Perbrominated 2-nitrotetraphenylporphyrins: electrochemical and axial ligation properties

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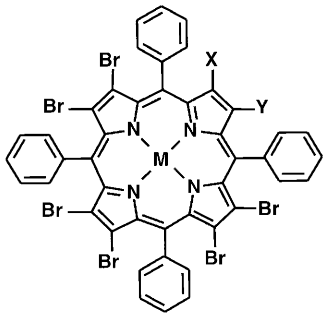
A new series of perbrominated 2-nitro-5,10,15,20-tetraphenylporphyrins, $H_2TPPBr_n(NO_2)$ (n = 6 and 7) and their metal (Cu^{II} and Zn^{II}) complexes have been synthesised and characterised. The presence of mixed electron withdrawing (bromo- and nitro-) substituents at the β-pyrrole positions induces interesting electrochemical and axial ligation properties. Perbrominated nitroporphyrins exhibit two successive one electron redox potentials with a positive shift of >100 mV relative to their corresponding octabromotetraphenylporphyrin ($MTPPBr_8$) complexes. Axial ligation of various nitrogenous bases to $ZnTPPBr_n(NO_2)$ complexes showed facile ligand binding with >50% enhancement in the equilibrium constants, K_{eq}, relative to $ZnTPPBr_8$. Surprisingly, $MTPPBr_n(NO_2)$ complexes show similar axial ligation and electrochemical redox behaviour. The anodic shift in electrochemical redox potentials and enhanced K_{eq} of $MTPPBr_n(NO_2)$ complexes have been attributed to the increased electron deficiency of the porphyrin π-system.

Over the past decade, perhaloporphyrins have aroused considerable interest due to their unusual physical and chemical properties. High-valent metalloperhaloporphyrins serve as catalysts for the oxidative transformation of organic substrates.[1] The stability of metalloporphyrin catalysts has been attributed to both electronic and steric factors.[1e] There are two classes of metalloperhaloporphyin catalysts; (*a*) those with electron withdrawing substituents only on the *meso*-phenyl positions[2,3] and (*b*) those with electron withdrawing substituents on both the β-pyrrole and *meso*-phenyl positions.[4,5] These increase the electron deficiency of the porphyrin macrocycle, and the latter type, in particular, have shown dramatic increases in catalytic activity.[4,5] The increased stability of the catalyst towards oxidative degradation is due to the stabilisation of the HOMO of the porphyrin macrocycle by the halogens at the porphyrin periphery.[4a,b,1d]

Perhaloporphyrins exhibit remarkable electronic, electrochemical redox and stereochemical properties, which make these porphyrins unique.[6] Furthermore, β-perbromoporphyrins have been employed as precursors in the synthesis of a variety of other substituted porphyrins, incorporating the desired donor–acceptor substituents using Suzuki cross-coupling reactions.[7] These highly functionalised porphyrins, are otherwise synthetically inaccessible. A large number of reports can be found in the literature on dodeca-substituted porphyrins with similar substituents at the pyrrole carbons.

Synthesis of porphyrins with mixed substituents is of increasing interest, due partly to the differences in their chemical reactivities and also in order to generate unusually substituted porphyrins.[8] A variety of porphyrins with mixed (alkyl and bromo) groups at the β-pyrrole positions have been reported by Senge and co-workers[9] and they exhibit interesting stereochemical features. The degree of non-planarity of the porphyrin ring influences the physico-chemical properties of the porphyrin π-system.[10] Porphyrins with mixed substituents have been largely unexplored. To our knowledge, $MTPPBr_7(NO_2)$ is the first dodeca-substituted asymmetric porphyrin with electron withdrawing hetero substituents at the β-pyrrole positions. We report here the synthesis, electrochemical redox and axial ligation properties of a series of perbrominated 2-nitrotetraphenylporphyrins, 2-nitro-7,8,12,13,17,18-hexabromo-5,10,15,20-tetraphenylporphyrin, $H_2TPPBr_6(NO_2)$ and 2-nitro-3,7,8,12,13,17,18-heptabromo-5,10,15,20-tetraphenylporphyrin, $H_2TPPBr_7(NO_2)$ and their Zn^{II} and Cu^{II} complexes.



