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Studies on some new *meso*-aryl substituted octabromo-porphyrins and their Zn(II) derivatives

Regimol G. George, M. Padmanabhan *

School of Chemical Sciences, Mahatma Gandhi University, P.D. Hills, Kottayam 686560, Kerala, India

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Abstract

A series of porphyrins with various tolyl (H_2TTHP) and naphthyl substituents (H_2TNHP) at the *meso*-positions, their octabromoderivatives (H_2TTBP and H_2TNBP) with Br substituents at β-pyrrole positions and also their Zn(II) derivatives have been synthesised and characterised by ^{1}H NMR, electronic, fluorescence and electrochemical studies. These have the *meso*-carbons bonded to tolyl moieties at *ortho*-, *meta*- and *para*-positions of the tolyl groups and at the α- or β-position of the naphthyl group. For the octabromoporphyrins, pronounced deshielding of NH protons and a moderate shift of *meso*-aryl protons to a lower δ value are observed compared to their nonbrominated species. The electronic spectra of ZnTTHP and ZnTNHP have almost the same B and Q bands while the B band of their free-base analogues have H_2TNHP absorbing at a higher wavelength than H_2TTHP. All the octabromoderivatives exhibit a pronounced red shift for both B and Q bands (compared to their nonbrominated forms) and show *meso*-substituent dependent change in both free-base and metallated forms. The above observations are interpreted in terms of moderate conjugative interaction of the aryl substituent with the π framework and also in terms of energy level reordering which alters the HOMO–LUMO gap. Consistent with the absorption spectral data the emission bands of all the bromoporphyrins were also seen to be red shifted considerably. Significant decrement in quantum yield (ϕf) was observed for the bromocompounds. While the ϕf of nonbrominated porphyrins is seen to be higher than their Zn(II) derivatives the reverse order is observed for the bromoderivatives. The ability of the Zn^{2+} ion to make the bromoporphyrins resistant to distortion by bridging the central cavity can be attributed as the cause for this interesting observation. Cyclic voltammetric studies exhibit characteristic quasi-reversible/irreversible oxidation–reduction features for all the free-bases and Zn(II) derivatives. The bromoderivatives on the other hand manifest marginally harder oxidation and very easy reduction features. The data are interpreted in terms of electron withdrawing ability of Br atoms and to reordering of HOMO and LUMO levels due to distortion in the porphyrin ring.

Keywords: Tetratolylporphyrins; Tetranaphthylporphyrins; Octabromoporphyrins; Zn(II) porphyrins; Electronic properties; Fluorescence properties; Electrochemical studies

1. Introduction

A porphyrin macrocycle provides a versatile platform for building elaborate molecular superstructures and this feature coupled with a rich and well-developed synthetic chemistry has led to the synthesis of several catalytically important metalloporphyrins and interesting model compounds of diverse functions [1–3]. The electronic and redox tuning of metalloporphyrins are of active interest as they can bring about significant modification in the chemical, catalytic and photochemical properties of the macrocycle [4–6]. Just as the type of the central metal ion, their oxidation and spin states modify the chemical properties of the metalloporphyrins, the nature and extent of substituents on the peripheral positions have a pronounced effect on the porphyrin macrocycle. It has been demonstrated that electrophilic substitution at the β-pyrrole positions is capable of bringing about major modifications in the electronic and redox properties of the systems. In this context metalloporphyrins bearing halogen substituents on the pyr-

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* Corresponding author. Fax: +91-481-731009.
E-mail address: padman_mgu@yahoo.co.in (M. Padmanabhan).

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role β-positions of the macrocycle are of great interest since they show a high catalytic efficiency for the oxidation of organic substrates [7–9]. Since such a substitution is known to bring about substantial red shift for both B and Q bands leading to intense absorptions in almost the near IR region, they have been proved to be excellent candidates for use as photosensitisers in photodynamictherapy [10,11].

Recent studies from this laboratory have shown that the optical, fluorescent and redox properties of porphyrins can be significantly influenced by the molecular environment around the porphyrin macrocycle, especially by polymer matrices [12–16]. We have also demonstrated that by providing congenial molecular surroundings and also by imparting ionic environments around the porphyrin framework several catalytic and enzymatic reactions like those of *catalase* and *peroxidase* could be efficiently carried out [17,18]. In continuation of our earlier work [19,20] we report the synthesis and characterisation of some new perbromoderivatives of a series of porphyrins with different *meso*-aryl substituents and their Zn(II) derivatives. Attempts are made to study the effect of various *meso*-aryl substituents on all the free-bases and their Zn(II) derivatives by spectral (electronic and fluorescent) and electrochemical methods and also to compare the properties of the brominated porphyrins with their corresponding nonbrominated species.

