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FACE TO FACE PORPHYRINS AS SYNTHETIC HOST MOLECULES †

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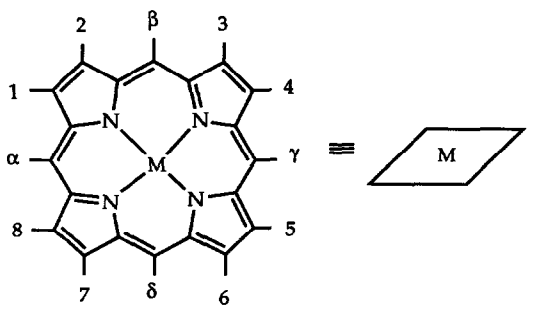
Abstract *The bis-zincporphyrins 9 and 11 were prepared from the bis-(3'-hydroxyphenyl)-porphyrin 6. Both bis-zincporphyrins formed complexes in $CHCl_3$ with a variety of amines and showed a strong preference for diamines, such as $H_2N(CH_2)nNH_2$ and 4,4'-dipyridyl. The limited degree of chain length recognition for the diamine guests by both hosts is associated with conformational flexibility of both host and guest but the rigid guest, 4,4'-dipyridyl, is selectively complexed through operation of the chelate effect.*

Many metalloporphyrins **1** have the ability to bind one or two electron rich ligands to form the complexes **2** and **3**. Such complexes have been studied as analogues of natural metalloporphyrin complexes such as the oxygen carriers haemoglobin and myoglobin,[1] oxidation catalysts [2] such as cytochrome C oxidase, and models for.the photosynthetic centre [3] of plants and microorganisms. Although such biomimetic studies have been a major incentive for the development of metalloporphyrin chemistry they have also been studied as synthetic receptor molecules [4] and as potential catalysts for singlet oxygen generation.[5]



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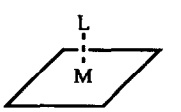

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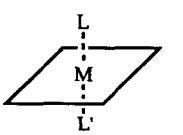

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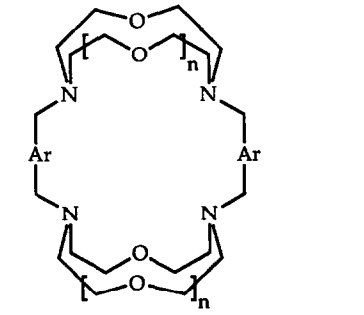
† This paper is dedicated to Professor Charles Rees on the occasion of his 65th birthday.

There have, however, been rather few studies of metalloporphyrins as synthetic host molecules for guests other than oxygen and carbon monoxide in spite of their attractively well defined rigid molecular geometry, possibly because there appears to be rather little selection of the ligands L and L' except through the heteroatom that binds to the metal atom of the metalloporphyrin. Guest selectivity in biomimetic studies has been obtained [1] through the introduction of caps and other steric barriers that limit guest size.

Earlier work [6] that demonstrated that very high selectivity can be obtained in the complexation of bis-alkylammonium cations $H_3N^+(CH_2)_nN^+H_3$ by the face to face crown ethers **4** suggested that the face to face metalloporphyrins, shown diagramatically in **5** might show similar selectivity.



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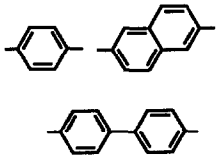

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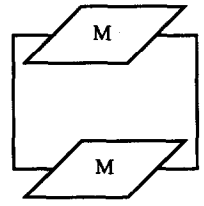

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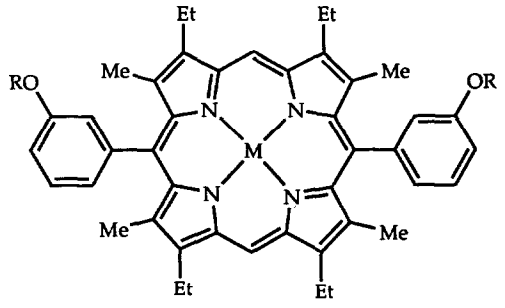
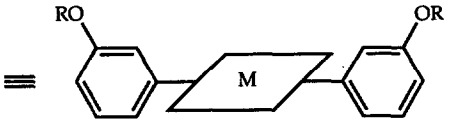
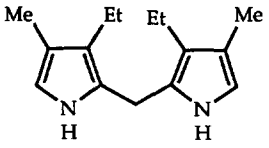




