*-tetrakis(4-hydroxyphenyl)porphyrin (4), is described here which gives porphyrins with a wide variety of substituents and charge types.

The porphyrin (4) forms the tetraphenoxide (6) in base, which reacts further with alkyl halides to form porphyrins with photolytically stable ether linkages. The alkyl groups are modified in accordance with the working medium of the porphyrins. Thus the neutral porphyrin (7), with octadecyloxyphenyl groups, is soluble in low-boiling alkane solvents and can be surface-coated onto glass and semiconductor powders, by evaporation. The tetra-anionic porphyrin (10), with sulphonated undecyloxyphenyl groups, sensitises water photo-oxidation on colloidal titanium dioxide more efficiently than the porphyrin (2). [In contrast, the porphyrin (11), with sulphonated phenyl groups, does not produce oxygen under these conditions.²] The octa-cationic viologen-porphyrin (13) was synthesised for a similar sensitising role on colloidal titanium dioxide. The viologen subunits would not only quench the photo-generated porphyrin triplet¹ but should also interact with the band structure of the semiconductor, curtailing the rate of unwanted back electron transfer from the reduced viologen to the porphyrin π -cation.¹

Porphyrin aggregates are important in photosynthetic and metabolic processes.^{5,6} Thus a chlorophyll antenna of a photosynthetic organism contains 2 to 300 closely spaced chlorophyll molecules embedded in a lipoprotein matrix. When one chlorophyll molecule is photoexcited, the excitation rapidly delocalises over the antenna. Properly constituted polymeric porphyrins could model this behaviour. Also, polymeric porphyrins containing different metal centres could have application as catalysts in, for example, the Fischer-Tropsch process. In order to test these ideas, the pentameric porphyrin (15) was synthesised using the porphyrin (4) as the starting material.

Results and Discussion

The porphyrin (4) was obtained quantitatively from the porphyrin (5) by demethylation with boron tribromide.⁷⁻⁹ This was found to be superior to 48% hydrobromic acid as a demethylating reagent for tetra-arylporphyrins with methoxy substituents.¹⁰ Also, the porphyrin (5) is easier to prepare¹¹ and purify by column chromatography, and is more stable than *meso*-tetrakisacetylphenylporphyrin, as used by Little *et al.*¹² The resulting porphyrin (4) can be chromatographed on silica gel.

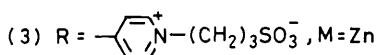
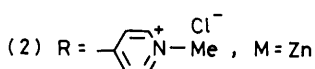
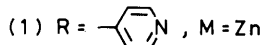
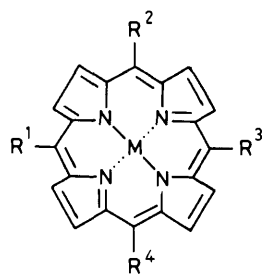
Prior to further reaction, the porphyrin (4) is activated by conversion into an olive-green intermediate,¹² probably the tetraphenoxide (6) either in solution, with potassium carbonate and dimethylformamide,¹³ or as a green solid, by reaction with methanolic KOH. On further reaction the olive-green colour returns to the characteristic red of the free-base porphyrin. This colour change was used as an indication of reaction progress.

The olive-green colour of (6) is rationalised in terms of delocalisation onto the central nitrogen atoms of the negative charges on the phenoxide oxygens of the intermediate (Figure 1a). The resulting porphyrin 'dianion-like' species should be spectroscopically similar to the dication,¹⁴ *i.e.* collapse of the free-base porphyrin's four-banded visible spectrum to two, more intense red-shifted bands (Figure 2a and c). A two-banded spectrum is observed (Figure 2b), but it is blue shifted and of lower intensity, with respect to the dicationic visible band of the porphyrin (4).