2. Experimental

Pyrrole (Fluka) was distilled over KOH pellets, under reduced pressure before use. The α-naphthaldehyde and β-naphthaldehyde (E-Merck) were used as received. All the solvents employed in the present study were of spectral grade and were distilled before use. Liquid bromine procured from Ranbaxy and basic alumina obtained from Acmes were used as received. The metal salts used in the preparation were BDH make and used without further purification. NMR spectra were recorded at 300 MHz with $CDCl_3$ as the solvent using a Bruker-300 MHz spectrometer. Elemental analysis were done using a Perkin–Elmer CHN analyzer. The UV–Vis spectral measurements were carried out with a Shimadzu 160A UV–Vis spectrophotometer. Emission spectra were recorded on a Spex-Fluorolog, F112-X equipped with a 450 W Xe lamp and Hamamtsu R 928 photomultiplier tube. Cyclicvoltammetric studies were carried out by using a BAS CV 50 W voltammetric analyser.

2.1. Preparation of 5,10,15,20-tetrakisarylporpyrins

The tolyl porphyrins *meso*-tetrakis(x-tolyl)porphyrins; x = *o*, *m*, *p* (H_2TToHP, H_2TTmHP and H_2TTpHP) were prepared from pyrrole and the respective tolualdehyde by Adler's method [21] incorporating some modifications. Pyrrole (1.04 ml, 14.5 mmol) and tolualdehyde (1.8 ml, 14.98 mmol) were added to 200 ml propionic acid and heated on a boiling waterbath for 6 days. In the case of *meso*-tetrakis(α-naphthyl)porphyrin (H_2TNαHP) and *meso*-tetrakis(β-naphthyl)porphyrin (H_2TNβHP), α-naphthaldehyde (2 ml, 14.7 mmol) or β-naphthaldehyde (2.3 g, 14.7 mmol) were used for the condensation with pyrrole (1.04 ml, 14.9 mM) and the heating on a waterbath was done for about 10 days. The solid residue obtained after distilling of the propionic acid under reduced pressure was washed with water and dried and purified by soxhlet extraction using $CHCl_3$ as solvent. The extracted mixture was further purified by column chromatography on basic Al_2O_3 using $CHCl_3$ as the eluent. The compounds were characterized by elemental analysis, ^{1}H NMR and electronic spectroscopy. The yields of the compounds were in the range 20–25%. *Anal.* Calc. for H_2TToHP: $C_{48}H_{38}N_4$ (mol. wt. 670.31); C, 85.94; H, 5.71; N, 8.35. Found: C, 86.21, H, 5.82; N, 7.97%. *Anal.* Calc. for H_2TTmHP: $C_{48}H_{38}N_4$ (mol. wt. 670.31); C, 85.94; H, 5.71; N, 8.35. Found: C, 85.90; H, 5.94; N, 8.16%. *Anal.* Calc. for H_2TTpHP: $C_{48}H_{38}N_4$ (mol. wt. 670.31); C, 85.94; H, 5.71; N, 8.35. Found: C, 86.28; H, 5.65; N, 8.07%. *Anal.* Calc. for H_2TNαHP: $C_{60}H_{38}N_4$ (mol. wt. 814.97); C, 88.43; H, 4.70; N, 6.87. Found: C, 88.53; H, 4.81; N, 6.66%. *Anal.* Calc. for H_2TNβHP: $C_{60}H_{38}N_4$ (mol. wt. 814.97); C, 88.43; H, 4.70; N, 6.87. Found: C, 88.71; H, 4.94; N, 6.35%.

2.2. Preparation of Zn(II) complexes of nonbrominated meso-tetrakisarylporpyrins

The Zn(II) metallation of all the porphyrins were carried out by the reported procedure. The free-base tolyl porphyrins (0.5 g, 0.74 mmol) or free-base naphthylporphyrins (0.5 g, 0.61 mmol) were dissolved in a suitable solvent mixture ($CHCl_3$:CH_3OH, 1:1, v/v). To this, the metal carrier $Zn(CH_3COO)_2 \cdot 4H_2O$ (9.1 g, 41.5 mmol) dissolved in glacial acetic acid (1.5 ml) was added. Sodium acetate was employed to facilitate buffer action. On refluxing the reaction mixture on a waterbath, the metallation was seen to get initiated. The metallation usually gets completed within 2 h. The mixture was washed free of the unreacted metal salts and the metal(II) derivative formed was purified by column chromatography using $CHCl_3$ as eluent. Metallation was confirmed by UV–Vis spectra. The yields were found to be 85–90%. *Anal.* Calc. for ZnTToHP: $C_{48}H_{36}N_4Zn$ (mol. wt. 734.164); C, 78.52; H, 4.94; N, 7.63. Found: C, 78.76; H, 5.02; N, 7.30%. *Anal.* Calc. for ZnTTmHP: $C_{48}H_{36}N_4Zn$ (mol. wt. 734.164); C, 78.52; H, 4.94; N, 7.63. Found: C, 78.46; H, 4.98; N, 7.58%. *Anal.* Calc. for ZnTTpHP: $C_{48}H_{36}N_4Zn$ (mol. wt. 734.164); C, 78.52; H, 4.94; N, 7.63. Found: C, 78.61; H, 4.86; N, 7.52%. *Anal.* Calc. for ZnTNαHP: $C_{60}H_{36}N_4Zn$