6 R = H, M = H_2

10 R = H, M = Zn

12 R = $(CH_2)_nBr$, M = H_2



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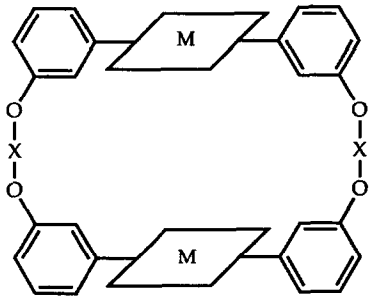
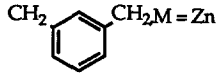
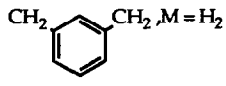
Although a number of face to face porphyrins have been reported,[7] in many cases the metal....metal separation in these compounds had only been appropriate for small guests such as molecular oxygen. More substantial separation appeared to be readily achievable by linking two diarylporphyrin sub-units. Accordingly the bis-(3'hydroxyphenyl)-porphyrin **6** was synthesised by standard methods from the dipyrrylmethane **7**. Reaction of the phenolic porphyrin **6** with 1,6-dibromohexane gave the face to face porphyrin **8** in rather low yield, and the metal-free bis-porphyrin **8** was converted into the bis-zincporphyrin **9** by reaction with zinc acetate. In an alternative synthesis, reaction of the zinc derivative **10** of the phenolic porphyrin **6** with α,α'-dibromo-*p*-xylene gave [8] the face to face bis-zincporphyrin **11**, again in low yield. An alternative synthesis of **8** and analogous compounds by reacting a bis-(3'-ω-bromoalkyloxyaryl)-porphyrin **12** with the phenolic porphyrin **6** gave no improvement in yield.



8 X = $(CH_2)_6$, M = H_2

9 X = $(CH_2)_6$, M = Zn

11 X = 

13 X = 

The bis-zincdiarylporphyrins **9** and **11** had spectroscopic properties that were very similar to those of a simple zincdiarylporphyrin indicating that there is little interaction between the two porphyrin systems in the ground state conformation.[9] The complexation of guest amines and diamines by the bis-zincporphyrins **9** and **11** in dichloromethane was examined using a spectroscopic method based upon the shift in the Soret band of the free zincporphyrin (λ_{max} 408 nm) on complexation (λ_{max} 418 nm). A computation procedure, based upon the formation of 1:1 pentacoordinated zinc complexes (*cf* **2**) with no formation of 2:1 hexacoordinated zinc complexes (*cf* **3**), was used to determine association constants. The results of this study are summarised in Table 1, which also summarises association constants for the complexation of similar guests by the mono-zincporphyrin **12**. The data in Table 1 shows that, as expected, the face to face porphyrins complex most strongly with the bidentate guests, 1,n-diamines, 4,4'-dipyridyl, histamine and 1,4-diazabicyclooctane.

The complexation of 1,n-diamines shows relatively little chain length selectivity, with a rather small ratio of K_a's for pairs of guests $H_2N(CH_2)_nNH_2$ and $H_2N(CH_2)_{n+1}NH_2$, and in both cases a wide range of diamines is complexed strongly. This contrasts with face to face crown ethers which generally select [6] only 3 or 4 members of the series of bis-alkylammonium cations $H_3N^+(CH_2)_nN^+H_3$ and often show ratios of >10:1 for pairs of guests which differ only by a single CH_2 group.

Table 1. Association constants for complexation of amines and diamines by bis-zincporphyrins **9** and **11** and zincporphyrin **12** (n=4, M=Zn)

Guest	Association constant[a]		
	bis-zincporphyrin **9**[b]	bis-zincporphyrin **11**[c]	zincporphyrin **12** (n=4, M=Zn)[d]
n-butylamine	$5.0\pm0.2\times10^3$	$5.0\pm0.5\times10^3$	$5.8\pm0.2\times10^3$
1,2-diaminoethane	$1.2\pm0.1\times10^6$	$6.0\pm2.0\times10^5$	$1.1\pm0.1\times10^4$
1,3-diaminopropane	$1.7\pm0.2\times10^6$		$1.4\pm0.1\times10^4$
1,4-diaminobutane	$5.0\pm0.5\times10^6$	$6.0\pm2.0\times10^5$	
1,5-diaminopentane	$5.5\pm0.5\times10^6$	$1.0\pm0.2\times10^6$	$1.4\pm0.1\times10^4$
1,6-diaminohexane	$4.5\pm0.5\times10^6$	$3.0\pm1.0\times10^6$	
1,7-diaminoheptane	$2.5\pm0.25\times10^6$	$2.0\pm1.0\times10^6$	$1.6\pm0.1\times10^4$
1,8-diaminooctane	$1.9\pm0.2\times10^6$	$3.0\pm0.5\times10^5$	
1,9-diaminononane	$2.6\pm0.2\times10^6$		$1.6\pm0.1\times10^4$
1,10-diaminodecane	$1.4\pm0.2\times10^6$		
pyridine	$1.05\pm.05\times10^3$	$1.4\pm0.2\times10^3$	$1.9\pm0.1\times10^3$
4,4'-dipyridyl	$2.4\pm0.5\times10^7$	$3.0\pm1.0\times10^7$	$3.5\pm0.2\times10^3$
imidazole	$1.0\pm0.1\times10^4$		$8.4\pm0.3\times10^3$
histamine	$7.5\pm1.0\times10^6$		$2.5\pm0.2\times10^4$
quinuclidine	$4.1\pm0.3\times10^4$		$8.5\pm0.5\times10^4$
1,4-diazabicyclooctane	$2.0\pm0.5\times10^8$		$1.5\pm0.1\times10^5$

[a] For solutions of porphyrin in CH_2Cl_2 at 10^{-6} mol dm^{-3} and 25° C.
[b] λ_{max} (host) 408 nm, (complex) 418 nm or 420 nm.
[c] λ_{max}(host) 407 nm, complex 418 nm.
[d] λ_{max}(host) 410 nm, (complex) 422 nm.

