Effect of Porphyrin Ring Distortion on the Spectral and Electrochemical Properties of Short-chain Basket-handle Porphyrins

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The effect of porphyrin ring distortion on the spectral and electrochemical properties of short-chain basket-handle porphyrins has been investigated. The covalent attachment of opposite phenyl rings of *meso*-5,10,15,20-tetraphenylporphyrin (H_2tpp) by short bridging groups of varying nature and length induces distortion in the porphyrin ring. Optical absorption studies indicate large bathochromic shifts (502–1139 cm^{-1}) for both Q and Soret bands and the magnitude of these shifts are linearly correlated with the degree of distortion. The potential values for the porphyrin ring oxidation and reduction were shifted to less-positive (180–260 mV) and to more-negative (280–390 mV) values respectively relative to planar H_2tpp. The magnitude of the shifts in the optical absorption bands and redox potentials are independent of the nature of the bridging chain. The origin of these shifts are traced to structural effects caused due to the introduction of a short bridging group rather than to the electronic effect of the bridging group. Introduction of Cu^{2+} into the porphyrin core does not affect the degree of distortion and ESR studies indicate no significant change in the electronic structure of the Cu^{2+} ion relative to [Cu(tpp)].

Porphyrins and metalloporphyrins are involved in several biomolecules of diverse functions. The ability of the porphyrin ring system to exist in many non-planar conformations such as ruffled, domed and saddle structures is believed to be an important criterion for this involvement.[1–3] A better understanding of the structure–function relationship is possible by studying model porphyrin systems in different distorted conformations. Recent attempts in this direction by many research groups have provided valuable information. Thus, Stolzenberg and co-workers[4–6] have related the distorted conformation of nickel hydroporphyrins to the stability of the macrocycle. They showed that the greatly enhanced stability of oxidized radical species is not a consequence of the redox activity of the co-ordinated nickel but rather of the ruffled conformation of the porphyrin macrocycle. Fujita and Fajer[7] have attributed the strong antiferromagnetic coupling observed between the iron centre and the porphyrin radical centre to the distorted conformation of the porphyrin ring. Recently, Scheidt and Lee[8] have emphasized the relationship between the stereochemistry of a variety of metallotetrapyrroles and their function.

Recent studies from this laboratory have shown that significant distortion can be induced in the porphyrin ring by covalent attachment of a short bridging chain across its periphery. The distortion was reflected in the altered spectroscopic properties both of the ground and excited states.[9] In continuation of our efforts towards an understanding of the structure–function relationship we have investigated the effect of (*i*) the nature of the bridging chain and (*ii*) the length of bridging chain on the spectroscopic and electrochemical properties of the most distorted isomer. The bridging chains selected include simple alkyl, alkyl containing an aromatic ring and alkyl containing an aromatic ring with electron-withdrawing substituents. Furthermore, it has been possible to insert Cu^{2+} into the porphyrin core despite the steric hindrance. It has been shown that for the series described in this work the distortion effects are independent of the nature of the bridging chain. However, the degree of distortion is dependent on the length of the bridging chain.

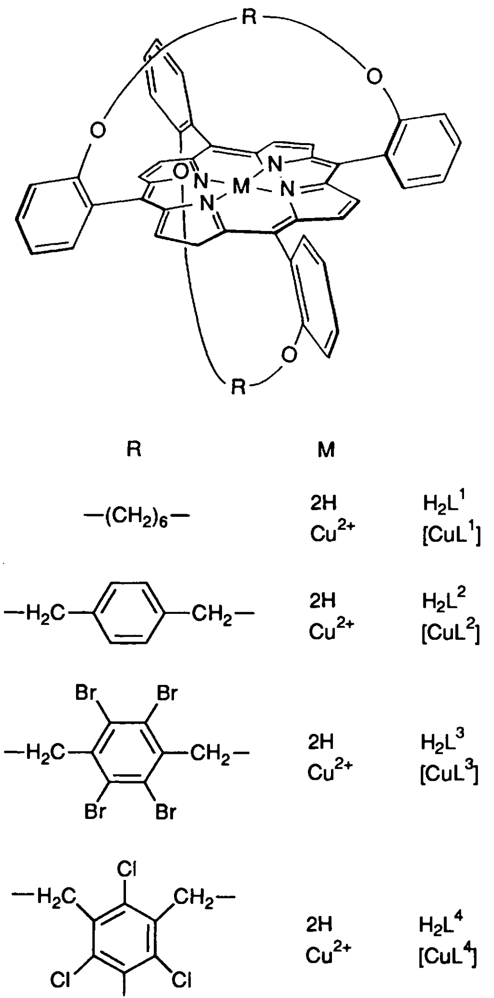

Table 1 Electronic spectral data of various cross-*trans*-linked basket-handle porphyrins and their copper(II) derivatives in $CHCl_3$