(mol. wt. 878.36); C, 82.05; H, 4.13; N, 6.38. Found: C, 82.16; H, 4.23; N, 6.16%. *Anal.* Calc. for ZnTNβHP: $C_{60}H_{36}N_4Zn$ (mol. wt. 878.36); C, 82.05; H, 4.13; N, 6.38. Found: C, 82.14; H, 4.23; N, 6.20%.

2.3. Preparation of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakisarylporphyrins

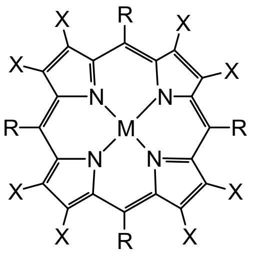
The bromoderivatives of tolylporphyrins (H_2TToHP, H_2TTmHP and H_2TTpHP) and naphthyl porphyrins (H_2TNαHP and H_2TNβHP) were synthesised by a known procedure [22] with some modification. The copper(II) porphyrins employed for the bromination reaction are generated as follows. The free-base tolyl porphyrins (0.5 g, 0.74 mmol) or free-base naphthyl porphyrins (0.6 g, 0.74 mmol) were dissolved in a suitable solvent mixture ($CHCl_3$: CH_3OH, 1:1, v/v) and reacted with the metal carrier, $Cu(CH_3COO)_2 \cdot 4H_2O$ (1.4 g, 7 mol) by refluxing on a waterbath. The metallation was seen to get initiated and gets completed within 2–3 h. The mixture was washed free of the unreacted metal salt and the Cu(II) derivative thus formed was purified by column chromatography on a basic Al_2O_3 column using $CHCl_3$ as eluent. The compound was characterised by electronic spectra. Copper(II) tolylporphyrin (0.30 g 0.41 mmol), generated as above, was dissolved in 100 ml of $CCl_4/CHCl_3$ (1:1, v/v) mixture, and liquid bromine (0.5 ml, 9.7 mmol) in 25 ml of the solvent mixture was added over a period of 2 h at room temperature. The stirring was continued for a further period of 24 h. Pyridine (1.5 ml) in 40 ml of the same solvent mixture was then added over 2 h. The solution was stirred for another period of 3 days. The reaction mixture was treated with 20% aqueous sodium metabisulphite solution to destroy excess bromine. The organic layer was dried using anhydrous Na_2SO_4. The product was chromatographed on a basic Al_2O_3 column using $CHCl_3$ as eluent. The demetallation of the brominated porphyrin was affected by perchloric acid (70%, 10 ml) which was added to the solution of CuTTBP formed (0.1 g, 0.07 mmol) in 50 ml of $CHCl_3$. The reaction mixture was stirred for 12 h. The organic layer was separated, neutralised with 20% aqueous sodium carbonate solution, and dried over anhydrous Na_2SO_4. The resulting solution was concentrated and was purified by column chromatography on basic alumina using $CHCl_3$ as eluent. In the preparation of H_2TNαBP and H_2TNβBP the Cu(II)naphthyl porphyrin taken was 0.36 g (0.41 mmol) and the period of addition of liquid bromine and pyridine was about 3.5 h. ^{1}H NMR and electronic spectral methods were employed for the characterisation of the compounds. The yields of the compounds were in the range 75–80%. *Anal.* Calc. for H_2TToBP: $C_{48}H_{30}Br_8N_4$ (mol. wt. 1302.01); C, 44.28; H, 2.32; N, 4.30; Br, 49.10; Found; C, 43.96; H, 2.57; N; 4.24; Br, 49.23%. *Anal.* Calc. for H_2TTmBP: $C_{48}H_{30}Br_8N_4$ (mol. wt. 1302.01); C, 44.28; H, 2.32; N, 4.30; Br, 49.10. Found; C, 44.21; H, 2.36; N, 4.31; Br, 49.12%. *Anal.* Calc. for H_2TTpBP: $C_{48}H_{30}Br_8N_4$ (mol. wt. 1302.01); C, 44.28; H, 2.32; N, 4.30; Br, 49.10. Found; C, 44.41; H, 2.36; N; 4.33 Br, 48.90%. *Anal.* Calc. for H_2TNαBP: $C_{60}H_{30}Br_8N_4$ (1446.04); C, 49.83; H, 2.09; N, 3.87; Br, 44.20. Found; C, 50.16; H, 2.23; N, 3.65; Br, 43.96%. *Anal.* Calc. for H_2TNβBP: $C_{60}H_{30}Br_8N_4$ (1446.04); C, 49.83; H, 2.09; N, 3.87; Br, 44.20. Found; C, 49.86; H, 2.06; N, 3.82; Br, 44.26%.