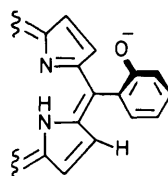
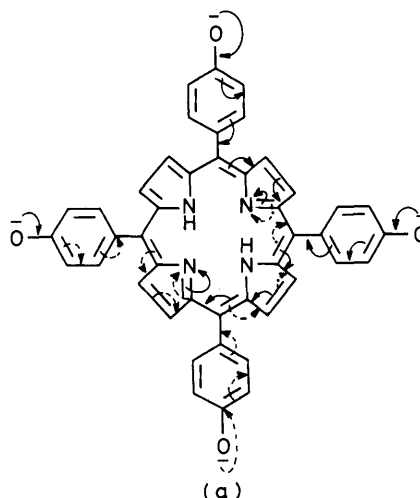
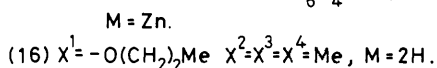
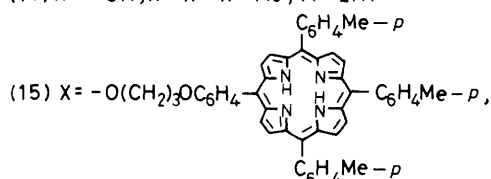
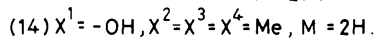
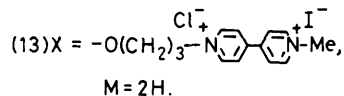
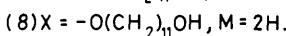
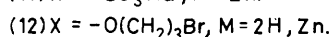
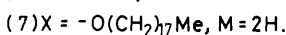
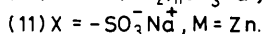
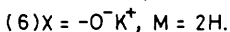
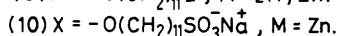
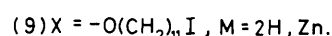
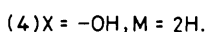
The two tetrakis(4-hydroxyphenyl)porphyrin isomers of (4) do not show these base-induced colour and spectroscopic changes. The 2-hydroxyphenyl group is sterically hindered from freely rotating into the plane of the porphyrin ring for delocalisation. In fact, atropoisomers are formed.¹⁰ The 3-hydroxyphenyl group can not delocalise charge over the porphyrin ring (Figure 1b and c).

The fluorescence emission from basic solutions of the porphyrin (4) is much reduced compared with that from the neutral free-base and the acidic dication. This may be due to intramolecular electron transfer quenching of the porphyrin excited state,^{8,9} by the peripheral negatively charged phenoxide groups.

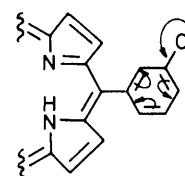
The synthetic routes to new porphyrins are shown in the Scheme. The porphyrin (4), in basic media, was treated with



For porphyrins (4)–(16) R = *p*-XC₆H₄; for all except (14) and (16) R¹ = R² = R³ = R⁴



(b)



(c)

Figure 1. Three isomeric *meso*-tetra(hydroxyphenyl)porphyrins as their phenoxides: a, 4-isomer-phenoxide negative charges can delocalise over phenyl rings and porphyrin macrocycle; b, 2-isomer-phenoxide negative charges are unable to delocalise over the macrocycle because of steric hindrance to phenyl rings rotating into the plane of porphyrin; c, 3-isomer-phenoxide negative charges are in the wrong position on the phenyl ring to delocalise over the macrocycle

1-bromoundecanol to give the porphyrin (8). Excess of methyl(triphenoxy)phosphonium iodide,^{15,16} smoothly and quantitatively iodinated (8) to (9). After zinc insertion, (9) was quantitatively converted into (10) with tetraethylammonium sulphite.¹⁶

U.v. visible spectroscopy indicates that (10) aggregates in aqueous solution (Figure 3). The porphyrin *B* band at 428 nm is extensively broadened, with a shoulder at 410 nm, and of greatly reduced intensity¹⁷ compared with the usual porphyrin *B* band absorption. Addition of methanol or surfactants, such as sodium tetradecyloxyethylene sulphate, narrows and intensifies the *B* band to a sharp peak at 426 nm, demonstrating aggregate dissociation. Similar behaviour is observed for the *Q* bands.

Using the technique of Little¹³ the porphyrin (4) was treated with 1,3-dibromopropane, to give the porphyrin (12). This compound was then further treated with 4,4'-bipyridyl, followed by iodomethane to give the porphyrin (13). This has eight positive charges and cyclic voltammetry shows that it possesses the typical two-electron reduction-wave of a viologen (see Table 1). Moreover, after one reduction, the compound forms an insoluble film on the working electrode, reminiscent of viologens with large attached groups.¹⁸ As the steric bulk

of the substituent increases, there is a positive shift in the viologen's first half-wave reduction potential, $E_4(1)$.¹⁸ This is shown in Table 1. The more positive value of $E_4(1)$ for the porphyrin (13), however, might also be due to its larger positive charge when compared with a normal viologen.