M = 2H, Cu(II), Zn(II)
X = Y = Br, $MTPPBr_8$
X = NO_2, Y = Br, $MTPPBr_7(NO_2)$
X = NO_2, Y = H, $MTPPBr_6(NO_2)$

Fig. 1 Molecular structure of perbrominated 2-nitrotetraphenylporphyrins.

Results and discussion

The porphyrins with mixed substituents at the β-pyrrole positions of the *meso*-tetraphenylporphyrin, $MTPPBr_n(NO_2)$ ($n = 6$ and 7) (Fig. 1) were synthesised by direct bromination of the complex $CuTPP(NO_2)$ followed by acid demetallation. In addition to the desired products [$CuTPPBr_n(NO_2)$ ($n = 6$ and 7)], the formation of $CuTPPBr_8$ was also observed. This is possibly due to nucleophillic substitution[8,11] of the nitro group by the bromo group. With increasing bromine concentration, there is an increase in the yield of $CuTPPBr_8$ relative to the $CuTPPBr_n(NO_2)$ complexes. When the ratio of liquid Br_2 to $CuTPP(NO_2)$ was 100 : 1, the product distribution was exclusively of $CuTPPBr_8$ (55%) and $CuTPPBr_7(NO_2)$ (45%) complexes. Under our optimised conditions, the $CuTPPBr_n(NO_2)$ (n = 6, 7) complexes were generated in good yields.

Table 1 UV–Visible absorption spectral data[a] of MTPPBr$_n$(NO$_2$) complexes in toluene at 25 °C

Porphyrin	B (Bands)	Q (Bands)
H_2TPPBr_8	368(4.30), 471(5.21)	570(3.88), 623(4.05), 740(3.76)
$H_2TPPBr_7(NO_2)$	373(4.31), 474(5.13)	573(3.80), 629(3.93), 747(3.75)
$H_2TPPBr_6(NO_2)$	269(4.32), 469(5.17)	570(3.85), 623(4.06), 738(3.75)
$CuTPPBr_8$	368(4.43), 472(5.11)	585(4.21), 628(3.84)
$CuTPPBr_7(NO_2)$	370(4.31), 475(4.98)	589(4.03), 634(3.78)
$CuTPPBr_6(NO_2)$	365(4.37), 470(5.05)	587(4.12), 633(3.87)
$ZnTPPBr_8$	355(4.50), 472(5.37)	603(4.04), 658(3.99)
$ZnTPPBr_7(NO_2)$	354(4.43), 474(5.34)	607(3.97), 664(4.03)
$ZnTPPBr_6(NO_2)$	352(4.31), 471(5.26)	603(3.89), 657(3.91)

[a] λ/nm. The values in parentheses refer to log (ε/dm^3 mol^{-1} cm^{-1}) values.