Porphyrin	Soret band[a] B (0,0)	Q bands[b] Q_y (1, 0)	Q_y (0, 0)	Q_x (1, 0)	Q_x (0, 0)
H_2tpp[c]	419 (46.4)	515 (18.7)	548 (8.6)	592 (5.5)	647 (3.9)
H_2L^1[d]	428 (22.8)	526 (11.5)	562 (5.1)	602 (4.5)	658 (1.7)
H_2L^2[c]	433 (22.2)	529 (11.7)	566 (5.2)	605 (4.3)	663 (1.2)
H_2L^3	436 (16.0)	532 (7.16)	568 (2.5)	606 (2.6)	663 (0.5)
H_2L^4	440 (14.7)	537 (11.7)	576 (5.4)	610 (4.8)	667 (1.3)
[Cu(tpp)]	417 (41.69)	540 (19.50)		580	
$[CuL^1]$	427 (31.26)	556 (13.07)		594 (2.29)	
$[CuL^2]$	432 (14.82)	562 (6.97)		600 (1.46)	
$[CuL^3]$	435 (21.53)	563 (10.52)		603 (2.06)	
$[CuL^4]$	440 (12.61)	569 (5.80)		611 (1.55)	

[a] λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1}). [b] λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1}). [c] Ref. 9(*a*). [d] Ref. 11(*a*).

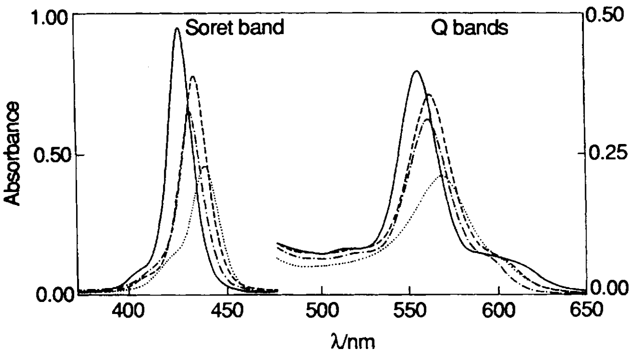

Fig. 1 Comparison of the optical absorption spectra of various copper(II) porphyrins in chloroform in the Soret- and Q-band regions. The concentrations used were ≈5 × 10^{-6} for Soret and ≈5 × 10^{-5} mol dm^{-3} for Q bands. ——, $[CuL^1]$; – – –, $[CuL^3]$; – · –, $[CuL^2]$; · · ·, $[CuL^4]$

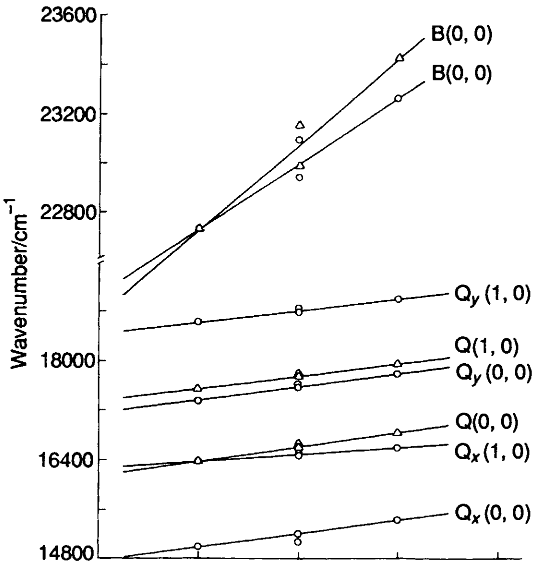

Fig. 2 Plot of absorption band shifts in the Soret- and Q-band region, for various free bases (○) and copper(II) derivatives (△) *versus* the number of atoms (6 for H_2L^4 and $[CuL^4]$; 7 for H_2L^2, H_2L^3, $[CuL^2]$ and $[CuL^3]$; 8 for H_2L^1 and $[CuL^1]$) in the bridging chain