The porphyrin (12) was treated, as its zinc chelate, with an excess of the previously¹² synthesised porphyrin (14). The resulting pentaporphyrin (15) was characterised by microanalysis, t.l.c., u.v./visible spectroscopy and fast-atom bombardment spectroscopy (FABS). The latter gives a parent molecular ion between 3 586 and 3 594 a.m.u. (the molecular weight of zinc pentaporphyrin is 3 592).

In the u.v./visible region, the zinc pentaporphyrin has *Q* band extinction coefficients expected by superimposing four free-base porphyrins onto one zinc porphyrin. This might suggest that the five porphyrin chromophores are not interacting electronically. However, the *B* band extinction coefficient is 25% below that expected for five non-interacting chromophores (see Table 2). Similar behaviour has been noted by other workers^{13,19–22} for porphyrin dimers and may be due to interaction of the molecular states of the component monomers, leading to weak singlet-energy transfer.

Lastly, the synthesis of the zinc pentaporphyrin (15) allows the preparation of, conceivably, a novel homogeneous Fischer-Tropsch catalyst. After iron or ruthenium insertion into the peripheral metal-free porphyrins of the pentamer, the zinc atom, in the central porphyrin, can be removed by treatment with acid and then replaced by ruthenium or iron.

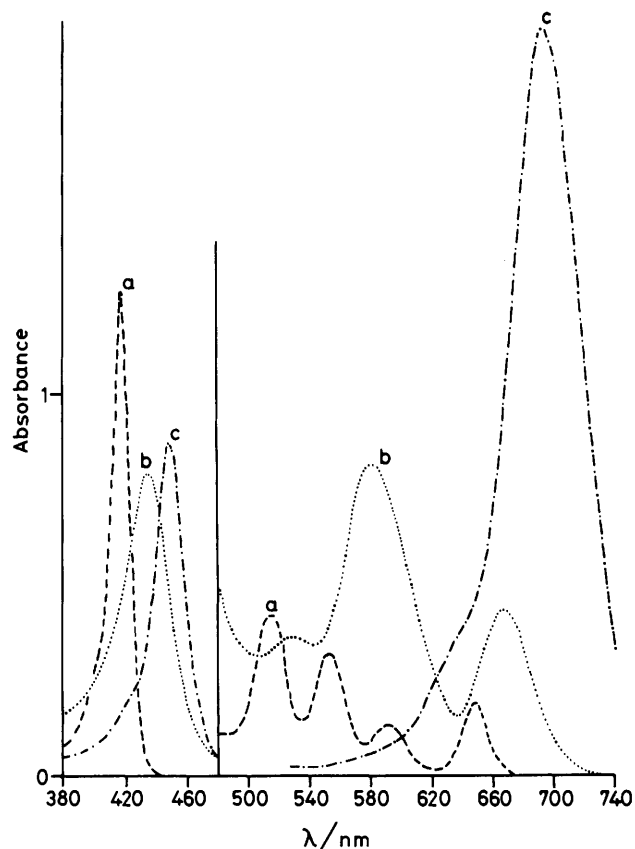


Figure 2. U.v.-visible spectra of the porphyrin (4). $3.5 \times 10^{-5}M$ -Solutions in a, methanol (free-base); b, $1M$ -KOH in methanol [tetraphenoxide (6)]; c, methanol plus two drops CF_3CO_2H (dication)

Table 1. Cyclic voltammetry (E_1 values in mV) of the porphyrin (13)* compared to heptylviologen, HV^{2+} , and benzylviologen, BV^{2+} (ref. 18)