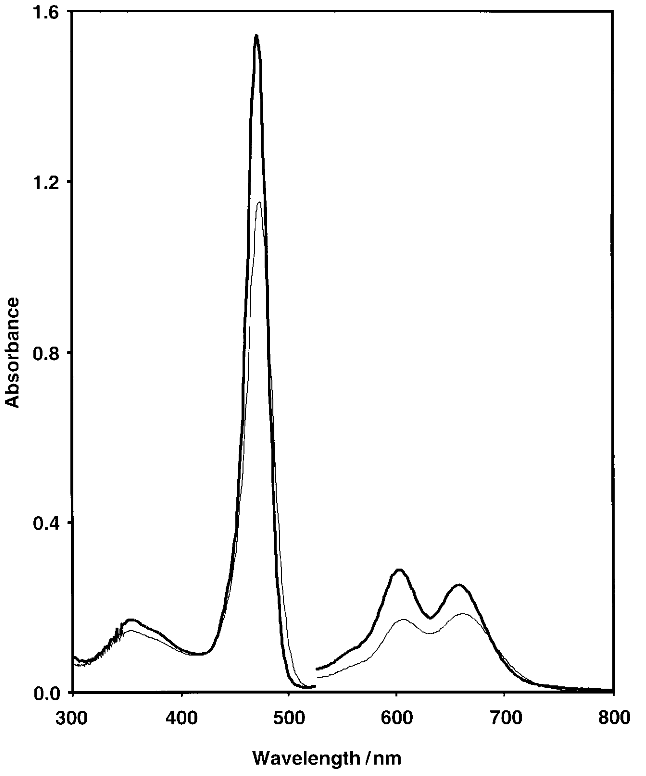


Fig. 2 Electronic absorption spectra of $ZnTPPBr_8$ (heavy line) and $ZnTPPBr_7(NO_2)$ (thin line) in toluene.

The synthesised complexes were characterised by ^{1}H NMR, UV–Visible and mass spectroscopic methods. Optical absorption spectra of the Zn^{II}-perbrominated porphyrins are shown in Fig. 2. Electronic absorption spectral data of the porphyrin complexes are given in Table 1. MTPPBr$_n$(NO$_2$) complexes exhibit similar spectral features to MTPPBr$_8$ complexes.[12a] Interestingly, the UV–Visible absorption spectra of MTPPBr$_7$(NO$_2$) (M = 2H, Zn^{II} and Cu^{II}) complexes show red-shifted B and Q bands relative to their corresponding MTPPBr$_8$ or MTPPBr$_6$(NO$_2$) complexes. The Q(0,0) bands in ZnTPPBr$_n$(NO$_2$) complexes show an increase in intensity relative to their Q(1,0) transitions in toluene. According to the four-orbital-model,[13] the highest occupied molecular orbitals, a_{1u} and a_{2u}, bear electron density at the β-pyrrole carbons and at the *meso*-carbons and imino nitrogens, respectively. The increase in intensity of Q(0,0)/Q(1,0) in ZnTPPBr$_n$(NO$_2$) is possibly due to a further lifting of the degeneracy of the a_{1u} and a_{2u} orbitals by stabilisation of the a_{1u} relative to the a_{2u} orbital, in contrast to that of ZnTPPBr$_8$. The relative intensity Q(0,0)/Q(1,0) for the perbrominated porphyrins follows the order ZnTPPBr$_7$(NO$_2$) > ZnTPPBr$_6$(NO$_2$) > ZnTPPBr$_8$. Synthesised perbrominated 2-nitrotetraphenylporphyrins were found to be non-fluorescent due to the heavy atom effect of the bromine substituents.[12a]

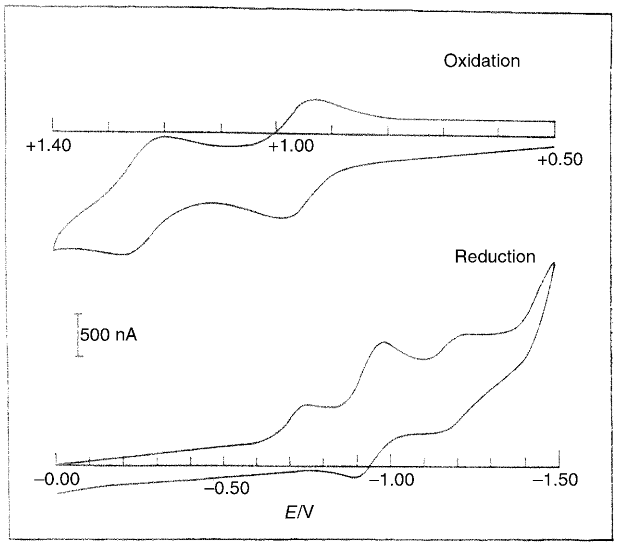


Fig. 3 Cyclic voltammograms of $ZnTPPBr_7(NO_2)$ in CH_2Cl_2 with TBAHFP as the supporting electrolyte at a scan rate of 100 mV s^{-1}.