2.4. Synthesis of Zn(II) complexes of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakisarylporphyrins

The metallation method employed for all the bromoderivatives was similar to those employed for the nonbrominated ones. However the reaction in this case could be carried out at room temperature. The metal salt was usually $Zn(CH_3COO)_2 \cdot 4H_2O$ and the solvent employed was $CHCl_3/CH_3OH$ mixture (2:1, v/v). In some cases, both acetic acid and sodium acetate were used for buffer action, if found necessary. Purification was carried out by column chromatography after removing the unreacted metal salt. Metallation was confirmed by UV–Vis spectra. Yields were found to be 97–99%. *Anal.* Calc. for ZnTToBP: $C_{48}H_{28}Br_8N_4Zn$ (mol. wt. 1365.29); C, 42.22; H, 2.07; N, 4.10; Br, 46.80. Found: C, 41.94; H, 2.20; N, 4.05, Br, 47.01%. *Anal.* Calc. for ZnTTmBP: $C_{48}H_{28}Br_8N_4Zn$ (mol. wt. 1365.29); C, 42.22; H, 2.07; N, 4.10; Br, 46.80. Found: C, 42.08; H, 2.10; N, 4.03, Br, 46.96%. *Anal.* Calc. for ZnTTpBP: $C_{48}H_{28}Br_8N_4Zn$ (mol. wt. 1365.29); C, 42.22; H, 2.07; N, 4.10; Br, 46.80. Found: C, 42.39; H, 2.01; N, 4.18, Br, 46.56%. *Anal.* Calc. for ZnTNαBP: $C_{60}H_{28}Br_8N_4Zn$ (mol. wt. 1509.43); C, 47.75; H, 1.87; N, 3.71; Br, 42.34. Found: C, 47.36; H, 1.95; N, 3.64, Br, 42.69%. *Anal.* Calc. for ZnTNβBP: $C_{60}H_{28}Br_8N_4Zn$ (mol. wt 1509.43); C, 47.75; H, 1.87; N, 3.71; Br, 42.34. Found: C, 46.88; H, 2.12; N, 3.88, Br, 42.76%.

3. Results and discussion

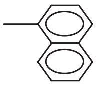
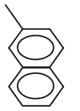
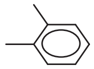
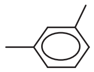
As mentioned in the preparatory section all the porphyrins were purified by column chromatography. The compounds were characterised by elemental analysis, ^{1}H NMR and electronic spectra. The free-base porphyrins and their Zn(II) derivatives prepared are summarised in Table 1, specifying the nature of substituents on **1.** Synthesis of a few of the nonbrominated porphyrins are reported [23–25] but we have considered them here to compare the properties with their brominated forms and also to look into the effect of various *meso* substituents on their overall electronic and redox properties.



1

During the bromination process it was observed that some of the copper porphyrins yielded their bromoderivatives in the metallated form itself while some others were found to be partly or completely demetallated. Almost complete demetallation was observed during the synthesis of H_2TTmBP, H_2TTpBP and H_2TNβBP while in the case of H_2TToBP and H_2TNαBP the parent copper derivatives were found to be resistant towards demetallation during the bromination reaction. This can be attributed to the overall structural disposition of porphyrin system rather than any electronic effects. In all cases we have carried out the demetallation reaction after the bromination processes to assure the complete conversion to free-bases. While carrying out Zn(II) metallation reactions from the free-bases it is seen that among the nonbrominated porphyrins the naphthyl derivatives undergo easier metallation than the tolyl derivatives which could be attributed to the distortional change brought about on the porphyrin ring by the bulkier *meso*-naphthyl groups. One of the significant observations with regard to the metallation of brominated porphyrins is the easier conversion to their metalloderivatives even in mild reaction conditions. While the distortion brought about on the porphyrin π-framework by the bulky naphthyl groups could be one of the factors which facilitate the metallation reaction (as in the case of nonbrominated naphthylporphyrins), the major factor which comes into play for the ease of metallation (in the case of bromoderivatives) can be the concerted electron-withdrawing ability of the eight Br atoms which could make NH protons more acidic. So the deprotonation of the NH protons could be an easy process facilitating the metallation with divalent Zn^{2+}.