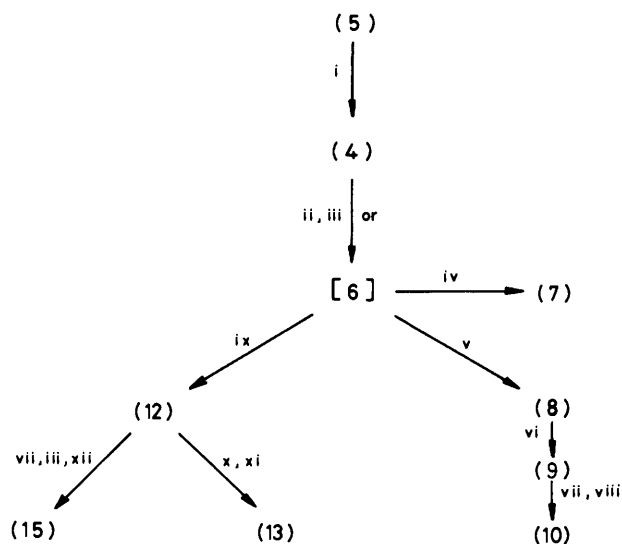
HV^{2+}		BV^{2+}		Porphyrin (13)	
$E_1(1)$	$E_1(2)$	$E_1(1)$	$E_1(2)$	$E_1(1)$	$E_1(2)$
-359 †	-559	-332	-549	-195	-575
-600 ‡	-800	-573	-790	-435	-815

* In $0.1M$ -KCl solution, deoxygenated with pure N_2 , using a copper or gold-disc working electrode. † Top-line potentials vs. normal hydrogen electrode. ‡ Bottom-line potentials vs. standard calomel electrode.

Experimental

All u.v.-visible spectra were recorded on a Pye Unicam SP8-400 spectrophotometer. Chromatographic separations were performed on columns made from slurries of either neutral alumina (Brockmann activity grade III, B.D.H.) or silica gel (Kieselgel 60, Merck). Thin-layer chromatography plates were obtained ready-made from Merck. Dowex 1-X8-100 ion-exchange resin was water-washed before use and was supplied by B.D.H. Solvents were used as supplied except where stated. DMF was vacuum distilled and stored over molecular sieve type 3A.

5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrin.—All glassware was cleaned and dried before use in a vacuum oven at



Scheme. Synthetic routes to porphyrins via the porphyrin (4). Reagents: i, BBr_3 , CH_2Cl_2 , $-80^\circ C$; ii, KOH -MeOH; iii, K_2CO_3 -DMF; iv, $C_{18}H_{37}Br$ -EtOH and heat; v, $Br(CH_2)_{11}OH$ -EtOH and heat; vi, $[(PhO)_3PMe]^+I^-$ -DMF and heat; vii, $Zn(OAc)_2$ -MeOH and heat; viii, Et_4NSO_3 -dioxane- H_2O and heat; ix, $C_3H_6Br_2$; x, 4,4'-bipyridyl; xi, MeI; xii, the porphyrin (14)

$100^\circ C$. Boron tribromide (Aldrich) (1 ml) was added to dry distilled (from phosphorus pentoxide) methylene dichloride and the mixture cooled in an acetone-solid CO_2 bath to $-80^\circ C$. The apparatus was fitted with a calcium chloride drying tube. 5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin (5) (292 mg, 0.4 mmol), previously synthesised by literature methods¹¹ in the minimum volume of dry distilled methylene dichloride, was placed in a self-regulating funnel and slowly added during 20 min. On mixing, the solution immediately turned emerald green, characteristic of the porphyrin dication. The mixture was stirred for 1 h at $-80^\circ C$ and then allowed to come to room temperature, with stirring, over 24 h. After cooling to $0^\circ C$ with an ice-bath, excess of methanol was added to hydrolyse the excess of boron tribromide and break down the porphyrin-boron tribromide complex.⁷ Triethylamine was added to neutralise the mixture which was then evaporated to dryness, taken up in ethyl acetate, and the solution washed several times with water in a separating funnel. The ethyl acetate layer was separated, dried ($MgSO_4$), filtered, evaporated to dryness, and taken into acetone. This solution was chromatographed on silica gel with acetone-light petroleum (b.p. 60 – $80^\circ C$) (1 : 1). The single red band was evaporated to dryness, taken into ethyl acetate, and crystallised with light petroleum (b.p. 60 – $80^\circ C$) (277 mg, 98%), m.p. $>300^\circ C$. The compound was used without further purification.