The ^{1}H NMR spectra of MTPPBr$_6$(NO$_2$) (M = 2H and Zn^{II}) complexes exhibit proton resonances arising from the β-pyrrole and *meso*-phenyl protons, while those of MTPPBr$_7$(NO$_2$) complexes showed no resonances due to β-pyrrole protons. The integrated intensities are in accordance with the proposed structures. The presence of a singlet at 8.70 ppm for the MTPPBr$_6$(NO$_2$) complexes indicates that the pyrrole ring with the nitro group is free of bromine substitution. For the MTPPBr$_7$(NO$_2$) complexes, the *ortho*-phenyl protons show an asymmetric multiplet, in contrast to their corresponding MTPPBr$_8$ complexes, indicating the lowered symmetry of the MTPPBr$_7$(NO$_2$) complexes.

A wide variety of perhaloporphyrins have been examined in non-aqueous media.[6a,b,j,12] The electrochemical redox properties of a series of perbrominated porphyrins have been examined in CH_2Cl_2 using tetrabutylammonium hexafluorophosphate (TBAHFP) as the supporting electrolyte. The cyclic voltammogram of a representative ZnTPPBr$_7$(NO$_2$) complex is shown in Fig. 3. For comparison, MTPPBr$_8$ complexes were also examined under similar conditions. Table 2 lists the electrochemical redox data of various asymmetric MTPPBr$_n$(NO$_2$) complexes. The observed redox potentials for the MTPPBr$_8$ complexes are in accordance with the reported values.[12] The MTPPBr$_n$(NO$_2$) (M = Cu^{II} and 2H) complexes exhibited two successive reduction and two oxidation potentials while the ZnTPPBr$_n$(NO$_2$) complexes showed two oxidation and three reduction potentials. The observed behaviour of the ZnTPPBr$_n$(NO$_2$) (n = 6 and 7) complexes is quite similar to that of the ZnTPPBr$_8$ complex.[12a] Interestingly, the porphyrins with mixed substituents showed >100 mV anodic shift in redox potential relative to their corresponding MTPPBr$_8$ complexes. This can be attributed to the increased electron deficiency of the

Table 2 Half-wave redox potentials[a] (mV) of $MTPPBr_n(NO_2)$ complexes in CH_2Cl_2 with 0.1 M TBAHFP at 25 °C

	Oxidation		Reduction		
Porphyrin	I	II	I	II	III
H_2TPPBr_8	960[b]	—	−680	−1070	—
$H_2TPPBr_7(NO_2)$	1050	1310	−580[b]	−950	—
$H_2TPPBr_6(NO_2)$	1055	1290	−650[b]	−955	—
$CuTPPBr_8$	910	1510	−865	−1090	—
$CuTPPBr_7(NO_2)$	1040	1545	−720	−925	—
$CuTPPBr_6(NO_2)$	1060	—	−725	−970	—
$ZnTPPBr_8$	880	1140	−935[b]	−1085	−1335
$ZnTPPBr_7(NO_2)$	955	1240	−740[b]	−945	−1180
$ZnTPPBr_6(NO_2)$	955	1220	−750[b]	−960	−1215

[a] *vs.* saturated calomel electrode. [b] Irreversible potentials.