Results and Discussion

The synthetic strategy involved the prior synthesis of the dialdehyde containing the short bridging group with appropriate substituents followed by condensation with pyrrole in propionic acid. This method of condensation results in the formation of three porphyrin isomers, cross *trans* linked, adjacent *cis* linked and adjacent *trans* linked which were separated by repeated column chromatography.[10]

The desired cross-*trans*-linked isomer was identified by its symmetric ^1H NMR spectrum relative to the other isomers. The chemical shifts of the *o*-*meso*-phenyl protons and inner NH ring protons has been used earlier as a marker to assess the degree of distortion of the porphyrin core due to the short bridging chain.[9,10] A comparison of the chemical shifts of these two types of protons shown below for different cross-*trans*-linked isomers suggests a higher degree of distortion for H_2L^4.

Compound	δ *o*-H	δ NH		δ *o*-H	δ NH
H_2L^1	8.85	−0.84	H_2L^4	8.88	+0.88
H_2L^2	8.85	−0.27	H_2L^3	8.85	−0.43

The site of attachment of the bridging chain to the phenyl groups in this isomer results in shorter and so tighter straps relative to the *para* isomer and this is reflected in the higher deshielding of the *ortho* and NH protons.

No report is available in literature on the metal derivatives of the porphyrin systems described here. It has been argued that the presence of short bridging groups symmetrically above and below the porphyrin plane provides steric hindrance to the entry of a metal ion from both faces.[11] However, we have successfully inserted Cu^{2+} into the porphyrin core of all the present derivatives. Fig. 1 shows a comparison of the optical spectra in $CHCl_3$ of all the copper(II) derivatives in the Soret and Q-band regions, and the data are listed in Table 1. Significant bathochromic shifts and broadening of all the Q and Soret bands with drastic reduction in intensity relative to the corresponding unstrapped derivatives are characteristic of distortion of the porphyrin ring.[9a,11a] Furthermore, the magnitude of the band shifts for these derivatives relative to [Cu(tpp)] (H_2tpp = 5,10,15,20-tetraphenylporphyrin) are comparable to the shifts observed for the free bases relative to their corresponding unstrapped derivatives, suggesting that the introduction of the Cu^{2+} ion does not alter the degree of distortion. The effect of electron-withdrawing substituents on the phenyl ring of the bridging group is reflected in a further reduction in intensity of the Soret and Q bands (Table 1).

We have pointed out earlier that the magnitude of the red shifts of Soret and Q bands relative to the corresponding unstrapped derivatives for short-chain basket-handle porphyrins depends on the chain length of the bridging group.[9] A plot of the magnitude of the shifts observed for the Soret and Q bands for various free bases and copper(II) derivatives *versus* the number of atoms in the bridging chain is linear (Fig. 2) suggesting that the magnitude of the red shifts can be directly related to the degree of distortion.

The distortion effects on the electrochemical behaviour were monitored by cyclic voltammetry. A comparison of the cyclic

