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meso-Substituted octabromoporphyrins: synthesis, spectroscopy, electrochemistry and electronic structure†

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The free-base, copper(II) and zinc(II) derivatives of 5,10,15,20-tetraarylporphyrin (aryl = phenyl, 4-methylphenyl or 4-chlorophenyl) and the corresponding brominated 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraarylporphyrin derivatives have been synthesized and their spectral and redox properties compared by UV/VIS, ^{1}H NMR, ESR and cyclic voltammetric methods. Substitution with the electron-withdrawing bromine groups at the pyrrole carbons has a profound influence on the UV/VIS and ^{1}H NMR spectral features and also on the redox potentials of these systems. On the other hand, electron-withdrawing chloro or electron-donating methyl groups at the *para* positions of the four phenyl rings have only a marginal effect on the spectra and redox potentials of both the brominated and the non-brominated derivatives. The ESR data for the copper(II) derivatives of all these systems reveal that substitution at either the β-pyrrole carbons and/or the *para* positions of the *meso*-phenyl groups does not significantly affect the spin-Hamiltonian parameters that describe the metal centre in each case. Collectively, these observations suggest that the highest-occupied (HOMO) and lowest-unoccupied molecular orbitals (LUMO) of the octabromoporphyrins involve the porphyrin π-ring system as is the case with the non-brominated derivatives. Investigations have been carried out to probe the electronic structures of these systems by three different approaches involving spectral and redox potential data as well as AM1 calculations. The results obtained suggest that the electron-withdrawing β-bromine substituents stabilize the LUMOs and, to a lesser degree, the HOMOs and that the extent of these changes can be fine-tuned, in a subtle way, by substituting at the *meso*-aryl rings of a given porphyrin.

Studies on the oxidation of organic and bioorganic substrates utilizing perhalogenated metalloporphyrins as catalysts continue to attract attention because of their relevance to biological monooxygenation and catalytic organic functional group transformation.[1–7] In general, two types of halogenated porphyrins have been prepared: (*i*) those having halogen substituents on the β-pyrrole position[8–17] and (*ii*) those having halogen substituents on the four phenyl rings of a tetraphenylporphyrin.[18–26] In recent years highly halogenated systems bearing chloro or bromo substituents on both the β-pyrrole and *meso*-phenyl rings of a tetraphenylporphyrin have also been synthesized and these show enhanced catalytic activity.[11,13,19,20,27–31] The metal ions incorporated into these porphyrin catalysts are mainly iron and manganese and, in a few cases, perhalogenated porphyrins complexed to other metal ions have also been reported.[7–10,13–16,28–31] The ability of a given porphyrin to serve as an oxidation catalyst is related to its electronic structure, which in turn is influenced by the location and number of electron-withdrawing substituents on the porphyrin periphery and also by the type of metal ion present in the porphyrin crevice.

The interesting catalytic properties of the halogenated porphyrins offer the scope to study their electronic structure. However, a survey of the literature suggested that only a few such studies have been carried out so far on this important class of compounds.[10,17,29,31] An attempt has been made here to probe the electronic structure of *meso*-phenyl-substituted octabromoporphyrins by the combined application of spectral (UV/VIS, ^{1}H NMR and ESR), electrochemical and theoretical methods.

Experimental

Materials

The chemicals and the solvents utilized (from either Aldrich Chemical Co., USA or BDH, India) were further purified using standard procedures.[32] The free base, copper(II) and zinc(II) derivatives of the 5,10,15,20-tetraarylporphyrins (aryl = phenyl, 4-methylphenyl or 4-chlorophenyl) were synthesized by standard methods.[33] The free base, copper(II) and zinc(II) derivatives of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (H_2obtpp) were synthesized according to the published methods.[10] The corresponding octabromo-tetra(4-chlorophenyl) and -tetra(4-methylphenyl) derivatives were synthesized using analogous procedures. Representative procedures are described below.

Preparation of [Cu(obtcpp)], H_2obtcpp and [Zn(obtcpp)]

The complex [Cu(obtcpp)] was synthesized by the reaction of bromine with [Cu(tcpp)] in $CHCl_3$–CCl_4 (1 : 1, v/v). The reaction conditions as well as the work-up and purification procedures were essentially the same as those employed earlier for the synthesis of [Cu(obtpp)][10] (yield: 75%).

This complex (0.20 g) was dissolved in $CHCl_3$ (100 cm^3), perchloric acid (20 cm^3) was added and the resulting mixture was stirred for 8 h at room temperature. The solution was neutralized with a saturated solution of Na_2CO_3 and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and the solvents were evaporated to dryness. The resulting green solid was chromatographed over basic alumina (activity 1) using $CHCl_3$ as the eluent. The first green fraction was collected and identified as the desired product (yield: 80%). The compound H_2obtcpp thus obtained, however, was not

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† *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

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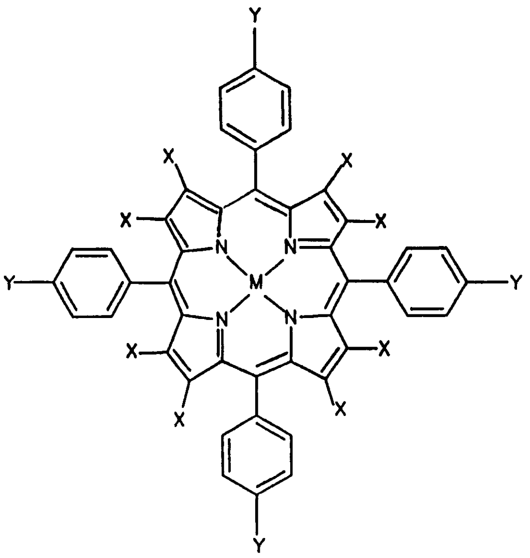