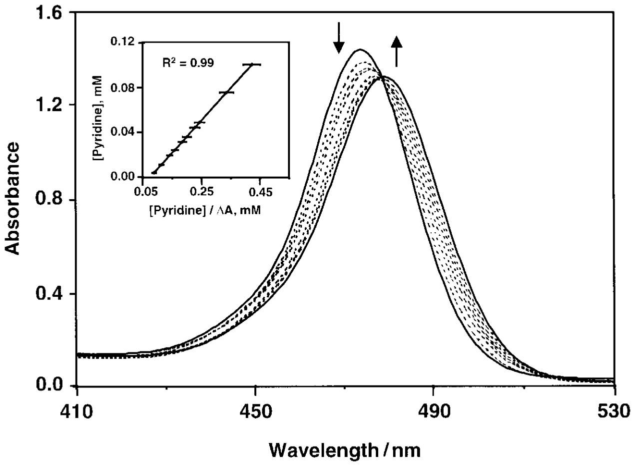


Fig. 4 Titration data is shown for the ligation of pyridine to the $ZnTPPBr_7(NO_2)$ complex in toluene. The main plot shows the electronic spectral change in the Soret region of the $ZnTPPBr_7(NO_2)$ complex on increasing addition of pyridine. The inset shows the plot of pyridine concentration, [pyridine] *vs.* [pyridine] divided by the change in absorbance at 474 nm.

porphyrin macrocycle of the $MTPPBr_n(NO_2)$ complexes. For the $MTPPBr_n(NO_2)$ ($M = Cu^{II}$, Zn^{II}) complexes, with an increase in electronegativity of the core metal ion a positive shift in redox potential was observed, as anticipated. It is of interest to note that the $MTPPBr_n(NO_2)$ ($n = 6, 7$) complexes showed similar redox potentials.

Ligation of nitrogenous bases to $ZnTPPBr_n(NO_2)$ complexes was performed to delineate the effect of mixed bromo- and nitro-substituents on the basicity of the Zn^{II} centre. Different bases were employed to probe the effect of basicity on the K_{eq} values. Optical absorption spectra of the $ZnTPPBr_7(NO_2)$ complex on successive additions of pyridine in toluene are shown in Fig. 4. On ligation of bases to Zn^{II}-perbrominated porphyrins, the $ZnTPPBr_n(NO_2)$ complexes show a red-shifted Soret and the visible bands, as in the case of ZnTPP.[14] The stoichiometry of the complexation between the Zn^{II} porphyrin and the ligand (L) were analysed using the Hill method[15] and in all cases the stoichiometry of the ligand binding to porphyrin was found to be one-to-one complexation [eqn. (1)].

$$[ZnTPPBr_n(NO_2)] + [L] \overset{K_{eq}}{\rightleftharpoons} [ZnTPPBr_n(NO_2)(L)] \quad (1)$$

For comparison with the representative plot for the ligation of pyridine[16] with $ZnTPPBr_7(NO_2)$ (shown in Fig. 4), the ligation of bases with $ZnTPPBr_8$ was also performed under similar conditions; these data[17] are presented in Table 3. It can be seen that the $ZnTPPBr_n(NO_2)$ complexes have >50% higher K_{eq}, relative to the $ZnTPPBr_8$ complex. The $ZnTPPBr_7(NO_2)$ and $ZnTPPBr_6(NO_2)$ complexes show quite similar K_{eq} values. The plot of log K_{eq} of $ZnTPPBr_7(NO_2)$ against the pK_a values for the various bases is shown in Fig. 5. The log K_{eq} values follow a fairly good linear relationship with the pK_a values. Interestingly, the additional bromo group in $ZnTPPBr_7(NO_2)$ has no significant influence over the K_{eq} value.