This difference is consistent with complexation of the diamines in a range of conformations having appropriate $H_2N...NH_2$ separations by the very broad cavity of the bis-porphyrin systems, in contrast with the narrow cavity of the face to face crown ether system which can accept bis-ammonium cations only in the fully extended conformation with all C-C bond in the anti conformation. Thus for the strong linear recognition found in earlier work [6] conformational restraint of the guest molecule is an essential feature. In addition, strong linear recognition would require a well defined Zn.....Zn separation in the bis-porphyrin systems **9** and **11**. Simple molecular mechanics calculations on a set of 100 conformations of each of the bis-porphyrins **8** and **13**, using the programs MACROMODEL [10] and CHARMm,[11] show that this is not the case. Thus each compound can adopt a considerable number of conformations within a calculated 10 kcal/mol energy range. These conformations have a range of distance and angular relationships between the two planes defined by the porphyrin systems. This conformational flexibility of both of the host molecules **9** and **11** is consistent

with the rather limited guest recognition implicit in the results summarised in Table 1. The other surprising feature of the face to face porphyrin system is the very strong complexation of 4,4'-dipyridyl (K_a *ca* $2\text{-}3\times10^7$ M^{-1}) as compared with the diamines (K_a *ca* $1\text{-}6\times10^6$ M^{-1}) in spite of the stronger complexation of butylamine (K_a *ca* 5×10^3 M^{-1}) as compared with pyridine [1] (K_a *ca* 1×10^3 M^{-}). The very strong binding of diazabicyclooctane is consistent with the stronger binding of quinuclidine (K_a *ca* 4×10^4 M^{-1}) as compared with butylamine.

Table 2. Chelation factors for binding bidentate ligands by bis-zincporphyrins **9** and **11**.

Bidentate ligand	Chelation factor mol dm^{-3} (K_{XX}/K_X^2)			
	Method A[a]		Method B[b]	
	Host **9**	Host **11**	Host **9**	Host **11**
1,2-diaminoethane	0.04	0.02	0.19	0.10
1,3-diaminopropane	0.035		0.27	
1,4-diaminobutane			0.80	0.10
1,5-diaminopentane	0.112	0.02	0.88	0.16
1,6-diaminohexane			0.72	0.48
1,7-diaminoheptane	0.039	0.03	0.40	0.32
1,8-diaminooctane			0.30	0.05
1,9-diaminononane	0.041		0.42	
1,10-diaminodecane			0.22	
4,4'-dipyridyl	7.84	9.8	87	61
histamine	0.048		0.60	
1,4-diazabicyclooctane	0.036		0.48	

[a] Based upon bidentate ligand binding to mono-zincporphyrin ($K_{obs}=2K_X$) and to bis-zincporphyrin ($K_{obs}=K_{XX}$).

[b] Based upon monodentate ligand binding to bis-zincporphyrin ($K_{obs}=2K_X$) and analogous bidentate ligand to bis-zincporphyrin ($K_{obs}=K_{XX}$).

The anomalous binding of 4,4'-dipyridyl appears to be a consequence of 'good fit' and rigidity. Thus the N...N separation in 4,4'-dipyridyl 7.2 Å requires a Zn...Zn separation of 11.5 Å based upon the known Zn...N separation of 2.14 Å in a simple pyridine complex of a zincporphyrin.[12] This fits the calculated Zn...Zn separation in one of the conformations of the face to face porphyrin **13** and it is not inconsistent with the range of Zn...Zn separations possible for the many possible conformations of the more flexible face to face porphyrin **8** . It may be noted that the $H_2N...NH_2$ separation in one or more of the diamines $H_2N(CH_2)_nNH_2$ will also fit the Zn...Zn separation but this is not associated with a strong enhancement of the association constant. However, 4,4'-dipyridyl loses no internal rotational freedom on complexation and this appears to be a feature that distinguishes it from the diamines. It was therefore of interest to examine the favourable statistical features of complexation involving

two site binding as compared with single site binding,[13] such favourable statistical features are often described as the *chelate effect*. Thus 1:1 complexation by a monotopic receptor is associated with an enthalpy of binding and loss of the rotational and translational freedom of the guest species, whereas 1:1 complexation of an analogous bidentate ligand by a ditopic receptor is associated with twice the binding enthalpy but the loss of rotational and translational entropy of only a single guest species. Thus if K_X is the association constant of a ditopic receptor and a guest with only a single binding site X and K_{XX} is the association constant of the same ditopic receptor and a guest with two binding sites X which are covalently interconnected, then potentially $K_{XX} >> K_X.K_X$ by a factor which represents the loss of rotational and translational entropy of the guest X on complexation. Estimates for this vary but a factor of 10^8 has been suggested [13] for small molecules. Experimental demonstrations of the validity of such large numbers do not appear to be available but a number of rather more modest values of the chelate effect have been reported or may be deduced [14] from reported association constants for two site binding and the analogous single site binding.