ML

M = 2H, Zn^{II} or Cu^{II}

L	X	Y
tpp	H	H
ttp	H	CH_3
tcpp	H	Cl
obtpp	Br	H
obttp	Br	CH_3
obtcpp	Br	Cl

spectroscopically pure. It contained traces (2–3%, as judged by TLC and UV/VIS spectroscopy) of unreacted [Cu(obtcpp)]. Pure samples were obtained by converting the free-base porphyrin first into its zinc(II) derivative [Zn(obtcpp)] and then demetallating using trifluoroacetic acid. The complex [Zn(obtcpp)] was obtained by refluxing a $CHCl_3$–MeOH (1 : 1, v/v) solution containing H_2obtcpp (97–98% pure, as given above) and zinc(II) acetate tetrahydrate for 1 h and repeated chromatography of the sample over basic alumina using $CHCl_3$ as the eluent (yield: 75%).

Methods

The UV/VIS spectra were recorded with a Shimadzu model UV-160A spectrophotometer, ^{1}H NMR spectra with a Bruker NR-200 AF-FT spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as an internal standard and ESR spectra with a JEOL JM-FE3X spectrometer for toluene solutions containing *ca.* 10^{-3} mol dm^{-3} copper(II) porphyrinate at 100 ± 3 K with diphenylpicrylhydrazide (dpph) as a *g* marker. Cyclic voltammetric experiments (CH_2Cl_2, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) were performed on a Princeton Applied Research (PAR) 174A polarographic analyser coupled with a PAR 175 universal programmer and a PAR RE 0074 X-Y recorder as detailed previously.[34–36] Care was taken to avoid the entry of direct, ambient light into the samples in all the spectroscopic and electrochemical experiments. Unless otherwise specified, all the experiments were carried out at 293 ± 3 K.

The electronic structures of the free-base porphyrins were investigated by the semiempirical AM1 method[37] using MOPAC[38] within the general framework of Gouterman's four-orbital model (FOM).[39] This model suggests that there are two nearly degenerate highest-occupied molecular orbitals (HOMOs) (b1 and b2 with a_{2u} and a_{1u} symmetry) and two nearly degenerate lowest-unoccupied molecular orbitals (LUMOs) (c1 and c2 with e_g symmetry). The ground-state configuration is $(b1)^2(b2)^2$. Configuration-interaction calculations were carried out involving all the excitations among five molecular orbitals bracketing the HOMO and the LUMO in the AM1 computations. Geometry optimization for the free-base porphyrins was done with reported crystal structural data for H_2tpp[40] and H_2obtpp[41] and by assuming that the structures of the tetra(4-methylphenyl) and tetra(4-chlorophenyl) derivatives are similar to those of the corresponding tetraphenyl compounds (*p*-phenyl substituents were appropriately replaced). Results on orbital energies, energy differences and atomic charge densities, obtained from the outputs, have been utilized for the discussion in this study. Molecular mechanics (MMX) calculations on the free-base derivatives were also carried out separately as described previously[34] using a standard software.[42]

Results and Discussion

Synthesis

The synthesis of free-base, copper(II) and zinc(II) derivatives of octabromoporphyrins substituted with either *p*-methyl or *p*-chloro groups at the *meso*-phenyl rings has been accomplished in good yields by closely following the methods reported for the synthesis of H_2obtpp and its metal(II) derivatives.[10] It was observed, during the synthesis of these porphyrins, that the presence of neither the electron-withdrawing chloro nor the electron-donating methyl substituents on the *meso*-phenyl groups has any adverse effect on the bromination occurring at the β-pyrrole positions. All the octabromoporphyrins synthesized were freely soluble in many organic solvents. Reaction of strong acids like CF_3CO_2H was seen to effect only demetallation of the metallooctabromo derivatives but not debromination of any of these porphyrins.

Spectroscopy

The ESR data for the copper(II) derivatives suggest that neither bromination nor *meso*-substitution has any significant effect on the spin-Hamiltonian parameters that describe the electronic structure of the metal centre (see Table 1). On the other hand, and as described below, substitution at the β-pyrrole positions results in dramatic changes in the ^{1}H NMR and UV/VIS spectral features of these porphyrins.

The ^{1}H NMR spectral data for each investigated diamagnetic porphyrin are given in Table 1 and the spectra of H_2tcpp and H_2obtcpp are compared in Fig. 1. A complete absence of the β-pyrrole proton resonances (δ 8.7–8.9) in the spectrum of H_2obtcpp reveals that all the pyrrole carbons are substituted with bromine. In addition, the proton resonance for the imino hydrogens of this porphyrin occurs in a deshielded region (δ −1.73, broad) relative to that observed for the non-brominated H_2tcpp (δ −2.72). This indicates a decreased electron density at the inner imino nitrogens for the octabromo derivative. A comparison of the spectral data for the remaining free base and zinc(II) porphyrins suggests that the situation is similar with these compounds in that bromination of the macrocycle brings about the disappearance of signals due to the β-pyrrole protons of each porphyrin and induces downfield shifts of the imino proton resonances in the case of the free-base porphyrins. The comparison also suggests that bromination has a marginal effect on the resonance positions of protons on the *meso*-aryl rings. This is illustrated in the inset of Fig. 1 which gives a plot of $\Delta(\delta_{ppm})$ (*i.e.* the difference in the chemical shifts of *meso*-aryl or imino protons, between the brominated and the non-brominated free-base porphyrins) *versus* Δ(atomic charges) (*i.e.* the corresponding difference in the atomic charges at the *meso*-aryl or imino positions, as derived from AM1 calculations). While the linear correlation between these two parameters as seen in the plot demonstrates a good correspondence between theory and experiment, the cluttering of points at the ends of the line clearly suggests that the electron-withdrawing effect of the bromine substituents located at the β-pyrrole positions is felt