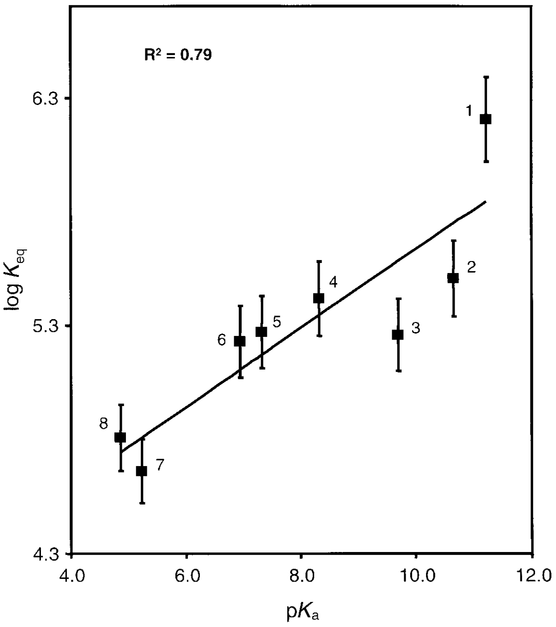


Fig. 5 A plot is given for log K_{eq} of $ZnTPPBr_7(NO_2)$/base against the corresponding pK_a values of the bases. The designated numbers for the bases are as given in Table 3.

In summary, a new class of asymmetric β-perbrominated 2-nitrotetraphenylporphyrins with mixed substituents have been synthesised and characterised. $MTPPBr_n(NO_2)$ complexes showed anodic shifts in electrochemical redox potentials and enhanced K_{eq} values relative to $MTPPBr_8$ complexes. This is interpreted in terms of an enhanced electron deficiency of the $MTPPBr_n(NO_2)$ complexes due to the introduction of a nitro group that is in direct conjugation with the porphyrin π-system.

Experimental

The majority of the solvents employed in this study were of reagent grade and were distilled before use. Toluene (Ranbaxy labs, India) was refluxed and distilled from sodium. CH_2Cl_2 (Qualigens, India) was refluxed and distilled over CaH_2. Liquid bromine, purchased from E. Merck, was used as received. Metal carriers, $Zn(OAc)_2 \cdot 2H_2O$ and $Cu(OAc)_2 \cdot H_2O$ were purchased from Ranbaxy labs (India) and used without further purification. Silica gel (60–120) was purchased from Acmes (India) and used as received. The nitrogenous bases, pyridine, 3-hydroxypyridine, imidazole and piperidine were procured from Fluka (Switzerland) and used as received. TBAHFP was procured from Fluka (Switzerland) and used without further purification.

Syntheses

$MTPPBr_n(NO_2)$ complexes. 2-Nitro-5,10,15,20-tetraphenylporphinatocopper(II), $CuTPP(NO_2)$ was synthesised using a reported procedure.[18] Perbrominated $H_2TPPBr_n(NO_2)$ ($n = 6, 7$) complexes were synthesised by bromination of $CuTPP(NO_2)$ with liquid bromine followed by demetallation. A 250 cm³ conical flask, equipped with a magnetic stir bar, was charged with $CuTPP(NO_2)$ (0.33 g, 0.44 mmol) in $CHCl_3$ (70 ml) at room temperature. To this solution, liquid Br_2 (4.36 g, 26 mmol)

Table 3 Equilibrium constants (K_{eq})[a] for the ligation of various nitrogenous bases and DMSO with Zn^{II}-perbrominated porphyrins in toluene at 25 °C

	$10^{-3}K_{eq}/M^{-1}$			
Base	$ZnTPPBr_8$	$ZnTPPBr_7(NO_2)$	$ZnTPPBr_6(NO_2)$	pK_a[b]
1. Piperidine	1003.77	1598.52	1598.86	11.22
2. Cyclohexylamine	192.79	320.23	301.04	10.66
3. 4-Dimethylaminopyridine	135.17	181.32	158.87	9.70
4. Morpholine	182.08	261.22	263.27	8.33
5. *N*-Methylimidazole	138.71	186.39	187.44	7.33
6. Imidazole	113.30	169.85	184.72	6.95
7. Pyridine	29.57	45.89	47.58	5.23
8. 3-Hydroxypyridine	39.02	64.21	62.02	4.86
9. DMSO	9.06	14.22	14.15	—