Further work is required with preorganised receptors and rigid guests to determine the importance of the chelate effect for enhancing host guest binding using multisite host-guest systems.

EXPERIMENTAL

Infra-red spectra were recorded using Pye Unicam SP 1025 and SP 298 spectrometers, solid samples were used as nujol mulls or KBr disks and spectra of liquids were taken using thin films. NMR spectra were recorded on Perkin Elmer R34 (220 MHz) and Bruker WM 250 (250 MHz) spectrometers using the solvents indicated. Mass spectra were measured using a VG 7070E spectrometer, FAB spectra were obtained using a 3-nitrobenzyl alcohol (NBA) matrix. Melting points were measured using a hot stage apparatus and are not corrected. UV and visible spectra were determined using a Perkin Elmer Lambda 5 spectrometer or a Hewlett Packard 8452A diode array spectrometer. Thin layer chromatography was carried out using Merck 5554 and 818133 pre-coated silica plates.

2,18,12,18-*Tetraethyl*-3,7,13,17-*tetramethyl*-5,15-*bis*(3'-*acetoxyphenyl*)*porphyrin* (**6**, R=$COCH_3$, M=H_2) - p-Toluenesulphonic acid (0.23 g, 1.3 mmol) was added to a solution of 4,4'-diethyl-3,3'-dimethyl-2,2'-dipyrrylmethane **7** (1.00 g, 4.35 mmol) and 3-acetoxy-benzaldehyde (0.71 g, 4.35 mmol) in de-aerated methanol (40 ml). The solution was stirred for 10 min then left for 6 h at room temperature and 12 h at 4 °C (shielded from light). The precipitate was removed by filtration, washed (methanol, 50 ml) and dried to give the porphyrinogen (1.24 g, 76%) as yellow crystals. A solution of DDQ (1.22 g, 5.12 mmol) in dry THF (20 ml) was added to a solution of the porphyrinogen (1.24 g, 1.66 mmol) in dry THF (200 ml) and the solution left at room temperature for 48 h. The solution was evaporated to dryness and the residual solid was treated with aqueous sodium hydroxide (200 ml, 5% w/w), stirred for 2 h, and the undissolved solid removed by filtration. The solid was washed with water and methanol and dried in vacuo to give the *bis(acetoxyphenyl)porphyrin* (**6**, R=$COCH_3$, M=H_2) (0.93 g, 76%) as a purple powder, mp > 300°C (Found: C, 77.6; H, 6.6; N, 7.3%. $C_{48}H_{50}N_4O_4$ requires C, 72.2; H, 6.8, N, 7.5%); δ (CDCl3) -2.48 (br. s, 2xN*H*), 1.76 (t, *J* 6 Hz, 4xCH_3CH_2), 2.36 (s, 2x$COCH_3$), 2.56 (s, 4xCH_3),

4.01 (q, *J* 8 Hz, 4xCH_3CH_2), 7.5-7.9 (m, 8 aryl-*H*), and 10.23 (s, 10-*H* and 20-*H*); m/z, 747 $(M+1)^+$. The corresponding *bis(hydroxyphenyl)porphyrin* **6** was obtained as a purple powder, mp > 300°C (Found: C, 78.2, H, 7.2,; N, 7.95%. $C_{44}H_{46}N_4O_2.CH_3OH$ requires C, 77.8; H, 7.2; N, 8.1%); δ ($CDCl_3$, TFA) -3.2 (br. s 4xN*H*$^+$), 1.42 (t, *J* 7 Hz, 4xCH_3CH_2), 2.39 (s, 4xCH_3), 3.83 (q, *J* 7 Hz, 4xCH_2CH_3), 7.56-7.90 (m, 8 aryl-*H*), and 10.30 (s 10-*H* and 20-*H*); m/z, 663 $(M+1)^+$.

3-(3'-bromopropyloxy)benzaldehyde - A Mixture of 3-hydroxybenzaldehyde (5.0 g, 41 mmol), 1,3-dibromopropane (12.50 ml, 120 mmol) and dry potassium carbonate (30 g) in dry acetone (200 ml) was heated under reflux for 1 h. The mixture was filtered and the filtrate evaporated to dryness. The residue was purified by flash chromatography using light petroleum (bp 60-80°C) followed by light petroleum-ether (80:20) to give the *product* (5.28 g, 53%) as a colourless oil (Found: C, 49.5; H, 4.6%. $C_{10}H_{11}O_2Br$ requires C, 49.4, H4.6%); ν_{max} 1690 cm^{-1}; δ ($CDCl_3$) 2.39 (m, CH_2CH_2Br), 3.65 (t, *J* 6 Hz, CH_2Br), 4.21 (t, *J* 6 Hz, CH_2O), 7.22-7.47 (m, 4 aryl-*H*), and 9.98 (s, C*H*O); m/z 243,245 $(M+1)^+$. Other 3-(ω-bromoalkyloxy)-benzaldehyde derivatives were prepared in a similar way.