Table 1 Proton NMR and ESR data

	^{1}H NMR[a] (δ)					ESR[b]		
Porphyrin	β-pyrrole	*o*-H of Ph	*m*-, *p*-H of Ph	CH_3	NH	$g_{\parallel}$	$g_{\perp}$	$10^4 a_{\parallel}^{Cu}/cm^{-1}$
H_2tpp	8.80 (s, 8 H)	8.20 (m, 8 H)	7.80 (m, 12 H)		−2.80 (s, 2 H)			
H_2ttp	8.87 (s, 8 H)	8.16 (d, 8 H)	7.61 (d, 8 H)	2.72 (s, 12 H)	−2.76 (s, 2 H)			
H_2tcpp	8.95 (s, 8 H)	8.23 (d, 8 H)	7.85 (d, 8 H)		−2.72 (s, 2 H)			
[Zn(tpp)]	8.91 (s, 8 H)	8.16 (m, 8 H)	7.72 (m, 12 H)					
[Zn(ttp)]	8.97 (s, 8 H)	8.12 (d, 8 H)	7.59 (d, 8 H)	2.73 (s, 12 H)				
[Zn(tcpp)]	8.90 (s, 8 H)	8.17 (d, 8 H)	8.13 (d, 8 H)					
H_2obtpp		8.22 (d, 8 H)	7.79 (m, 12 H)		−1.66 (br s, 2 H)			
H_2obttp		8.11 (d, 8 H)	7.59 (d, 8 H)	2.69 (s, 12 H)	−1.63 (br s, 2 H)			
$H_2obtcpp$		8.05 (d, 8 H)	7.69 (d, 8 H)		−1.73 (br s, 2 H)			
[Zn(obtpp)]		8.10 (m, 8 H)	7.73 (m, 12 H)					
[Zn(obttp)]		8.01 (d, 8 H)	7.52 (d, 8 H)	2.71 (s, 12 H)				
[Zn(obtcpp)]		7.93 (d, 8 H)	7.59 (d, 8 H)					
[Cu(tpp)]						2.190	2.075	204
[Cu(ttp)]						2.195	2.085	204
[Cu(tcpp)]						2.202	2.064	201
[Cu(obtpp)]						2.182	2.064	196
[Cu(obttp)]						2.182	2.062	198
[Cu(obtcpp)]						2.192	2.072	195

[a] Measured in $CDCl_3$–$SiMe_4$. Error limit: δ ±0.01 ppm. [b] Measured in toluene at 100 ± 3 K. Error limits: g ±0.001, $a_{\parallel}^{Cu}$ ± 5 × 10^{-4} cm^{-1}. In addition to these parameters, $a_{\parallel}^{N}$, $a_{\perp}^{N}$ and $a_{\perp}^{Cu}$ values of 14 ± 1 × 10^{-4}, 15 ± 1 × 10^{-4} and 30 ± 2 × 10^{-4} cm^{-1}, respectively, have also been estimated for these copper(II) porphyrins.

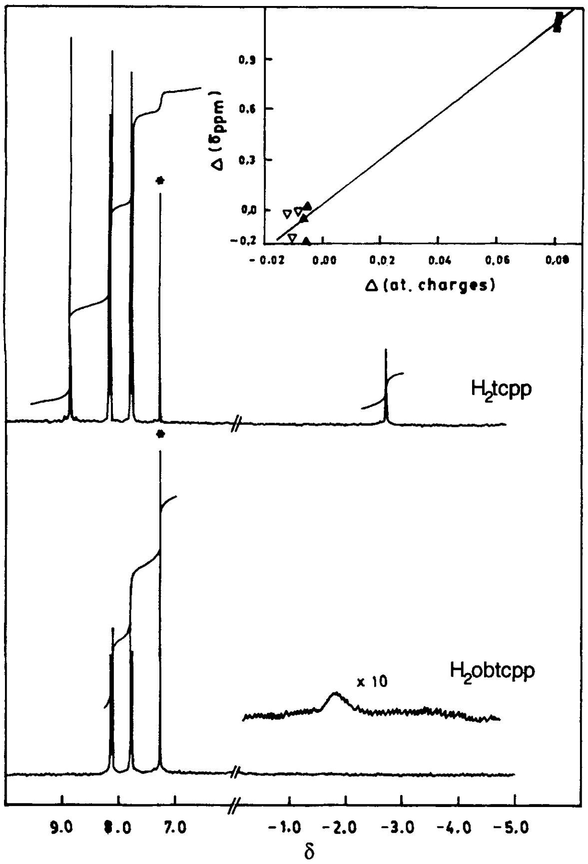

Fig. 1 Proton NMR spectra of H_2tcpp and $H_2obtcpp$ in $CDCl_3$–$SiMe_4$. The inset shows a plot of $\Delta(\delta_{ppm})$ (from ^{1}H NMR) *versus* Δ(atomic charges) (from AM1 calculations). The symbols ■, ▲ and ▽ refer, respectively, to ring imino, *meso*-phenyl *ortho* and *meta* protons of the three sets of free-base porphyrins compared. See text for further details