[a] Error ± 6%. [b] Values are taken from ref. 19.

in $CHCl_3$ (30 ml) was added dropwise over a period of 20 min. After complete addition of bromine, the reaction mixture was stirred for 4 h at room temperature. At the end of 4 h, pyridine (4.0 ml) in $CHCl_3$ (40 ml) was added dropwise over a period of 30 min. Then the reaction mixture was allowed to stir for a further 6 h and then treated with 100 ml of aqueous sodium metabisulfite solution (25%) followed by 150 ml of aqueous HCl (20%). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude product mixture was concentrated to a minimum volume and purified by column chromatography on silica gel with $CHCl_3$ as the eluant. The yield of the product was found to be 0.38 g (65%). The separation of the individual components $CuTPPBr_8$, and $CuTPPBr_n(NO_2)$ ($n = 6, 7$) was unsuccessful on silica or alumina columns due to the poor solubility of the product mixture in low polarity solvents. However, the separation the of mixture was effected by preparation of the Zn^{II} complexes.

The acid demetallation of perbrominated porphyrins was performed using conc. H_2SO_4. In a typical reaction, the Cu^{II} complex (0.10 g, 0.08 mmol) was dissolved in $CHCl_3$ (40 ml), and to this conc. H_2SO_4 (3 ml) was added. The reaction mixture was stirred for a period of 30 min, then washed with distilled water (2 × 100 ml) and the non-aqueous layer was neutralised with saturated aqueous $NaHCO_3$ solution. The organic solution was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure using a rotary evaporator. Yield of the free base product was found to be 0.085 g (90%). The Zn^{II} insertion into the free base perbrominated porphyrins was carried out using the procedure employed for Cu^{II} insertion as described below and the yield of the product was almost quantitative. The individual Zn^{II} complexes of H_2TPPBr_8 and $H_2TPPBr_n(NO_2)$ ($n = 6,7$) were separated on a silica gel column using toluene as the eluant. The $ZnTPPBr_8$ complex was eluted first followed by the $ZnTPPBr_7(NO_2)$ and $ZnTPPBr_6(NO_2)$ complexes. Yields of the individual fractions were found to be $ZnTPPBr_8$ (40%), $ZnTPPBr_7(NO_2)$, (30%) and $ZnTPPBr_6(NO_2)$ (30%).

$H_2TPPBr_n(NO_2)$ complexes. These complexes were prepared by demetallation of their Zn^{II} complexes using conc. HCl. In a typical demetallation reaction, $ZnTPPBr_7(NO_2)$ (0.060 g, 0.05 mmol) was dissolved in 20 ml of $CHCl_3$. To this, 3 ml of conc. HCl (33%) was added with stirring for 15 min. the reaction mixture was then washed with distilled water (3 × 50 ml). The non-aqueous layer was neutralised with aqueous $NaHCO_3$ (15%) solution and dried over anhydrous Na_2SO_4. The yield of the porphyrin was found to be 0.055 g (90%).

$CuTPPBr_n(NO_2)$ complexes. The metal ion insertion was performed in a $CHCl_3$–CH_3OH solvent mixture using Cu^{II} acetate monohydrate as metal carrier. A round-bottomed flask (100 cm^3) was charged with $H_2TPPBr_7(NO_2)$ (0.075 g, 0.06 mmol) in $CHCl_3$ (25 ml). Cu^{II} acetate monohydrate (0.050 g, 0.22 mmol) in 3 ml of methanol was added and the solution was stirred at room temperature for 20 min. The solvent was then removed under reduced pressure and the crude material purified by silica gel column chromatography using $CHCl_3$ as the eluant. The yield of the porphyrin was almost quantitative.