3-(4'-*Bromobutyloxy)-benzaldehyde* (59% yield) was a colourless oil (Found: C, 51.1, H, 5.0%. $C_{11}H_{13}O_2Br$ requires C, 51.4; H, 5.1%);ν_{max} 1690 cm^{-1};δ ($CDCl_3$) 2.10 (m, $OCH_2CH_2CH_2CH_2Br$), 3.55 (t, *J* 5 Hz, CH_2Br), 4.12 (t, *J* 5 Hz, CH_2O) 7.21-7.45 (m, 4 aryl-*H*), and 9.94 (s, C*H*O); m/z 257, 259 $(M+1)^+$.

3-(5'-*Bromopentyloxy)-benzaldehyde* (58% yield) was obtained as a colourless oil (Found: C, 53.0; H,5.6%. $C_{12}H_{15}O_2Br$ requires C, 53.2; H, 5.6%);ν_{max} 1695 cm^{-1}; δ ($CDCl_3$) 1.6-2.0 (m, $CH_2CH_2CH_2CH_2CH_2$); 3.40 (t, *J* 5 Hz, CH_2Br), 3.99 (t, *J* 5 Hz, OCH_2), 7.11-7.35 (m, 4 aryl-*H*), and 9.90 (s, C*H*O); m/z, 271,273 $(M+1)^+$.

3-(6'-*Bromohexyloxy)-benzaldehyde* (52% yield) was obtained as a colourless oil (Found: C, 54.8; H, 6.2%. $C_{13}H_{17}O_2Br$ requires C, 54.8; H 6.0%); ν_{max} 1700 cm^{-1}; δ ($CDCl_3$) 1.5-2.0 (m, $CH_2CH_2CH_2CH_2CH_2CH_2$), 3.35 (t, *J* 5 Hz, CH_2Br), 3.95 (t, *J* 5 Hz, OCH_2), 7.10-7.35 (m, 4 aryl-*H*), and 9.88 (s, CH_2O); m/z, 285,287 $(M+1)^+$.

2,8,12,18-*Tetraethyl*-3,7,13,17-*tetramethyl*-5,15-*bis[3'*-(3"-*bromopropyloxyphenyl]-porphyrin* (**12**, n=3) - This was prepared from 3-(3'-bromopropyloxy)-benzaldehyde (1.08 g, 4.44 mmol) and the dipyrrylmethane **7** (1,02 g, 4.44 mmol) using a method similar to that used for the porphyrin **6**. The *bis(bromopropyloxy)porphyrin* (**12**, n=3) was obtained as a purple powder (1.01 g, 65%), mp >300 °C (Found: C, 66.8, H, 6.2, N, 6.2%. $C_{50}H_{56}N_4O_2Br$ requires C, 66.4; H, 6.2; N, 6.2%); δ ($CDCl_3$) -2.45 (br. s, 2xN*H*), 1.78 (t, *J* 7 Hz, 4xCH_3CH_2), 2.38 (m, 2x$OCH_2CH_2CH_2Br$), 2.58 (s, 4xCH_3), 3.67 (t, J 6 Hz, 2xCH_2Br), 4.03 (q, *J* 7 Hz, 4xCH_2CH_3), 4.27 (t, *J* 6 Hz, 2xCH_2O), 7.35-7.67 (m, 8 aryl-*H*), and 10.25 (s, 10-*H* and 20-*H*); m/z (FAB, 3NBA matrix) 902-908, peaks corresponding to $(M+1)^+$. Other bis (ω-bromoalkyloxyaryl)porphyrins were prepared by a similar method.

2,8,12,18-*Tetraethyl*-3,7,13,17-*tetramethyl*-5,15-bis[3'-(4"-*bromobutyloxy)phenyl]-porphyrin* (**12**, n=4) was obtained as a purple powder (77%), mp > 300°C (Found: C, 66.5; H, 6.5, N, 6.0%. $C_{52}H_{60}N_4O_2Br$ requires C, 67.0; H, 6.5; N, 6.0%); δ ($CDCl_3$) -2.44 (br. s, 2xN*H*), 1.78 (t, *J* 7 Hz, 4xCH_3CH_2), 2.06 (m, 2x$OCH_2CH_2CH_2CH_2Br$), 2.57 (s, 4xCH_3), 3.50 (t, *J* 6 Hz, 2xCH_2Br),4.03 (q, *J* 7 Hz, 4xCH_2CH_3), 4.15 (t, *J* 7 Hz, 2x OCH_2), 7.32-7.64 (m, 8 aryl-*H*), and 10.24 (s, 10-*H* and 20-*H*);