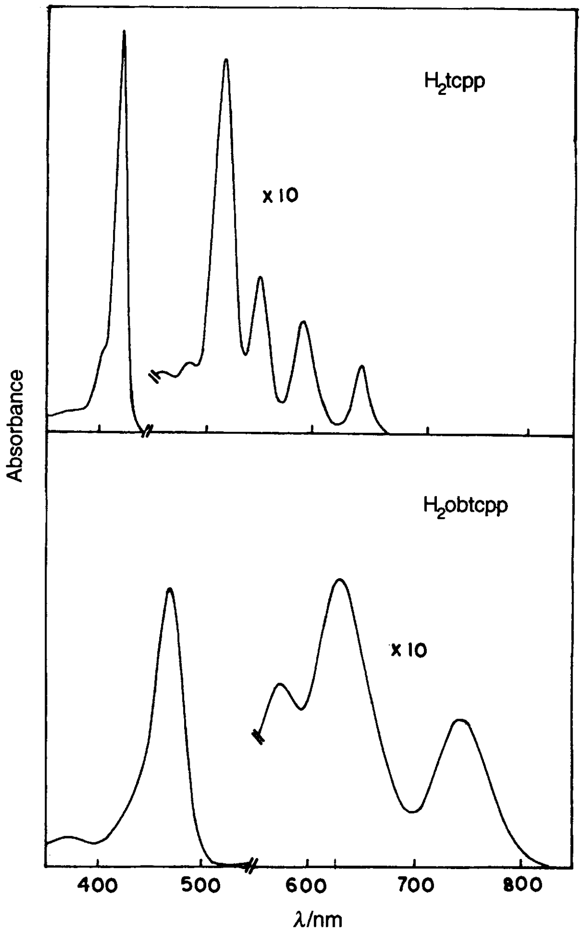

Fig. 2 The UV/VIS spectra of H_2tcpp and $H_2obtcpp$ in CH_2Cl_2

more by the porphyrin ring protons (*i.e.* imino) than by the protons on the *meso*-aryl groups.

There exist two main differences in the UV/VIS spectral features of the brominated and the non-brominated porphyrins as illustrated in Fig. 2 and Table 2. First, both the B and Q bands of the octabromoporphyrins show maxima at far more red-shifted wavelengths relative to those of the unsubstituted analogues. The second difference lies in the full-width at half-maximum (f.w.h.m.) and intensity of these transitions; by and large, the f.w.h.m. and oscillator strength [$f = 4.33 \times 10^{-9}(\text{f.w.h.m.})\varepsilon$ where ε is the molar absorption coefficient in dm^3 mol^{-1} cm^{-1} and f.w.h.m. is in cm^{-1}] of the

Table 2 The UV/VIS and redox potential data

		Redox potential data,[b] $E_{\frac{1}{2}}$/V *vs.* SCE			
		Oxidation		Reduction	
Porphyrin	UV/VIS,[a] λ_{max}/nm (log ε)	I	II	I	II
H_2tpp	647 (3.44), 590 (3.61), 548 (3.76), 514 (4.13), 417 (5.56)	1.00	1.25	−1.23	−1.59
H_2ttp	647 (3.73), 590 (3.74), 549 (3.90), 514 (4.26), 417 (5.37)	0.94	1.18	−1.27	−1.65
H_2tcpp	645 (3.45), 590 (3.66), 550 (3.83), 515 (4.18), 418 (5.37)	1.10	1.28	−1.15	−1.60
[Cu(tpp)]	572 (3.60), 538 (4.49), 414 (6.04)	0.98	1.21	−1.33	−1.80
[Cu(ttp)]	573 (3.55), 540 (4.35), 416 (5.94)	0.93	1.23	−1.37	−1.83[c]
[Cu(tcpp)]	573 (3.50), 539 (4.37), 416 (5.89)	1.07	1.26	−1.30	−1.75
[Zn(tpp)]	585 (3.51), 547 (4.23), 419 (5.67)	0.80	1.02	−1.35	−1.67
[Zn(ttp)]	587 (3.53), 549 (4.16), 420 (5.68)	0.77	1.01	−1.40	−1.72
[Zn(tcpp)]	586 (3.59), 548 (4.21), 420 (5.71)	0.83	1.16	−1.34	−1.64
H_2obtpp	741 (3.83), 627 (4.07), 566 (3.85), 468 (5.43), 367 (4.52)	0.96[c]	1.37[c]	−0.82[c]	−1.24[c]
H_2obttp	743 (3.86), 628 (4.04), 563 (3.87), 467 (5.56), 369 (4.65)	0.85[c]	1.10[c]	−0.85[c]	−1.26[c]
H_2obtcpp	742 (3.79), 628 (4.08), 571 (3.87), 470 (5.37), 373 (4.41)	0.96[c]	—	−0.72[c]	−1.08[c]
[Cu(obtpp)]	623 (3.84), 582 (4.24), 467 (5.35), 451 (sh), 365 (4.64)	0.96	1.41	−0.87	−1.12
[Cu(obttp)]	625 (3.81), 580 (4.12), 464 (5.12), 450 (sh), 353 (4.49)	0.89	1.41	−0.90	−1.16
[Cu(obtcpp)]	623 (3.73), 582 (4.14), 467 (5.02), 453 (sh), 368 (4.33)	1.02	1.49	−0.75	−1.03
[Zn(obtpp)]	654 (3.93), 596 (3.84), 466 (5.24), 352 (4.67)	0.84	1.07	−0.95[c]	−1.16[c]
[Zn(obttp)]	654 (3.98), 594 (3.97), 469 (5.33), 346 (4.57)	0.74	1.01	−1.02[c]	−1.20[c]
[Zn(obtcpp)]	652 (3.95), 596 (3.93), 467 (5.31), 349 (4.69)	0.93	1.18	−0.86	−1.10[c]

[a] Measured in CH_2Cl_2. Error limits: λ_{max} ± 1 nm; log ε ±10%. [b] Measured in CH_2Cl_2, 0.1 mol dm^{-3} NBu_4ClO_4. Error limit: $E_{\frac{1}{2}}$, E_p ±0.04 V. [c] Quasi-reversible/irreversible.

octabromo derivatives are higher than those of the non-brominated analogues. One important difference between the spectra of the non-brominated and brominated free-base porphyrins concerns the number of Q bands. As seen in Fig. 2, while H_2tcpp shows four Q bands consistent with Gouterman's four-orbital model,[39,43] only three such bands are discernible in the spectrum of the brominated analogue. The former spectrum can be interpreted in terms of vibronic mixing which results in the appearance of Q*y*(0,1), Q*y*(0,0), Q*x*(1,0) and Q*x*(0,0) transitions in order of decreasing intensity, whereas the unusually large f.w.h.m. value of the band at 628 nm of H_2obtcpp suggests a possible overlap of the Q*y*(0,0) and Q*x*(0,0) transitions.[10] Finally, the data in Table 2 suggest that *meso* substituents affect the spectral parameters of the octabromoporphyrins in as much as they do so in the case of the non-brominated analogues.