Table 1
Substituted free-base porphyrins and their Zn(II) derivatives developed in the study

R	X	M	Porphyrin
	H	2H	H_2TNαHP
	Br	2H	H_2TNαBP
	H	Zn	ZnTNαHP
	Br	Zn	ZnTNαBP
	H	2H	H_2TNβHP
	Br	2H	H_2TNβBP
	H	Zn	ZnTNβHP
	Br	Zn	ZnTNβBP
	H	2H	H_2TToHP
	Br	2H	H_2TToBP
	H	Zn	ZnTToHP
	Br	Zn	ZnTToBP
	H	2H	H_2TTmHP
	Br	2H	H_2TTmBP
	H	Zn	ZnTTmHP
	Br	Zn	ZnTTmBP
	H	2H	H_2TTpHP
	Br	2H	H_2TTpBP
	H	Zn	ZnTTpHP
	Br	Zn	ZnTTpBP

3.1. ^{1}H NMR spectra

^{1}H NMR spectra of the brominated and nonbrominated free-base porphyrins and their Zn(II) derivatives were recorded in $CDCl_3$. The chemical shifts observed are given in Table 2.

All the porphyrins gave reasonably good ^{1}H NMR signals. The integrated intensities of the signals provided complete characterisation of the porphyrins. The complete absence of pyrrole proton resonances and the presence of only $–CH_3$ and *meso*-aryl group resonances in the ^{1}H NMR spectra of bromoporphyrins revealed that all the protons of the pyrrole carbons were substituted with Br atoms. The pyrrolic proton resonances of H_2TToHP are seen to occur in a more shielded region compared to those in other nonbrominated porphyrins. The inevitable steric interaction of *o*-methyl group with the porphyrin π-framework accounts for this. It is seen that the methyl group in H_2TToHP and H_2TToBP appear at low δ compared to their *meta* and *para* analogs. This could be attributed to the nature of disposition of the methyl groups above the porphyrin π-framework in a manner that the methyl proton lies in the shielded region of the magnetic anisotropy. In the *meta*- and *para*-analogs since the methyl groups are located away from the porphyrin π-framework, such a shielding does not occur. Very interestingly, the $–CH_3$ signals of H_2TToHP appear as a multiplet containing four signals at 1.99, 2.03, 2.06 and 2.08 ppm while the *meta* and *para* isomers (H_2TTmHP and H_2TTpHP) give only singlets for the $–CH_3$ groups. This is because of the possibility of having four atropisomers (αααα, αβαβ, ααββ and αααβ) only in the case of the ortho isomer [1,2]. We assign the four $–CH_3$ signals observed to αααα, αβαβ, ααββ and αααβ atropisomers respectively. The same features are observed in its bromo (H_2TToBP) and its Zn(II)derivatives (ZnTToHP and ZnTToBP). Their meta and para analogues give only one singlet for $–CH_3$ protons. The proton resonances of imino hydrogens of octabromotetraarylporphyrins occurred in a appreciably deshielded region of −1.3 to −1.65 ppm relative to that observed for the corresponding nonbrominated free-base porphyrins (−2.65 ppm), consistent with significant

Table 2
^{1}H NMR data of brominated and nonbrominated free-base porphyrins and their Zn(II) derivatives