m/z (FAB, 3NBA matrix) 930-936, peaks corresponding to $(M+1)^+$. The zinc derivative was prepared by heating a solution of the porphyrin (**12**, n=4) (50 mg, 0.054 mmol) in chloroform (20 ml) with saturated methanolic zinc acetate (1 ml). After 30 m the solution was cooled, washed with water (3x30 ml), dried ($MgSO_4$), and evaporated to give the *zinc porphyrin* (quantitative yield) as a purple solid, mp>300°C (Found: C, 62.6; H, 5.8; N, 5.4%. $C_{52}H_{58}N_4O_2Br_2Zn$ requires C, 62.7; H, 5.9; N, 5.6%); δ ($CDCl_3$) 1.72 (t, *J* 7 Hz, 4xCH_3CH_2), 1.97-2.16 (m, 2x$OCH_2CH_2CH_2CH_2Br$), 2.51 (s, 4xCH_3), 3.50 (t, *J* 6 Hz, 2xCH_2Br), 3.97 (q, *J* 7 Hz, 4xCH_2CH_3), 4.15 (t, *J* 6 Hz, 2xOCH_2), 7.29-7.66 (m, 8 aryl-*H*), and 10.06 (s, 10-*H* and 20-*H*); m/z (FAB, NBA matrix) 992-1001, peaks corresponding to M^+.

2,8,12,18-*Tetraethyl*-3,7,13,17-*tetramethyl*-5,15-*bis*[3'-(5"-*bromopentyloxy*)*phenyl*]*porphyrin* (**12**, n=5) was obtained as a purple powder (47%), mp>300°C (Found: C, 67.2; H, 6.7; N, 5.7%. $C_{54}H_{64}N_4O_2Br_2$ requires C, 67.5; H, 6.7; N, 5.8%); δ ($CDCl_3$) -2.45 (br.s, 2xN*H*), 1.57-2.02 (m, 4xCH_2CH_3 + 2x$OCH_2CH_2CH_2CH_2CH_2Br$), 2.56 (s, 4xCH_3, 3.44 (t, *J* 7 Hz, 2xCH_2Br),4.03 (q, *J* 7 Hz, 4xCH_2CH_3), 4.13 (t, *J* 7 Hz, 2xOCH_2), 7.34-7.64 (m, 8 aryl-*H*), and 10.24 (s, 10-*H* and 20-*H*); m/z (FAB, 3NBA matrix) 958-964, peaks corresponding to $(M+1)^+$.

2,8,12,18-*Tetraethyl*-3,7,13,17-*tetramethyl*-5,15-*bis*[3'(6"-*bromohexyloxy*)*phenyl*]-*porphyrin* (**12**,n=6) was obtained as a purple powder (60%), mp >300°C (Found: C, 68.0; H, 7.0; N, 5.6%. $C_{56}H_{68}N_4O_2Br_2$ requires C, 68.0; H, 6.9; N, 5.7%); δ ($CDCl_3$) -2.45 (br. s, 2xN*H*); 1.44-1.83 (m, 2x $OCH_2CH_2CH_2CH_2CH_2CH_2Br$), 1.90 (t, *J* 7 Hz, 4x$CH_3CH_2$), 2.48 (s, 4x$CH_3$), 3.42 (t, *J* 7Hz, 2x$CH_2Br$), 3.92 (q, *J* 7 Hz, 4x$CH_2CH_3$), 4.15 (t, *J* 7 Hz, 2x$OCH_2$), 7.36-7.68 (m, 8 aryl-*H*), and 10.18 (s, 10-*H* and 20-*H*); m/z (FAB, 3NBA matrix) 986-992, peaks corresponding to $(M+1)^+$.

Bis-zincporphyrin **9**- A stirred mixture of the bis(3'hydroxyphenyl)porphyrin **6** (0.50g, 0.78mmol), 1,6-dibromopropane (0.184 g, 0.76 mmol) and caesium carbonate (2.46 g, 7.55 mmol) in DMF (100ml) was heated at 75°C for 5 days. The solvent was evaporated and the residual solid extracted with hot chloroform. The extract was filtered, washed with water (2x20 ml), dried ($MgSO_4$) and evaporated to give a purple powder which was purified by chromatography [Kieselgel 60H, 50 g, eluent CH_2Cl_2-EtOH (99.25:0.75) containing a trace of ammonia]. The early fractions were combined and evaporated to give a purple powder which crystallised from $CHCl_3$-hexane to give the *bis-porphyrin* **8** (34 mg, 6%) as a purple powder mp> 300°C; δ ($CDCl_3$) -2.67 (br. s, 4xN*H*),1.62 (t, *J* 7 Hz, 8xCH_2CH_3),1.65-1.90 (m, 2x$CH_2(CH_2)_4CH_2$), 2.48 (s, 8xCH_3), 3.86-4.12 (m, 8xCH_2CH_3 + 4xOCH_2), 7.27-7.77 (m, 16 aryl-*H*), and 10.03 (s, 10-*H* and 20-*H*, 10'-*H* and 20'-*H*): m/z (FAB, NBA matrix) 1491 $(M+1)^+$. The *bis-zincporphyrin* **9** was prepared by heating the bis-porphyrin (**8**) (30 mg, 0.02 mmol) in $CHCl_3$ (10 ml) with saturated methanolic zinc acetate (1 ml). After 30 m the solution was cooled, washed with water (3x20 ml), dried ($MgSO_4$) and evaporated to give the *bis-zincporphyrin* **9** (*ca* 100%) as a purple powder mp>300°C (Found: C, 66.3; H, 5.9; N, 6.1%. $C_{100}H_{108}N_8O_4Zn_2.2CHCl_3$ requires C, 66.0; H, 6.0; N, 6.0%); λ_{max} (CH_2Cl_2) 408 (ε 600 000), 536 (ε 34 000), and 574 nm (ε 19 000); δ ($CDCl_3$) 1.64 (t, *J* 7 Hz, 8xCH_3CH_2), 1.70-1.90 (m, 2x$OCH_2(CH_2)_4CH_2O$), 2.45 (s, 8xCH_3), 3.87-4.12 (m, 8xCH_2CH_3 + 4x OCH_2), 7.31-7.74 (m, 16 aryl *H*), and 9.99 (s, 10-*H* and 20-*H*, 10'-*H* and 20'-*H*); m/z (FAB, 3NBA matrix) 1614-1623, peaks corresponding to $(M+1)^+$.