Electrochemistry

Redox potential data for all the porphyrins investigated are summarized in Table 2 and representative voltammograms depicting the changes that occur upon bromination of [Zn(tcpp)] are shown in Fig. 3. Each porphyrin investigated was seen to undergo up to two stepwise, one-electron oxidation reactions and up to three stepwise, one-electron reductions. While all of the electrode processes of the non-brominated compounds and also the first one-electron oxidation and first one-electron reduction of most of the brominated compounds are reversible [$i_p/v^{\frac{1}{2}}$ = constant, $E_{pa} - E_{pc}$ = 60 ± 10 mV and i_{pc}/i_{pa} = 0.9–1.0 in the scan rate (v) range 100–500 mV s^{-1}], the remaining oxidation and reduction processes of the brominated compounds are either quasi-reversible ($E_{pa} - E_{pc}$ = 90–200 mV and i_{pc}/i_{pa} = 0.2–0.7 in this scan rate range) or totally irreversible, as judged by the wave analysis.[44] In each case the electron transfer is assumed to involve the porphyrin ring and not the metal ion as was true for H_2tpp, H_2obtpp and their copper(II) and zinc(II) derivatives.[10,45]

An inspection of the data given in Fig. 3 and Table 2 reveals that while the ring reduction potentials of the brominated derivatives are shifted anodically by 380–720 mV in comparison with those of the non-brominated analogues, the corresponding anodic/cathodic shifts in the ring oxidation potentials are relatively less dramatic (maximum shift *ca.* 200 mV). These observations indicate that the presence of electron-withdrawing bromine substituents at the β-pyrrole carbons makes the porphyrin ring easily reducible and slightly difficult/easier to oxidize relative to the non-brominated analogue. On the other hand, substitution at the *meso*-phenyl rings is comparatively less effective in modulating the ring redox potentials. Nonetheless, in general, the redox potentials of the *meso*-*p*-chloro-substituted porphyrins are more positive compared to the *p*-methyl-substituted porphyrins (see Table 2) consistent with the electron-withdrawing or -donating properties of these substituents.[45]

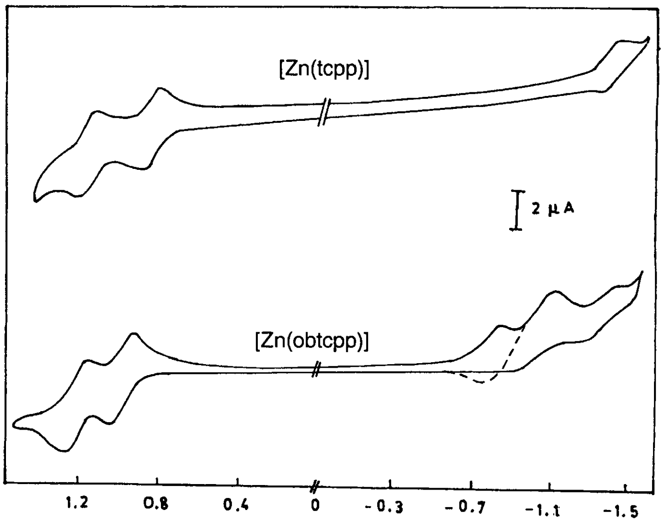

Fig. 3 Cyclic voltammograms of [Zn(tcpp)] and [Zn(obtcpp)] in CH_2Cl_2, 0.1 mol dm^{-3} NBu_4ClO_4. The potential axis is with respect to the saturated calomel electrode (SCE)

An interesting aspect that is related to the electrochemistry of only the zinc(II) octabromo derivatives is concerned with the third reduction peak observed at around −1.35 V for these systems as exemplified in Fig. 3 for [Zn(obtcpp)]. The third reduction peak appears at almost the same potential as that where the non-brominated [Zn(tcpp)] undergoes its first one-electron reduction. In addition, this peak is electrochemically reversible unlike the first and the second reduction peaks which are irreversible when the potential is scanned beyond *ca.* −1.3 V for each zinc(II) octabromoporphyrinate (see Fig. 3). In their recent study on the cobalt(II) derivatives of hexa-, hepta- and octa-bromoporphyrins D'Souza *et al.*[16] have shown that further reduction of the singly reduced species of each of these brominated complexes leads to stepwise elimination of Br groups to give $[\mathrm{Co^I(tpp)}]^-$ as a final product in solution. The irreversible nature of the first and the second one-electron reduction peaks together with the subsequent appearance of a reversible, third reduction peak at −1.35 V in the voltammograms of [ZnL] (L = obttp, obtpp or obtcpp) suggest that, as was the case with the cobalt complexes, electrochemical reduction of these zinc(II) porphyrins may also lead to elimination of Br groups culminating in the generation of the corresponding non-brominated porphyrin in each case. Curiously, the electrochemical behaviour of the zinc(II) octabromoporphyrinates reported here is in stark contrast with that of [octahalogeno-*meso*-tetra(pentafluorophenyl)-porphyrinato]zinc(II) complexes.[30] All of the latter porphyrinates were oxidized in a single, reversible, two-electron transfer step and reduced in successive, reversible, two one-electron transfer steps in CH_2Cl_2, 0.1 mol dm^{-3} NBu_4PF_6.