Porphyrin	δ values (ppm)					
	Pyrrole H	*meso*-aryl protons			Methyl H	Imino H
		ortho	*meta*	*para*		
H_2TToHP	8.63(8H), s		8.03–7.96 (*m*-8H), m	7.69–7.52 (*p*-8H), m	2.08–1.99(12H), m	−2.63(2H), s
H_2TTmHP	8.93(8H), s	8.06(*o*-8H), d		7.68(*p*-8H), s	2.7(12H), s	−2.65(2H), s
H_2TTpHP	8.92(8H), s	8.08(*o*-8H), d	7.54(*m*-8H), d		2.71(12H), s	−2.65(2H), s
H_2TNαHP	8.93(8H), s	7.87–8.72 (28H), m (all naphthyl H's)				−2.59(2H), s
H_2TNβHP	8.84(8H), s	7.69–8.68(28H), m (all naphthyl H's)				−2.57(2H), s
ZnTToHP	8.62(8H), s		8.01–7.95 (*m*-8H), m	7.66–7.52 (*p*-8H), m	−2.07–1.99(12H), m	
ZnTTmHP	8.93(8H), s	8.07(*o*-8H), d		7.65(*p*-8H)	2.7(12H), s	
ZnTTpHP	8.92(8H), s	8.05(*o*-8H), d	7.52(8H), d		2.71(12H), s	
ZnTNαHP	8.92(8H), s	7.52–8.54(28H), m (all naphthyl H's)				
ZnTNβHP	8.83(8H), s	7.68–8.68(28H), m (all naphthyl H's)				
H_2TToBP			7.9(*m*-8H), s	7.69–7.53(8H), m	2.35–2.05(12H), m	−1.4(2H), bs
H_2TTmBP		8.01(*o*-8H), s		7.63(8H), s	2.68(12H), s	−1.65(2H), bs
H_2TTpBP		8.08(*o*-8H), d	7.57(*m*-8H), d	–	2.69(12H), s	−1.66(2H), bs
H_2TNαBP		7.57–8.31(28H),m (all naphthyl H's)				−1.3(2H), bs
H_2TNβBP		7.51–8.72(28H), m (all naphthyl H's)				−1.5(2H), bs
ZnTToBP			7.86(*m*-8H), s	7.67–7.52(*p*-8H), m	2.35–2.04(12H), m	
ZnTTmBP		7.99(*o*-8H), s		7.61(*p*-8H), s	2.68(12H), s	
ZnTTpBP		7.99(*o*-8H), d	7.54(*m*-8H), d		2.7(12H), s	
ZnTNαBP		7.33–8.31(28H), m (all naphthyl H's)				
ZnTNβHP		7.33–8.29(28H), m (all naphthyl H's)				

The chemical shift values are in ppm.

electron-withdrawing effect of eight Br atoms. In all the bromoderivatives the aryl protons are seen to be getting shielded because of the distortion and also due to the presence of electron withdrawing Br atoms at β pyrrole positions which deplete the π electron cloud of the porphyrin. Almost all of the free-base porphyrins and Zn(II) derivatives gave a complex multiplet for the aryl protons. However, the *para* tolyl porphyrins H_2TTpHP and H_2TTpBP showed typical AB pattern for the aryl protons, both in the free-base and metallated forms. In H_2TTpHP the *o*-H of the aryl moiety is seen at 8.08 ppm and *m*-H at 7.54 ppm both with AB type splitting.

3.2. Electronic spectra

The optical spectral data of the nonbrominated and brominated free-base porphyrins and their Zn(II) derivatives are given in Table 3. A perusal of the spectral data indicated the following salient features: (1) The Q bands of all the nonbrominated free-base porphyrins show the four banded etio-type spectrum and have almost the same absorption maxima. (2) The B bands of all the tolylporphyrins also have similar absorption maxima, but in the case of naphthylporphyrins the B band was seen to be appearing at higher wavelength. (3) The absorption spectral features of octabromoderivatives are significantly different from those of nonbrominated compounds, all being highly red shifted. (4) Among the bromoderivatives H_2TTpBP has the most red shifted Q band (λ_{max} 748 nm) while H_2TToBP has the lowest (λ_{max} 724 nm). (5) While the nonbrominated Zn(II) porphyrins have more or less the same B band absorption maxima for all the porphyrin derivatives, the corresponding bromoderivatives show variation depending on the *meso*-substituent.

The similar λ_{max} for the Soret band of all the tolylporphyrins (nonbrominated) indicates that the tolyl groups have no $-CH_3$ position dependent influence on the porphyrin framework. This is expected as the tolyl groups can be considered to lie with almost the same degree of tilt with the porphyrin plane. But the case of naphthylporphyrins is seen to be different. It can be expected that the presence of bigger naphthyl groups bring about more red shift than less bulkier tolyl groups because the ground state of the π bond system would be smaller than the excited state due to weaker bonding in the more deformed naphthyl porphyrin [26]. In addition, since the *meso*-aryl groups are known to lie not totally orthogonal to the porphyrin plane, but slightly tilted, this would make the *meso* group get into some conjugative interaction with the main porphyrin framework. In such a situation, the naphthyl derivatives would have better conjugation than the tolyl derivatives making the former to absorb at higher λ_{max} for the B band of naphthylporphyrins compared to tolylporphyrins. In the case of octabromotetraarylporphyrins the presence of electronegative and bulkier Br atoms at the β-pyrrole positions leads to dramatic changes in their electronic

Table 3
Electronic spectral data of brominated and nonbrominated free-base porphyrins and their Zn(II) derivatives in $CHCl_3$ at 298 K