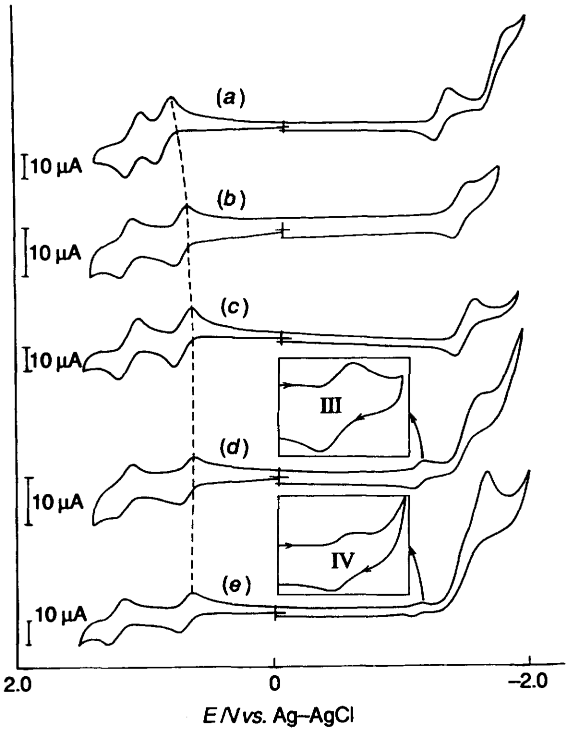

Fig. 3 Cyclic voltammograms of (*a*) [Cu(tpp)], (*b*) [CuL^2], (*c*) [CuL^1], (*d*) [CuL^4] and (*e*) [CuL^3]. The concentrations used were $\approx 5 \times 10^{-4}$ mol dm^{-3}. Scan rate 100 mV s^{-1}. The inset shows the reversible nature of the bridging phenyl ring reduction. The potentials are *versus* Ag–AgCl with NBu_4ClO_4 as the supporting electrolyte

Table 2 Electrochemical redox data[a] for the free bases and their copper(II) derivatives in CH_2Cl_2

	Ring oxidation, $E_{\frac{1}{2}}$		Bridging phenyl ring reduction	Ring reduction, $E_{\frac{1}{2}}$	
Porphyrin	I	II		I	II
H_2tpp	1.03	1.30	—	−1.11	−1.52
H_2L^1	0.85	1.23	—	−1.40	—
H_2L^2	0.85	1.23	—	−1.39	−1.78
H_2L^3	0.77	1.32	−1.14	−1.45	—
H_2L^4	0.85	1.32	−1.13	−1.69[b]	—
[Cu(tpp)]	1.06	1.31	—	−1.14	−1.74
[CuL^1]	0.81	1.25	—	−1.50	—
[CuL^2]	0.85	1.30	—	−1.45	—
[CuL^3]	0.74	1.30	−1.14	−1.66[b]	—
[CuL^4]	0.76	1.26	−1.14	−1.51	—

[a] Potentials in volts *vs.* Ag–AgCl. [b] Corresponds to peak potential.

voltammograms of the copper(II) derivatives with that of [Cu(tpp)] in CH_2Cl_2 is made in Fig. 3. All the free bases, and copper(II) derivatives exhibit two separate one-electron porphyrin-ring-centred oxidations corresponding to the formation of mono- and di-cations respectively.[12] Both the oxidations are reversible [$\Delta(E_a - E_c)$ = 55–65 mV] with the ratio of peak currents close to unity. However, the first oxidation potentials were found to be shifted to less-positive values (180–260 mV) relative to H_2tpp and [Cu(tpp)] respectively indicating easier oxidations (Table 2). The one-electron reductions of the porphyrin ring were observed in both the free bases and the copper(II) derivatives suggesting the formation of monoanions. This reduction was irreversible in H_2L^4 and [CuL^4]. Furthermore, the first reduction potentials in both metal and free-base derivatives are shifted to more negative values (280–390 mV) suggesting harder ring reductions relative to [Cu(tpp)] and H_2tpp. The easier oxidations are interpreted in terms of loss of coplanarity resulting in decreased electron delocalization,[13] and the harder reductions are attributed to the destabilization of anions due to steric hindrance of the strapping group to approach of the solvent.[14] Earlier studies from this laboratory[9a] as well as from other laboratories[15] on strapped porphyrins showed a similar electrochemical behaviour.

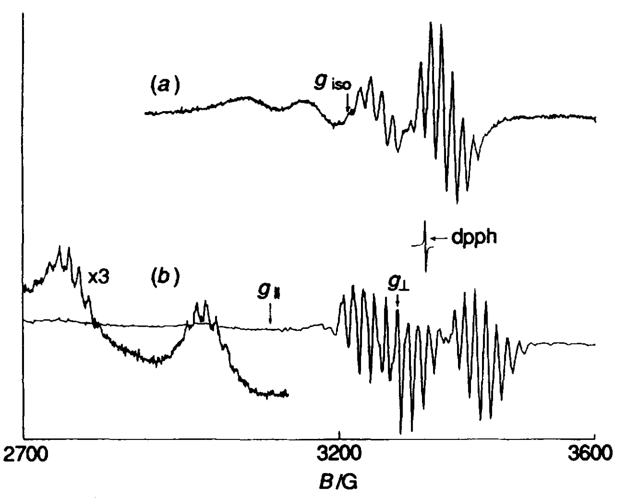

Fig. 4 The ESR spectra in chloroform–toluene (1 : 1) of (*a*) [CuL^1] at 27 °C and (*b*) [CuL^3] at −140 °C. dpph = Diphenylpicrylhydrazyl; G = 10^{-4} T