To sum up, the spectral and electrochemical data presented collectively suggest that the HOMO and LUMO of the octabromoporphyrins reported involve the porphyrin π-ring system and that they possess maximum coefficients on the macrocyclic π-ring atoms as is the case with their parent unsubstituted porphyrins.[43]

Electronic structure

Three different methods have been employed for elucidating the electronic structures of the porphyrins investigated: (*i*) an approach reported by Binstead *et al.*[46] which utilizes both UV/VIS and redox potential data, (*ii*) a method reported by Shellnut and Oritz[47] which utilizes only the quantitative UV/VIS data and (*iii*) AM1 calculations.

Briefly, the method of Binstead *et al.*[46] relates the shifts observed in the centre of gravity of Q and B bands in the absorption spectra (ΔE_{cg}) and the redox potentials (ΔE_{ox} and ΔE_{red}) due to the substituent to the energy shifts of the HOMO (a_{1u} and a_{2u}) and LUMO (e_g), equations (1)–(3). Here ML′

$$\Delta E_{red} = E_{red}[\mathrm{ML}] - E_{red}[\mathrm{ML'}] = -\delta\varepsilon_k \quad (1)$$

$$\Delta E_{ox} = E_{ox}[\mathrm{ML}] - E_{ox}[\mathrm{ML'}] = -\delta\varepsilon_j \quad (2)$$

$$\delta\varepsilon_i = 2(-\Delta E_{cg} + \delta\varepsilon_k - \tfrac{1}{2}\delta\varepsilon_j) \quad (3)$$

refers to either the free base, zinc(II) or copper(II) derivative of a given non-brominated tetraarylporphyrin and ML to the corresponding octabromoporphyrinate. The values of $\delta\varepsilon_i$, $\delta\varepsilon_j$ and $\delta\varepsilon_k$, so obtained follow the trend $\delta\varepsilon_k > \delta\varepsilon_i \gg \delta\varepsilon_j$ for the octabromoporphyrins as seen from the data given in Table 3. This trend, which is similar to that observed for several 2-substituted porphyrins[36,46] and also for the tetra- and octa-bromo derivatives of basket-handle porphyrins,[15] can be rationalized if *i* and *j* are identified with the a_{1u} and a_{2u} levels and *k* with the e_g levels. Thus, the a_{1u} and, more importantly, the e_g levels seem to be sensitive to the presence of bromo substituents at the β-pyrrole carbons.

The above supposition is further supported by the results of AM1 calculations and also by the redox potential data for the free-base derivatives. In Table 3 are summarized the energies of the HOMO [a_{2u} (b_1) and a_{1u} (b_2)] and the LUMO [e_g (c_1 and c_2)] levels of each of the free-base porphyrins and Fig. 4(*a*) (top) shows the difference between these energies [ΔE (HOMO − LUMO)] for the non-brominated and brominated derivatives as derived from AM1 calculations. While there exists minimum modulation of the ΔE (HOMO − LUMO) values upon substitution at the *meso*-phenyl positions for both the brominated and the non-brominated porphyrins, as such, the values are smaller for the former derivatives. Similarly, the excitation energies (ground state ⟶ first excited singlet state), as derived from the AM1-CI calculations, are also lower (1.92 ± 0.02 eV) for the brominated porphyrins in comparison with those (2.18 ± 0.02 eV) for the non-brominated compounds. These theoretical results are consistent with the redox potential data as shown in Fig. 4(*a*) (bottom) which clearly illustrates that bromination of a given porphyrin ring brings about a drastic reduction in its ΔE (HOMO − LUMO) value (*i.e.* the difference between the ring oxidation and reduction potentials, in this case[45]).

The results of the AM1 calculations further suggest that the observed lower ΔE (HOMO − LUMO) values of the octabromoporphyrins is a consequence of the stabilization of both the HOMO and the LUMO of these compounds with respect to the energy levels of the non-brominated species and that there is a greater stabilization for the LUMOs (average 0.64 eV) compared to that for the HOMOs (average 0.23 eV) (see Table 3). As the porphyrin ring reduction involves an electron addition to the LUMO and the ring oxidation involves an electron abstraction from the HOMO,[45] the greater LUMO stabilization, as obtained from AM1 calculations, for the free-base octabromoporphyrins is consistent with the redox potential data of all of the brominated derivatives where larger ΔE_{red} values (= +0.38 to +0.55 V, between the first reduction potentials of the non-brominated and the brominated derivatives) in comparison with the ΔE_{ox} values (= +0.14 to −0.10 V, between the corresponding first oxidation potentials) have been noted (see Table 2). Interestingly, the negative ΔE_{ox} values observed in this study for [Zn(obtpp)] and [Zn(obtcpp)] suggest that these octabromoporphyrins are easier to oxidize than the corresponding non-brominated analogues as is the case with previously reported tetramesityl derivatives.[17]

It is instructive to inquire whether the observations made above with regard to the relative energies of the frontier orbitals of the free-base derivatives, as obtained by AM1 calculations, are relevant to the electronic structures of the corresponding metalloporphyrins. This aspect has been addressed here by employing a method recently reported by Shellnut and Oritz[47] which utilizes quantitative UV/VIS data for the metalloderivatives. The method, which is again based on the FOM approach, considers the presence of substituents on the peripheral positions of a metalloporphyrin to be a perturbation leading to a multitude of configuration interactions (CIs). The nature of the peripheral substituents stabilizes or destabilizes the one-electron excited-state configurations to different extents. As will be shown below, the results obtained by the application of this semiempirical method indicate that, indeed, the observations made for the free-base octabromoporphyrins hold good for the corresponding metalloderivatives as well.