5,10,15,20-Tetrakis(4-octadecyloxyphenyl)porphyrin (7).—The porphyrin (4) (100 mg, 0.15 mmol) was dissolved in 5% (w/v) methanolic potassium hydroxide. The resulting deep olive-green solution was evaporated to dryness, sodium-dried benzene added (25 ml), and the suspension evaporated to a green solid. A solution of 5% (w/v) octadecyl bromide in absolute ethanol (10 ml) was added and the mixture refluxed under nitrogen for 2 h. The solution changed colour from green to red and the product precipitated from the reaction mixture. The solvent was evaporated and the residue taken into benzene-chloroform (3 : 1, v/v) and chromatographed on a column of neutral alumina. The fastest running

Table 2. Comparison of extinction coefficients for zinc pentaporphyrin (ϵ_{ZnP}) with those for the porphyrin (16) (ϵ_{16}) and the zinc porphyrin (12) (ϵ_{Zn12})

	Q bands				B bands
	q_1	q_2	q_3	q_4	
ϵ_{16}^*	5.1	5.2	10	17.8	494
$4\epsilon_{16}$	20.4	20.8	40	71.2	1 976
ϵ_{Zn12}		6.9	16.3		490
$4\epsilon_{16} + \epsilon_{Zn12}$	20.4	27.7	56.3	71.2	2 466
ϵ_{ZnP}	21.9	27.9	57.8	70.8	1 834

Q band ratios				B band ratios
Theoretical ($4\epsilon_{16} + \epsilon_{Zn12}$)		Found (ϵ_{ZnP})		
q_4/q_3	q_4/q_2	q_4/q_3	q_4/q_2	$\frac{\epsilon_{ZnP}}{4\epsilon_{16} + \epsilon_{Zn12}}$
$71.2/56.3 = 1.26$	$71.2/27.7 = 2.57$	$70.8/57.8 = 1.22$	$70.8/27.9 = 2.54$	$1 834/2 466 = 0.74\ddagger$

* See ref. 13, compound (16). † Found ϵ_{ZnP} for B band is ca. 25% reduced compared with theoretical B band extinction coefficient ($4\epsilon_{16} + \epsilon_{Zn12}$) calculated on the assumption of no interchromophoric interaction.

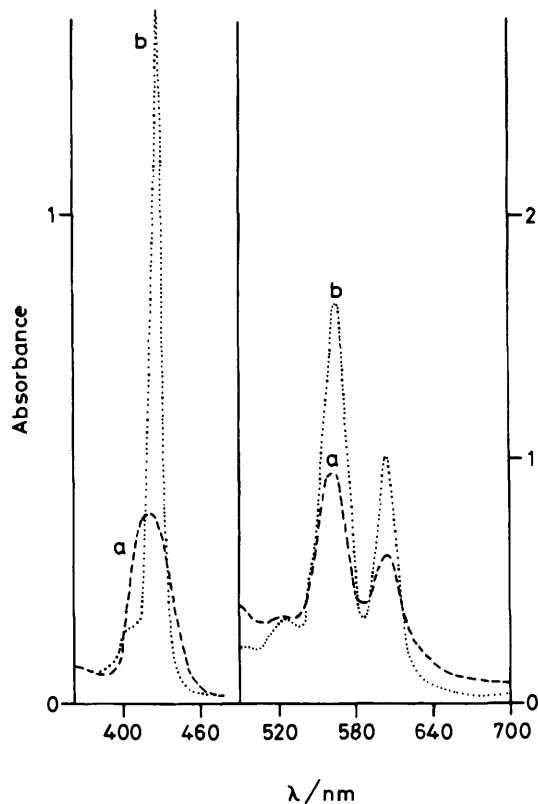


Figure 3. U.v.-visible spectra of porphyrin (10) in a, water; b, methanol. B-bands, 2.5×10^{-5} M-solutions; Q-bands, 10^{-4} M-solutions

band, eluted with benzene, was evaporated to dryness, refluxed in ethanol, filtered, washed with hot ethanol, and dried at 100°C to give the porphyrin (7) (73 mg, 30%) as purple plates, m.p. $118\text{--}120^\circ\text{C}$ (Found: C, 82.7; H, 10.45; N, 3.35. $\text{C}_{116}\text{H}_{174}\text{N}_4\text{O}_4$ requires C, 82.56; H, 10.32; N, 3.32).