Fig. 3 shows an additional couple marked III and IV at −1.14 V for [CuL^3] and [CuL^4]. The corresponding free bases also show this couple at the same potential. These are reversible in all cases (Fig. 3 inset) when scanned separately [$\Delta(E_a - E_c)$ = 60–64 mV with peak current ratio to unity]. Furthermore, this couple was not observed for H_2L^1, H_2L^2 and their copper(II) derivatives. It is assigned to the reduction of the bridging phenyl ring containing electron-acceptor substituents. To confirm this, the electrochemical reduction of the dialdehyde containing the bridging group was monitored under the same conditions. 2,3,5,6-Tetrabromo-*p*-phenylenedimethylenedioxybis(benzaldehyde) in CH_2Cl_2 exhibits a reversible couple at −1.015 V, while 2,4,5,6-tetrachloro-*m*-phenylenedimethylenedioxybis(benzaldehyde) 4 shows an irreversible peak at −1.34 V. This intramolecular electron transfer from donor to acceptor in these porphyrins is interesting from the point of view of photoinduced electron transfer since the donor and the acceptor have a fixed orientation with respect to each other at a short distance.[16] Experiments are underway to explore this aspect in detail.

A representative ESR spectrum obtained at room temperature in chloroform–toluene (1 : 1) and of a frozen glass at −140 °C are displayed in Fig. 4. All the room-temperature spectra were composed of four resolved copper lines with superhyperfine structure for two high-field copper lines.[17] However, the low-temperature spectra show axial symmetry and the parallel components of the spin-Hamiltonian parameters, $g_\parallel$, $A_\parallel{}^{Cu}$ and $A_\parallel{}^{N}$ can be determined with a precision adequate for our purpose. However, the exact evaluation of such parameters from the high-field part of the spectra required computer simulation. The details of the simulation program used have been described.[18] The spin Hamiltonian parameters evaluated from the simulated spectra are in Table 3.

The principal tensor components of the superhyperfine interaction between the pyrrole nitrogens and the unpaired electron in the parallel and perpendicular regions were almost the same, indicating a predominantly isotropic superhyperfine interaction, as expected for a CuN_4 moiety in an approximately tetragonal crystal field.[17,19] Furthermore, the equally spaced nitrogen hyperfine lines indicate that the non-planarity of the porphyrin ring has little influence on the ESR spectra and the unpaired electron is coupled equally to the four pyrrole

Table 3 The ESR data for the copper(II) derivatives in chloroform–toluene (1 : 1)[a]

Compound	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{Cu}$	$A_{\perp}^{Cu}$	$A_{\parallel}^{N}$	$A_{\perp}^{N}$	α^2	g_o	A_o^{Cu}	A_o^{N}
[Cu(tpp)]	2.187	2.067	218	32.80	14.5	16.40	0.7500	2.107	97.70	15.90
[CuL^1]	2.155	2.057	205	32.50	n.r.	16.25	0.7239	2.090	90.00	16.30
[CuL^2]	2.159	2.054	202	32.88	n.r.	16.44	0.7212	2.089	89.51	15.85
[CuL^3]	2.161	2.056	205	32.00	14.9	15.99	0.7332	2.091	89.70	15.85
[CuL^4]	2.161	2.042	200	30.22	14.0	15.11	0.7234	2.081	86.96	16.30

n.r. = Not resolved.
[a] A values in 10^{-4} cm^{-1} and the sign of A is negative. [b] From ref. 17(*a*).

nitrogens. This is not surprising as the non-planarity observed in X-ray structural work on [Cu(tpp)] was not manifested in the ESR[17] spectrum.