Porphyrin	B band (nm) $\varepsilon \times 10^{-4}$[a]		Q bands (nm) $\varepsilon \times 10^{-4}$[a]			$\Delta\bar{\nu}$ (cm^{-1})[b]
	B(0,0)	$Q_y(1,0)$	$Q_y(0,0)$	$Q_x(1,0)$	$Q_x(0,0)$	
H_2TToHP	417(44.67)	514(1.74)	546(0.51)	577(0.63)	648(0.32)	
H_2TTmHP	418(42.66)	516(1.62)	551(0.69)	588(0.54)	648(0.33)	
H_2TTpHP	418(45.71)	517(1.69)	551(0.66)	590(0.52)	648(0.30)	
H_2TNαHP	425(43.65)	515(1.62)	550(0.56)	589(0.65)	647(0.34)	
H_2TNβHP	425(44.67)	515(1.66)	550(0.67)	590(0.52)	648(0.35)	
H_2TToBP	466(21.38)		563(1.51)	610(0.79)	724(0.35)	2500
H_2TTmBP	470(21.88)		565(0.89)	631(1.41)	741(0.42)	2600
H_2TTpBP	471(21.88)		568(0.90)	632(1.59)	748(0.43)	2700
H_2TNαBP	474(20.89)		567(1.32)	623(0.81)	734(0.39)	2400
H_2TNβBP	473(21.38)		566(0.90)	629(1.25)	734(0.41)	2380
ZnTToHP	421(39.81)	548(2.24)			587(1.10)	
ZnTTmHP	420(40.74)	549(2.04)			590(1.07)	
ZnTTpHP	420(41.69)	548(2.14)			590(1.05)	
ZnTNαHP	421(40.74)	549(2.09)			589(1.09)	
ZnTNβHP	422(42.66)	550(2.14)			588(1.07)	
ZnTToBP	464(24.55)	594(1.318)			655(1.23)	2200
ZnTTmBP	463(25.70)	595(1.38)			656(1.26)	2210
ZnTTpBP	465(26.30)	593(1.31)			657(1.26)	2304
ZnTNαBP	473(25.70)	594(1.31)			652(1.20)	2611
ZnTNβBP	472(25.12)	593(1.26)			653(1.29)	2510

[a] Molar extinction coefficient ε in $10^{-4}/dm^3\ mol^{-1}\ cm^{-1}$.
[b] $\Delta\bar{\nu} = \bar{\nu}_2 - \bar{\nu}_1$; energy of the B band in cm^{-1} for brominated porphyrin ($\bar{\nu}_1$) and nonbrominated porphyrin ($\bar{\nu}_2$).

spectra compared to their nonbrominated derivatives. This can be explained by looking at the various factors which influence the energies of both HOMO and LUMOs of the porphyrins. As evident, the eight Br substituents at the β-pyrrole positions would drain out electron density from the porphyrin framework which would make it more susceptible to reduction. This amounts to lowering of the LUMOs of the porphyrin ring and consequent reduction in the HOMO–LUMO gap and hence the significant red shift. Coupled with this electronic effect there is also a significant steric factor. The bulky Br atoms at the eight β-positions would bring about major structural distortion within the porphyrin framework as evident from the numerous X-ray data [22,27]. Such a distortion would cause a significant break up in conjugation, the effect of which would be major alteration of π energy levels including destabilisation of the HOMO and some lowering of the LUMO. INDO/s level calculation has testified this [28].

Interestingly, the Q bands of octabromotolylporphyrins (especially *p*- and *m*-) are more red shifted compared to octabromonaphthylporphyrins. This could be explained in terms of the inductive effect that is originating from the electron-donating $–CH_3$ group of the *meso*-tolyl moiety. It is likely that the *meso*-aryl groups can get into some extent of conjugative interaction with the porphyrin framework (by slight tilting), which would make the methyl moiety release an appreciable electron density to the porphyrin unit. The effect of such a +I effect would lift the HOMO, resulting in the reduction of the HOMO–LUMO gap and hence the larger redshift. It is worthwhile to note that among all the brominated porphyrins H_2TTpBP has the Q band, red shifted to maximum. The higher red shift observed in the *para*-derivative is due to the *para* effect of the $–CH_3$ moiety which also accounts for the large spectral shift of the B band between the brominated and nonbrominated *meso*-tetra(*p*-tolyl)porphyrins. Among all the brominated porphyrins the least red shifted compound is H_2TToBP. The major reason for this is attributed to the unavoidable steric repulsion between the $–CH_3$ moiety at the *ortho* position and the bulky Br atom preventing the *meso*-aryl moiety from taking part in conjugative interaction with the macrocyclic π-framework by tilting. As indicated already, octabromoporphyrins have three discernible Q bands in contrast to the four-banded visible spectra of nonbrominated porphyrins. The origin of the four bands is known to be due to vibronic mixing, resulting in the appearance of $Q_y(1,0)$, $Q_y(0,0)$, $Q_x(1,0)$ and $Q_x(0,0)$ positions in the order of decreasing energy and intensity [29,31]. It is noteworthy that in the case of H_2TTmBP, H_2TTpBP and H_2TNβBP the peak in the range 569 nm is a weaker one than the peak at 625 nm. The nature of the peak at 625 nm suggests a possible overlap of the $Q_y(0,0)$ and $Q_x(1,0)$ transitions which is evident from its intensity and broadness. But in the case of H_2TToBP and also in H_2TNαBP the peak near 570 nm was more intense compared to that at 625 nm. This suggests a possible overlap of $Q_y(1,0)$ and $Q_y(0,0)$ bands for these porphyrins. The steric interaction of the bulky α-naphthyl group and *ortho*-methyl group with the Br atoms in the respective porphyrins can be expected to contribute to this.