5,10,15,20-Tetrakis[4-(11-hydroxyundecyloxy)phenyl]-porphyrin (8).—The porphyrin (4) (100 mg, 0.15 mmol) was treated with methanolic potassium hydroxide as above. To the green solid was added ethanolic 11-bromoundecan-1-ol

(2 ml; 30%, w/v). The mixture was refluxed under nitrogen for 4 h, the olive-green colour changing to deep red. The solution was evaporated to dryness and the residue taken into methanol-chloroform (2 ml; 5%, v/v) and chromatographed on a column of neutral alumina. The eluted red band was evaporated to dryness and precipitated from chloroform with light petroleum (b.p. $60\text{--}80^\circ\text{C}$). The amorphous solid was filtered and dried to give the porphyrin (8) (120 mg, 60%), m.p. $138\text{--}140^\circ\text{C}$ (Found: C, 75.5; H, 8.6; N, 3.9. $\text{C}_{88}\text{H}_{118}\text{N}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ requires C, 75.75; H, 8.75; N, 4.02); λ_{max} (ϵ mmol l^{-1}) in benzene 426 (221), 518 (7), 547 (8.4), 582 (3), and 652 nm (2.3).

5,10,15,20-Tetrakis[4-(11-iodoundecyloxy)phenyl]porphyrin (9).—The previous porphyrin (8) (100 mg, 0.74 mmol) was mixed with a large excess of freshly prepared methyl(triphenoxy)phosphonium iodide (MTPPI) and dried in a pistol at 40°C for 4 h (MTPPI is moisture sensitive). Dry DMF (5 ml) was added and the solution stirred and heated at 60°C for 1.5 h. Excess of methanol was added to destroy remaining MTPPI and the required porphyrin precipitated. It was filtered off, dried, taken into a small volume of methylene dichloride, and chromatographed on neutral alumina, with methylene dichloride as eluant. The eluted red band was concentrated and crystallised from methanol. The purple crystals were filtered off, washed, and dried, to give the porphyrin (9) (124 mg, 94%), m.p. $133\text{--}135^\circ\text{C}$ (Found: C, 59.05; H, 6.45; N, 3.15. $\text{C}_{88}\text{H}_{114}\text{I}_4\text{N}_4\text{O}_4$ requires C, 58.73; H, 6.34; N, 3.11), λ_{max} (ϵ mmol l^{-1}) in benzene 423 (589), 518 (20.7), 554 (14.4), 590 (6.3), and 652 nm (7.6); in benzene plus two drops of trifluoroacetic acid 452 (418) and 683 (76).

5,10,15,20-Tetrakis[4-(11-sulphoundecyloxy)phenyl]-porphyrin (10).—The previous porphyrin was converted into its zinc chelate by literature methods.²³ This porphyrin (26 mg, 0.014 mmol) was dissolved in dioxane (1 ml; freshly chromatographed on an alumina column to remove the stabiliser). To this solution was added a solution of aqueous tetraethylammonium sulphite (1 ml; 0.75M) prepared by bubbling sulphur dioxide into tetraethylammonium hydroxide.¹⁶ The mixture was refluxed for 6 h and then evaporated to dryness. The residue was taken into water (5 ml) and warmed. A saturated sodium chloride solution (30 ml) was added and the porphyrin salted out. The red precipitate was filtered off, washed with sodium perchlorate solution (50%, w/v) and ethanol, and then dried to give the porphyrin (10) as a red amorphous powder of (24 mg, 99%), m.p. $>300^\circ\text{C}$

(Found: C, 57.45; H, 6.25; N, 3.05. $C_{88}H_{112}N_4O_{16}S_4Na_4Zn \cdot 4H_2O$ requires C, 57.39; H, 6.53; N, 3.05), λ_{max} . (ϵ mmol l^{-1}) in water 410 (s, 144), 428 (156), 558 (9.6), and 601 nm (6.2); in methanol 426 (570), 559 (16.4), and 600 nm (10.2).