This model, in essence, parametrizes the interaction of the one-electron states that give rise to the π–π* absorption spectrum of metalloporphyrins. The four parameters are the energies and the dipoles of the excited-state MO configurations. These configurations result from promotion of one electron from the nearly degenerate highest-filled a_{2u} and a_{1u} orbitals to the lowest-unoccupied e_g orbital. Electron–electron repulsion causes the MO configurations to interact and gives rise to a 2 × 2 matrix the elements of which are the parameters of the model. Exact diagonalization of the Hamiltonian matrix provides expressions for the eigenstate energies (E_B and E_Q) and the transition dipoles (q_B and q_Q) of the observed Soret band and the α band, respectively, in terms of the four MO parameters. The parameters that define the energies of the excited-state molecular orbital configurations are the matrix elements A_{1g} and A_{1g}' (which define the energies of the excited MO

Table 3 Frontier orbital energies and other related parameters for the octabromoporphyrins as derived from three different approaches

	Based on UV/VIS and redox data[a]			Based on AM1 data (eV)				Based on UV/VIS data[b] (cm^{-1})			
Porphyrin	$-\delta\varepsilon_i$	$\delta\varepsilon_j$	$-\delta\varepsilon_k$	$b_2(a_{1u})$[c]	$b_1(a_{2u})$[c]	$c_1(e_g)$[c]	$c_2(e_g)$[c]	q^2_Q/q^2_B	$E_B - E_Q$	$\frac{1}{2}(E_B + E_Q) = A_{1g}'$	$2A_{1g}$
H_2obtpp	0.21	0.04	0.41	−8.439	−7.441	−2.613	−2.568				
				(−7.871)	(−7.256)	(−2.042)	(−1.889)				
H_2obttp	0.18	0.09	0.42	−8.502	−7.494	−2.736	−2.665				
				(−7.804)	(−7.173)	(−1.969)	(−1.820)				
H_2obtcpp	0.14	0.14	0.43	−8.690	−7.703	−2.868	−2.814				
				(−8.117)	(−7.521)	(−2.299)	(−2.138)				
[Cu(obtpp)]	0.40	0.02	0.46					0.0618	5 362	18 735	−2 548
[Cu(obttp)]	0.42	0.04	0.47					0.0619	5 552	18 776	−2 552
[Cu(obtcpp)]	0.53	0.05	0.55					0.0688	5 362	18 732	−2 714
[Zn(obtpp)]	0.32	−0.04	0.40					0.0700	6 169	18 375	−2 741
[Zn(obttp)]	0.27	0.03	0.38					0.0634	6 031	18 306	−2 586
[Zn(obtcpp)]	0.41	−0.10	0.48					0.0614	6 075	18 375	−2 539

[a] $\delta\varepsilon_i$, $\delta\varepsilon_j$ and $\delta\varepsilon_k$ values estimated based on a method described in ref. 46. [b] Parameters estimated based on a method described in ref. 47. [c] Entries in parentheses refer to the frontier orbital energies of the corresponding non-brominated porphyrins.