Determination of Association Constants -- Measured quantities of guest amine or diamine in dichloromethane (ml quantities of $2.5x10^{-1}$ to $2.5x10^{-4}$ M solutions according to the value of K_a) were added to a solution of the host porphyrin **9** or **11** in dichloromethane ($1x10^{-6}$ M, 2.5 ml) and the change in absorbance at λ_{max} for the host and the host-guest complex was recorded. In all cases a good isobestic point was observed except for very high values of guest concentration. The face-to-face zincporphyrins were susceptible to degradation by light and air in very dilute solution and it was found necessary to correct the value of host concentration by factors ranging from 0.5 to 0.9 to allow for loss of host due to decomposition to obtain a good fit between calculated and observed absorbance at both of the selected wavelengths. The values of K_a given in Table 1 are best fit values, the quoted deviation represents the range of values of K_a for which the difference between calculated and observed absorbance does not exceed the experimental errors.

REFERENCES

1 Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Holbert, T. R.; Bunnenberg, E.; Linder, R. E.; LaMar, G. N.; Del Gaudio, J.; Lang, J.; Spartalian, K. *J. Am. Chem. Soc.* **1980**, *102*, 4182; Collman, J. P.; Brauman, J. I.; Collins, T. J.; Iverson, B.; Sessler, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 2450; Battersby, A. R.; Hartley, S. G.; Turnbull, M. D. *Tetrahedron Lett.*. **1978**, 3169; Baldwin, J. E.; Crossley, M. J.; Close, T.; O'Rear E. A.; Peters, M. K. *Tetrahedron* **1982**, *38*, 27; Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 898; Traylor, T. G.; Tsuchiya, S.; Campbell, D.; Mitchell, M.; Stynes, D.; Koga, N. *J. Am. Chem. Soc.* **1985**, *107*, 604; Boitrel, B.; Lecas, A.; Renko, Z.; Rose, E. *J. Chem. Soc., Chem. Commun.* **1985**, 1820; Proniewicz, L. M.; Bruha, A.; Nakamoto, K.; Kyuno, E.; Kincaid, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 7050; Guentin, C.; Lexa, D.; Momenteau, M.; Saveant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 1874; Baltzer, L.; Landegren, L. *J. Am. Chem. Soc.* **1990**,*112*, 2804; Lee, C. H.; Garcia, B.; Bruice, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 6434; Johnson, M. R.; Seok,W. K.; Ibers, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 3998.

2 Proniewicz, L. M.; Odo, J.; Goral, J.; Chang, C. K.; Nakamoto, K. *J. Am. Chem. Soc.* **1989**, *111*, 2105; Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Hampton, P. D.; Naruta, Y.; Sparapany, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3477; Kim, K.; Collman J. P.; Ibers, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4242; Battersby, A. R.; Howson W.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1982**, 1266.

3 Irvine, M. P.; Harrison, R. J.; Beddard, G. S.; Leighton, P.; Sanders, J. K. M. *Chem. Phys.* **1986**, *104*, 315; Lindsey, J. S.; Delaney, J. K.; Mauzerell, D. C.; Linschitz, H. *J. Am. Chem. Soc.* **1988**, *110*, 3610; Rodriguez, J.; Kirmaier, C.; Johnson, M. R.; Friesner, R. A.; Holten, D.; Sessler, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 1652; Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1991**, *113*, 4325; Gaines, G. L.; O'Neil, M. P.; Svec, W. A.; Niemczyk, M.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 719; Knapp, S.; Dhar, T. G. M.; Albaneze,J.; Gentemann, S.; Potenza, J. A.; Holten, D.; Schugar, H. J. *J. Am. Chem. Soc.* **1991**, *113*, 4010.

4 Dubowchik, G. M.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1987**, 293; Neumann, K. H.; Vogtle, F. *J. Chem. Soc., Chem. Commun.* **1988**, 520; Hunter, C. A.; Meah, M. N.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1988**, 692, 694; Ogoshi, H.; Hatakeyama, H.; Kotani, J.; Kawashima, A.; Kuroda, Y. *J. Am. Chem. Soc.* **1991**, *113*, 8181; Bonar Law, R. P.; Sanders, J. K.