Spectra

The synthesised free base perbrominated porphyrins and their metal complexes were characterised by ^{1}H NMR, UV–Visible, elemental and mass spectroscopic techniques. $ZnTPPBr_8$: δ_H (400 MHz, $CDCl_3$, TMS) 8.10 (m, 8H, aromatic H_o), 7.56 (m, 12H, aromatic $H_{m,p}$). FAB mass spectrum (*m*/*z*): 1308 (M^+, 100%), 1230 ($M^+ - Br$, 8%). The observed data are similar to those reported for $ZnTPPBr_8$.[12a]

$MTPPBr_6(NO_2)$ (M = 2H, Zn^{II}) complexes. $H_2TPPBr_6(NO_2)$: δ_H (400 MHz, $CDCl_3$, TMS) 8.71 (s, 1H, β-H), 8.21 (m, 8H, aromatic H_o), 7.70 (m, 12H, aromatic $H_{m,p}$), −1.50 (br s, 2H, NH) (Found: C, 46.35; H, 2.16; N, 6.10. $C_{44}H_{23}N_5O_2Br_6$ requires C, 46.86; H, 2.06; N, 6.21%). $ZnTPPBr_6(NO_2)$: δ_H (400 MHz, $CDCl_3$, TMS) 8.65 (s, 1H, β-H), 8.10 (m, 8H, aromatic H_o), 7.50 (m, 12H, aromatic $H_{m,p}$). FAB mass spectrum (*m*/*z*): 1197.0 [$(M + H)^+$, 100%], 1116.9 [$(M + H)^+ - Br$, 12%].

$MTPPBr_7(NO_2)$ (M = 2H, Zn^{II}) complexes. $H_2TPPBr_7(NO_2)$: δ_H (400 MHz, $CDCl_3$, TMS) 8.18 (m, 8H, aromatic H_o), 7.75 (m, 12H, aromatic $H_{m,p}$), −1.45 (br s, 2H, NH) (Found: C, 43.40; H, 1.91; N, 5.90. $C_{44}H_{22}N_5O_2Br_7$ requires C, 43.60; H, 1.83; N, 5.78%). FAB mass spectrum (*m*/*z*): 1213.6 [$(M + H)^+$, 100%]. $ZnTPPBr_7(NO_2)$: δ_H (400 MHz, $CDCl_3$, TMS) 8.12 (m, 8H, aromatic H_o), 7.73 (m, 12H, aromatic $H_{m,p}$). FAB mass spectrum (*m*/*z*): 1275.0 [$(M + H)^+$, 100], 1196.9 [$(M + H)^+ -$ Br, 11%].

Instrumentation

Electronic absorption spectra of free base porphyrins and their metal derivatives were recorded on a JASCO V-550 model UV–Visible absorption spectrophotometer using 1 cm path length quartz cells in toluene. ^{1}H NMR spectra of porphyrins were recorded on a 400 MHz FT-NMR spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. Cyclic voltammetric measurements of free base perbrominated porphyrins and their metal complexes were performed on a BAS-100 Bioanalytical system provided with a monitor and XY recorder. The electrochemical cell consists of a three-electrode cell assembly; a platinum-button-working electrode, a saturated calomel reference, SCE, and a platinum wire as the auxiliary electrode. The reference electrode, SCE was separated from the bulk solution by a glassy diaphragm connected to a bridge filled with the supporting electrolyte. The concentrations of the porphyrins employed were ~1 mM. All measurements were performed at 25 °C in CH_2Cl_2 under N_2 atmosphere using 0.1 M TBAHFP as the supporting electrolyte.

The ligation of various nitrogenous bases with the Zn^{II} perbrominated porphyrins was performed at 25 °C in toluene using a thermostat cell holder and the equilibrium constants, K_{eq}, were evaluated using reported procedure.[16b] K_{eq} were analysed[16b] at four different wavelengths and are found to be similar within the experimental error (6%). For a given base, three K_{eq} values were evaluated and average of three K_{eq} values has been taken for data analysis.

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