5,10,15,20-Tetrakis[4-(3-bromopropoxy)phenyl]porphyrin (12).—The porphyrin (4) (200 mg, 0.3 mmol) was stirred in DMF with 1,3-dibromopropane (3.2 g, 1.6 mmol) and potassium carbonate (2.4 g) for 3 days at room temperature. The reaction mixture was poured into aqueous methanol (200 ml; 170 ml water, 30 ml methanol). The precipitated porphyrin was dried in a vacuum oven at 100 °C (to remove excess of dibromopropane), taken into chloroform (3 ml), and chromatographed on a column of neutral alumina, with benzene as eluant; the eluted band was concentrated and crystallised with light petroleum (b.p. 60–80 °C) to give purple crystals of the porphyrin (12) (189 mg, 55%), m.p. >300 °C (Found: C, 60.0; H, 4.65; N, 4.70. $C_{56}H_{50}Br_4N_4O_4 \cdot C_6H_6$ requires C, 60.00; H, 4.52; N, 4.52), λ_{max} . (ϵ mmol l^{-1}) in chloroform 422 (519), 518 (18.1), 554 (12.1), 590 (5.6), and 649 nm (6.5); in chloroform with two drops of trifluoroacetic acid 450 (357) and 689 nm (60.3); λ_{max} . (ϵ mmol l^{-1}) for zinc chelate, in chloroform 426 (490), 554 (16.3), and 596 nm (6.9).

5,10,15,20-Tetrakis[4-[3-(4'-methyl-4,4'-bipyridinio)propoxy]phenyl]porphyrin Tetrachloride Tetraiodide (13).—The porphyrin (12) (100 mg, 0.086 mmol) and 4,4'-bipyridyl (Aldrich, 500 mg, 3.2 mmol) were stirred in DMF at 60 °C for 3 h and then overnight at room temperature. Excess of water was then added and the aqueous solution shaken with methylene dichloride. The aqueous layer was separated, evaporated to dryness, and then stirred with a suspension of pre-washed Dowex resin in water (8 g in 20 ml) for 24 h. The suspension was filtered through a pre-washed bed of Dowex resin and the filtrate evaporated to dryness; the residue was taken into a small volume of methanol and then precipitated with acetone, filtered off, and dried. From this solid (117 mg), an amount was taken (45 mg) and suspended in DMF (2 ml). Iodomethane (10 ml) was added and the mixture stirred at room temperature for 24 h. The mixture was dissolved in water and washed with chloroform. The aqueous layer was separated, evaporated to dryness, and the residue taken into the minimum of ethanol and precipitated with acetone to give a purple amorphous powder of the porphyrin (13) [31 mg, 40% from the porphyrin (12)], m.p. >300 °C (Found: C, 55.8; H, 4.75; N, 7.15. $C_{100}H_{94}Cl_4N_{12}O_4 \cdot 3C_3H_6O$ requires C, 55.66; H, 4.77; N, 7.15), λ_{max} . (ϵ mmol l^{-1}) in water 423 (311), 521 (9.6), 560 (12.3), 598 (7), and 645 nm (4); in water plus two drops of trifluoroacetic acid 446 (186) and 692 nm (46).

5,10,15,20-Tetrakis[4-{3-[4-(10,15,20-tri-4-tolylporphyrin-5-yl)phenoxy]propoxy}phenyl]porphyrinzinc (15).—The porphyrin (12) was converted into the zinc chelate by literature methods.²³ This porphyrin (20 mg, 0.016 mmol) and the previously synthesised porphyrin (14)¹² (100 mg, 0.149 mmol) were stirred together in DMF (2 ml) with potassium carbonate (400 mg) at room temperature for 5 days. The mixture was poured into water and the precipitate filtered off, washed with methanol, dried, taken into chloroform (1 ml), and chromatographed on a column of neutral alumina. The

front-running band was eluted with chloroform, concentrated, and the residue crystallised from methanol to give purple crystals of the pentaporphyrin (15) (40 mg, 70%), m.p. >300 °C (Found: C, 81.25; H, 5.25; N, 7.6. $C_{244}H_{188}N_{20}O_8Zn$ requires C, 81.58; H, 5.24; N, 7.81), λ_{max} . (ϵ mmol l^{-1}) in chloroform 422 (1 834), 519 (70.8), 554 (57.8) 594 (27.9), and 648 nm (21.9) [Found (FABS) M^+ (broad), between 3 586 and 3 594. Pentaporphyrin (15) requires M , 3 592]. T.l.c. (on alumina with chloroform as eluant) R_F (15), 0.92; R_F (12), 0.75; R_F (14), 0.29.

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