M. *J. Chem. Soc., Chem. Commun.* **1991**, 574; Aoyama, Y.; Yamagishi, A.; Tanaka, Y.; Toi, H.; Ogoshi, H.*J. Am. Chem. Soc.* **1987**, *109*, 4735; Aoyama, Y; Yamagishi, A; Asagawa, M; Toi, H; Ogoshi, H. *J. Am. Chem. Soc.* **1988**, *110*, 4076.

5 Some recent examples include :- O'Malley, S.; Kodadek, T. *J. Am. Chem. Soc.* **1989**, *111*, 9116; Collman, J. P.; Zhang, X.; Hembre, R. T.; Braumann, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 5356; Boitrel, B.; Lecas, A.; Rose, A. *J. Chem. Soc., Chem. Commun.* **1989**, 349; Groves, J. T.; Viski, P. *J. Org. Chem.* **1990**, *55*, 3628; Narata, Y.; Tani, F.; Ishihara, N.; Maruyama, K. *J. Am. Chem. Soc.* **1991**, *113*, 6865.

6 Johnson, M. R.; Sutherland, I. O.; Newton, R. F. *J. Chem. Soc., Chem. Commun.* **1979**, 309; Mageswaran, R.; Mageswaran, S.; Sutherland, I. O. *J. Chem. Soc., Chem. Commun.* **1979**, 722; Jones, N. F.; Kumar, A.; Sutherland, I. O. *J. Chem. Soc., Chem. Commun.* **1981**, 990; Kotzyba-Hibert, F.; Lehn, J.-M.; Vierling, P. *Tetrahedron Lett.* **1980**, 941; Kotzyba-Hibert, F.; Lehn, J.-M.; Saigo, K. *J. Am. Chem. Soc.* **1981**, *103*, 4226.

7 For example, as Cytochrome-c-oxidase models and see also:- Hamilton, A. D.; Lehn, J.-M.; Sessler, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5158; Tabushi, I.; Kugimiya, S.; Kinnaird, M. G.; Sasaki, T. *J. Am. Chem. Soc.* **1985**, *107*, 4192; Anderson, H. L.; Hunter, C. A.; Meah, M. N.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5780; Hunter, C. A.; Meah, M. N.; Sanders, J. K. M. *J. Am. Chem. Soc.*, **1990**, *112*, 5773; Bookser, B. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 4208; Karaman, R.; Bruice, T. C. *J. Org. Chem.* **1991**, *56*, 3470.

8 Danks, I. P.; Sutherland, I. O.; Yap, C. H. *J. Chem. Soc., Perkin Trans.* 1 **1990**, 421.

9 Osuka, A.; Maruyana, K. *J. Am. Chem. Soc.* **1988**, *110*, 4454.

10 Still,W. C., Macromodel Version V3.1X and BatchMin V3.1, Columbia University, 1990.

11 QUANTA 3.2 and CHARMm as supplied by the Polygen Corporation.

12 Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1969**, *92*, 3761; Abraham, R. J.; Bedford, G. R.; McNeillie, D.; Wright, B. *Org. Mag. Res.* **1980**, *14*, 418.

13 Page, M. I. in " Chemistry of Enzyme Action", Ed. Page, M. I., Elsevier, Amsterdam, 1984, ch. 1; Page, M. I. in "Enzyme Mechanisms", Eds. Page, M. I.; Williams, A., Royal Society of Chemistry, London, 1987, ch. 1; Kirby, A. J. in "Enzyme Mechanisms", Eds. Page, M. I.; Williams, A., Royal Society of Chemistry, London, 1987, ch. 5.

14 Zimmerman, S. C.; Mrksich, M.; Baloga, M. *J. Am. Chem. Soc.* **1989**, *111*, 8528; Zimmerman S. C.; van Zyl, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 7894; Zimmerman, S. C.; van Zyl, C. M.; Hamilton, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 1373; Breslow, R.; Greenspoon, N.; Guo, T.; Zorzycki, R. *J. Am. Chem. Soc.* **1989**, *111*, 8296; Kugimiya, S. I. *J. Chem. Soc., Chem. Commun.* **1990**, 432; Garcia-Tellado, F.; Goswami, S.; Chang, S.-K.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 7393; Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1989**,1714; Adrian, J. C.; Wilcox, C. S. *J. Am. Chem. Soc.* **1989**, *111*, 8055; Aoyama, Y.; Tanaka, Y.; Sugihara, S. *J. Am. Chem. Soc.* **1989**, *111*, 5397; Tanaka, Y.; Kato, Y.; Aoyama, Y. *J. Am. Chem. Soc.* **1990**, *112*, 2807; Aoyama, Y.; Asakawa, M.; Yamagishi, A., Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1990**, *112*, 3145; Breslow, R.; Chung, S. *J. Am Chem. Soc.* **1990**, *112*, 9659; Wiliams, D. H.; Cox, J. P. L.; Doig, A. J.; Gardner, M.; Gerhard, U.; Kaye, P. T.; Lal, A. R.; Nicholls, I. A.; Salter, C. J.; Mitchell, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 7020.