The tendency for $g_{\parallel}$ to increase and $A_{\parallel}^{Cu}$ to decrease with an increase in the extent of distortion has been reported for structurally well characterized complexes of Cu^{2+} with a variety of ligands containing N, O and S as donor atoms.[20] A closer inspection of the ESR parameters in Table 3 did not reveal any such correlation. However, the observed decrease in $A_{\parallel}^{Cu}$ and A_o^{Cu} values for distorted derivatives relative to [Cu(tpp)] is in accord with the literature reports on distorted copper(II) complexes.[19,20]

The α^2 value calculated from the experimental data represents the bonding coefficient of the b_1 molecular orbital and gives a qualitative idea about the strength of the Cu–N σ bond.[21] The stronger the in-plane σ bond between Cu^{2+} and nitrogen, the higher is the energy of the b_1 molecular orbital because of its antibonding character.[22] Thus, the small decrease in α^2 observed here indicates a lowering of the energy of the b_1 molecular orbital relative to that of [Cu(tpp)] and a weaker copper–nitrogen interaction in the distorted derivatives. A similar conclusion was arrived at to explain the higher value of α^2 for copper phthalocyanin ($\alpha^2 = 0.79$) compared to [Cu(tpp)].[22] Justification for such a conclusion was based on the X-ray structural data[23] which indicated a shorter Cu–N bond (by 0.05 Å) in the copper phthalocyanin relative to [Cu(tpp)]. However, confirmation of such a conclusion in the present study must await the results of a crystal structure determination of one of the copper derivatives.

Conclusion

It has been demonstrated that spectral and electrochemial properties can be altered significantly by a permanent deformation of the porphyrin ring. The linear correlation observed between the magnitude of the optical absorption band shifts and the degree of distortion is quite useful. Furthermore, the magnitude of the red shifts in the absorption spectra and the shifts of the redox potentials in cyclic voltammetry indicate that these shifts are structural rather than electronic in origin due to the nature of the bridging group, at least for the series studied here. The introduction of a metal into the porphyrin core does not seem to affect the degree of distortion. ESR data indicate no significant changes in the electronic structure of Cu^{2+}. Furthermore, the reduction of the bridging phenyl groups prior to ring reduction in the free base and in the copper(II) derivatives of H_2L^3 and H_2L^4 suggests the possibility of photoinduced electron transfer in these systems. A suitable modification of the bridging chain by incorporating an aromatic quinone ring instead of a simple benzene ring might result in very useful models of the photosynthetic electron transfer. Studies in this direction are in progress.

Experimental

Synthesis.—α,α′,2,3,5,6-*Hexabromo*-p-*xylene*. 2,3,5,6-Tetrabromo-*p*-xylene (1.0 g, 2.37 mmol) was dissolved in CCl_4 (100 cm^3) in a three-necked flask (500 cm^3) fitted with a dropping funnel (the tip of which extended to almost the bottom of the flask) and an efficient condenser leading to a gas absorption trap. The flask was heated with vigorous stirring and was illuminated with lamps (3 × 200 W) placed 5 cm from its upper portion. When the temperature of the oil-bath reached 125 °C, bromine (0.27 cm^3, 5.22 mmol) was added dropwise over 1 h. Stirring was continued at 125 °C under illumination for 30 min. The mixture was then cooled to 60 °C and poured into a beaker containing boiling light petroleum (100 cm^3). The solution was cooled slowly to room temperature with occasional stirring to prevent caking of the brown crystalline product which separated. The product was filtered off and washed thoroughly with light petroleum (b.p. 60–80 °C). It was recrystallized from chloroform–ethanol (3:1 v/v), yield 0.850 g (62%). ^{1}H NMR ($CDCl_3$): δ 4.99 (s, 4 H, CH_2).

α,α′-*Dibromo*-2,4,5,6-*Tetrachloro*-m-*xylene*. This was prepared from 2,4,5,6-tetrachloro-*m*-xylene (1 g, 4.09 mmol) and bromine (0.5 cm^3, 9.01 mmol) by following a similar procedure to that above. Yield 1.28 g (78%). ^{1}H NMR ($CDCl_3$): δ 4.8 (s, 4 H, CH_2).

2,3,5,6-*Tetrabromo*-p-*phenylenedimethylenedioxybenzaldehyde*. α,α′,2,3,5,6-Hexabromo-*p*-xylene (19 g, 32.7 mmol) and anhydrous K_2CO_3 (13.5 g, 98.3 mmol) were dissolved in dry dimethylformamide (dmf) and stirred for 5 min. Freshly distilled salicylaldehyde (12 g, 99.1 mmol) was added and stirring was continued for 7 h at room temperature. The completion of the reaction was monitored by TLC. Water (300 cm^3) was added to the reaction mixture and extracted with chloroform (3 × 100 cm^3). The chloroform layer was washed several times with water and sodium hydrogencarbonate solution followed by drying over sodium sulfate. Diethyl ether was added to the concentrated chloroform layer to obtain a white crystalline product (19.5 g, 90%). ^{1}H NMR ($CDCl_3$): δ 5.46 (s, 4 H, OCH_2), 6.9–7.9 (m, 8 H, Ph), and 10.4 (s, 1 H, CHO).