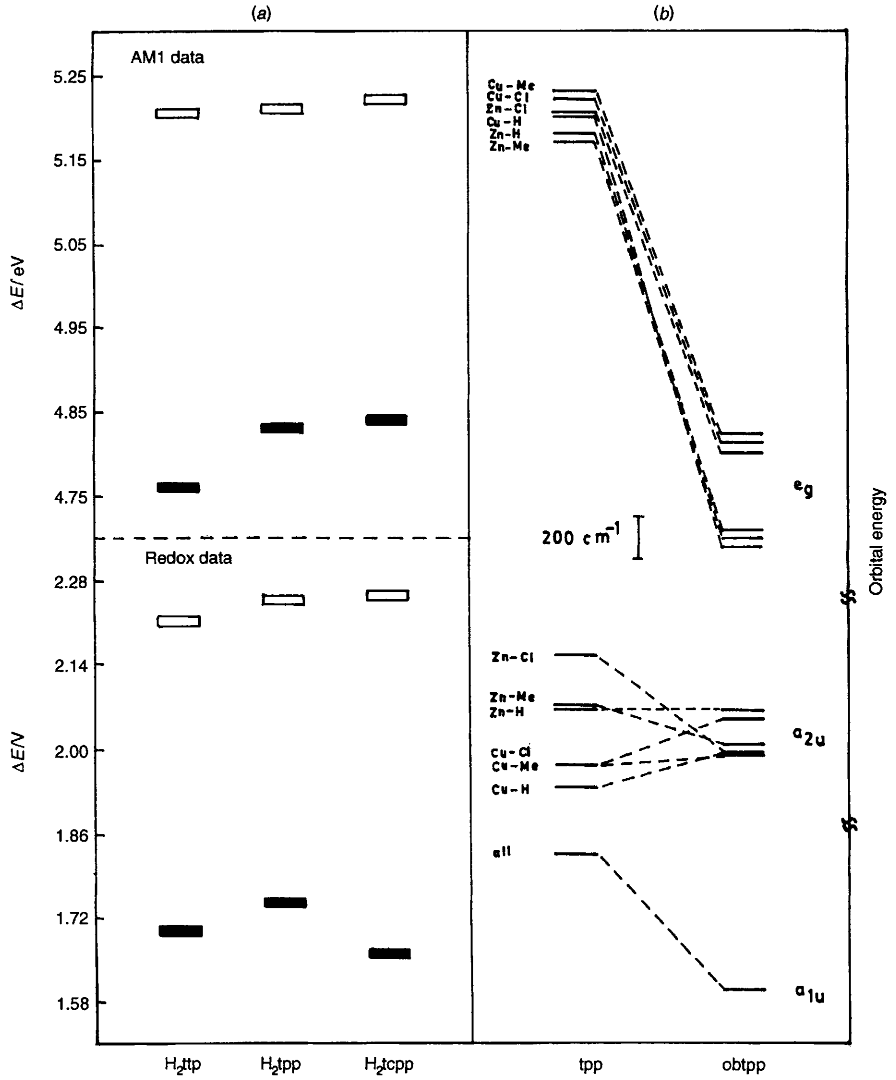

Fig. 4 (*a*) Difference between the energies of the HOMO and LUMO levels (ΔE) for the non-brominated (open rectangles) and brominated (filled rectangles) free-base derivatives as derived from the AM1 calculations (top) and redox potential values (bottom). Here, while H_2ttp and H_2tcpp refer, respectively, to porphyrins substituted with methyl and chloro groups at the *meso*-phenyl rings, H_2tpp refers to the unsubstituted porphyrin. (*b*) Frontier-orbital energy-level diagram of the copper(II) and zinc(II) derivatives of brominated (obtpp) and non-brominated (tpp) porphyrins as derived from an analysis of their quantitative UV/VIS data.[47] The entries refer to the identity of the metal ion and the *meso para* substituent in each case and the dashed lines indicate the extent of stabilization/destabilization of the orbitals

configurations), the off-diagonal CI element A_{1g}'' and the ratio of the transition dipoles r/R for one-electron states. While the matrix element $2A_{1g}$ directly represents the energy splitting of the a_{1U} and a_{2U} orbitals, it is possible to obtain the energy of the e_g level using the data on the average energy of the B and Q transitions (A_{1g}').[47]

These parameters can be estimated by employing the quantitative UV/VIS data following the literature method.[10,47] Here, an experimental plot of $E_B - E_Q$ values *versus* $q_Q{}^2/q_B{}^2$ is compared with theoretical curves obtained for assumed values of A_{1g}'' and r/R and by varying φ [equations (4) and (5)]. The

$$q_Q{}^2/q_B{}^2 = \frac{\sin 2\varphi - (r/R)\sin 2\varphi + r(R)^2 \cos 2\varphi}{\cos 2\varphi + (r/R)\sin 2\varphi + (r/R)^2 \sin 2\varphi} \quad (4)$$

$$\varphi = \tfrac{1}{2}\tan^{-1}(A_{1g}/A_{1g}'') \quad (5)$$

best fit for an experimental curve of $E_B - E_Q$ *versus* $q_Q{}^2/q_B{}^2$ for various octabromoporphyrins, including [Cu(obtpp)] and [Zn(obtpp)] was obtained earlier when $A_{1g}'' = 5050$ cm^{-1}, $r/R = 0.01$ and $\varphi = -15$ to $+14°$.[10] Assuming that the same values hold good for the *p*-chloro- and *p*-methyl-substituted derivatives, it was possible to estimate the relative energies of the a_{1u}, a_{2u} and e_g levels for the present copper(II) and zinc(II) porphyrins. The relevant parameters for the octabromoporphyrins are summarized in Table 3 and the energy levels of the copper(II) and zinc(II) derivatives of the octabromoporphyrins are compared with those of the corresponding non-brominated analogues in Fig. 4(*b*). The LUMOs of the brominated porphyrins are greatly stabilized to the tune of *ca.* 1500–2000 cm^{-1} and the HOMOs are either moderately stabilized (a_{1u}, average 620 cm^{-1}) or marginally destabilized {a_{2u}, *ca.* 20–200 cm^{-1} with the exception of [Zn(obtcpp)]}.

Thus, all of the three methods utilized here to probe the electronic structure of the octabromoporphyrins seem to suggest the same: the effect of electron-withdrawing bromine substituents is to reduce the energies of the LUMOs greatly and to alter the energies of the HOMOs to a lesser extent. This differential stabilization of the energy levels observed for the octahalogeno derivatives can be traced to a counteracting force in the form of a deformation of the porphyrin ring which preferentially destabilizes the HOMOs leaving the LUMOs largely unaffected.[29] The fact that bromination results in a large distortion of the macrocycle has been well documented[13,14,17,29,31] and it has been further verified here for the free-base derivatives by performing MMX calculations. The results suggest that while the π-ring system of each non-brominated porphyrin is nearly planar, there exists a two-fold rotation which reduces the molecular symmetry for the brominated compounds. Specifically, there is a saddling (in which the pyrrole β-carbons are alternatively above and below the mean porphyrin plane) and a ruffling (in which the *meso*-carbons are above and below the mean plane) for these octabromoporphyrins. The average displacement of the β-carbon atoms of the pyrrole rings relative to the mean plane of the four nitrogens in these cases is 1.08 ± 0.03 Å consistent with single-crystal structures of various free-base and metallooctabromoporphyrins reported earlier.[13,14,17,31]

In summary, the combined application of spectral, electrochemical and theoretical methods in this study for *meso*-substituted octabromoporphyrins has provided the relative ordering of the frontier orbitals of the macrocyclic systems. The effect of bromines is to alter the energies of the HOMOs to a minor extent and to stabilize the LUMOs to a greater extent. Substitution of 'innocent', divalent metal ions such as zinc(II) or copper(II) into the porphyrin crevice and that of electron-donating or -withdrawing groups at the *para* positions of the *meso*-phenyl rings of the macrocycle seem to serve only to 'fine-tune' the frontier orbital energies of the octabromoporphyrins. The negative values of $\delta\varepsilon_j$ observed for the zinc(II) octabromoporphyrins (Table 3) and also the stabilization of the a_{2u} orbital of [Zn(obtcpp)] [Fig. 4(*b*)] are noteworthy in this regard. Lowering as well as modulation of the energies of the HOMOs are important determinants of the activity and robustness of porphyrin-based catalyst systems. Keeping this fact in mind, we are currently engaged in both experimental and theoretical investigations on various highly halogenated metalloporphyrins.

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