2,4,5,6-*Tetrachloro*-m-*phenylenedimethylenedioxydibenzaldehyde*. α,α′-Dibromo-2,3,5,6-tetrachloro-*m*-xylene (1 g, 2.487 mmol) and anhydrous K_2CO_3 (1.7 g, 12.3 mmol) were added to dry dmf and stirred for 5 min. Salicylaldehyde (1.5 g, 12.39 mmol) was added and stirring was continued for 7 h at room temperature. Work-up of the reaction as above gave a white crystalline solid (1.22 g, 84%). ^{1}H NMR ($CDCl_3$): δ 5.72 (s, 4 H, OCH_2), 6.9–8.9 (m, 8 H, Ph) and 10.5 (s, 1 H, CHO).

H_2L^3. 2,3,5,6-Tetrabromo-*p*-phenylenedimethylenedioxydibenzaldehyde (4.5 g, 6.8 mmol) and pyrrole (0.913 g, 13.6 mmol) in propionic acid (500 cm^3) were heated under reflux for 2 h. The reaction mixture was set aside overnight and was filtered to remove the foam-type material. The solvent was evaporated under reduced pressure. The resultant crude compound was chromatographed over silica gel (60–120 mesh) in C_6H_6. The desired cross-*trans*-linked isomer was eluted first as a red band in C_6H_6. This was rechromatographed over silica gel (60–120 mesh) using C_6H_6 and the product obtained as a purple crystalline solid (0.309 g, 3%). No attempt was made to separate the other undesired isomers. FAB mass spectrum: *m/z* 1514. ^{1}H NMR ($CDCl_3$): δ 8.85 (m, 4 H, *o*-H of Ph), 8.55 (s, 8 H, pyrrole), 7.50 (m, 8 H, *m,m′*-H of Ph), 6.66 (m, 4 H, *p*-H of Ph), 4.53 (s, 8 H, bridge CH_2), and −0.43 (s, 2 H, NH).

H_2L^4. 2,4,5,6-Tetrachloro-*m*-phenylenedimethylenedioxydibenzaldehyde (1 g, 2.066 mmol) and pyrrole (0.277 g, 4.127 mmol) were added to boiling propionic acid (500 cm^3) and refluxed for 2 h. The crude product obtained as above was purified and separated by silica gel (60–120 mesh) column chromatography with C_6H_6. The desired least-polar cross-*trans*-linked isomer obtained in C_6H_6 was rechromatographed using silica gel (60–120 mesh) and the fraction eluted with C_6H_6 gave the pure crystalline solid (0.0496 g, 2.5%). FAB mass spectrum: *m*/*z* 1156. ^{1}H NMR ($CDCl_3$): δ 8.88 (m, 4 H, *o*-H of Ph), 8.60 (s, 8 H, pyrrole), 7.63 (m, 8 H, *m*,*m'*-H of Ph), 7.13 (m, 4 H, *p*-H of Ph), 3.48 (s, 8 H, bridge CH_2) and 0.88 (s, 2 H, NH).

The compounds H_2L^1 [ref. 11(*a*)] and H_2L^2 [ref. 9(*a*)] were synthesised following the published procedures.

Copper(II) *derivatives*. The free-base porphyrin and a two-fold excess of copper(II) acetate in dmf was heated under reflux at 160 °C for 8 h. The progress of the reaction was monitored by recording the absorption spectra of aliquots taken at different intervals of time. The reaction mixture was concentrated to small volume and poured into to a beaker containing water. Extraction with chloroform (3 × 100 cm^3) and drying over sodium sulfate gave the crude product. This was purified by column chromatography using neutral alumina and chloroform as eluent. FAB mass spectra: *m*/*z* 906, 1220 and 1577 for [CuL^1], [CuL^4] and [CuL^3] respectively.

The details of the spectrometers employed are described in our earlier work.[24]

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