As expected, Zn(II) porphyrins exhibit characteristic change in the electronic spectra as compared to their free-base porphyrins. It is seen that all the zinc(II) derivatives of nonbrominated porphyrins show more or less the same absorption maxima showing minimal dependency on the nature of the *meso*-substituent. This is especially so for the Soret band. But in the case of zinc(II) derivatives of brominated porphyrins we could see more prominent changes depending upon the *meso*-substituents. All the tolyl substituted Zn(II) bromoporphyrins show almost the same $\lambda_{\max}$ and have similar B and Q bands. However, the naphthyl derivatives have a B band appearing at higher wavelength than that of the tolyl species. The reason why the nonbrominated zinc(II) porphyrins have similar band positions for both tolyl and naphthyl derivatives, while in the bromoderivatives the tolyl and naphthyl species manifest a change could be explained in terms of puckering of the π framework and associated energy level changes. Since all the bromoderivatives have in themselves a strong steric interaction because of the bulky Br atoms on adjacent β pyrrole positions the bulky naphthyl group would cause additional steric disturbance in ZnTNαBP and ZnTNβBP. Since ZnTTBP (*o*-, *m*-, *p*-) have comparatively less bulkier *meso* substituents the steric interaction would not be so severe. As seen from Table 3 both ZnTNαBP and ZnTNβBP show conspicuous red shift in the B band as compared to the tolyl derivatives. As indicated in the case of free-base porphyrins we attribute this red shift to the mesomeric effect and distortion in the conjugative plane of the porphyrin.

3.3. Fluorescence spectra

The fluorescence emission was measured at room temperature in $CHCl_3$ and at a common excitation wavelength of 560 nm for all the compounds. The selection of λ_{ex} was done by overlaying the absorption spectra of all the compounds. Appreciable absorption was seen at 560 nm even for the Zn(II) derivatives of all the porphyrins. Besides, all solutions were adjusted to the appropriate concentrations so that they give the same absorbance at the chosen wavelength. All the quantum yields were calculated relative to the cresyl violet (CV) in EtOH which has a quantum yield of 0.59 [30]. The emission data are presented in Table 4.

Table 4
Fluorescence spectral data of brominated and nonbrominated free-base porphyrins and their Zn(II) derivatives in $CHCl_3$

Porphyrin	Emission peaks λ (nm)		Quantum yield ϕf ($\times 10^2$)
	Q(0, 0)	Q(0, 1)	
H_2TToHP	654	714	0.57
H_2TTmHP	654	717	0.53
H_2TTpHP	654	718	0.68
H_2TNαHP	654	716	0.08
H_2TNβHP	656	720	0.16
ZnTToHP	603	643	0.16
ZnTTmHP	600	649	0.27
ZnTTpHP	605	649	0.36
ZnTNαHP	603	652	0.05
ZnTNβHP	609	655	0.13
H_2TToBP		750	0.0034
H_2TTmBP		784	0.0037
H_2TTpBP		786	0.0040
H_2TNαBP		750	0.0032
H_2TNβBP		757	0.0034
ZnTToBP	654	730	0.11
ZnTTmBP	652	712	0.12
ZnTTpBP	654	732	0.13
ZnTNαBP	660	726	0.11
ZnTNβBP	645	720	0.12

An inspection of the emission data indicates the following: (1) Irrespective of the nature of the *meso*-aryl groups, free-bases of all the nonbrominated porphyrins have almost the same emission maxima. (2) Nonbrominated naphthylporphyrins have lower quantum yield compared to tolylporphyrins. The highest quantum yield is observed for H_2TTpHP and the lowest for H_2TNαHP. (3) In the case of octabromotetraarylporphyrins both Q(0, 0) and Q(0, 1) emission bands are shifted significantly to longer wavelength compared to their nonbrominated species as expected from the shifts observed in their absorption bands. (4) There is a broadening of the emission bands with significant quenching of the fluorescence intensity for all the bromoderivatives leading to a decrease in quantum yield relative to the nonbrominated ones. The nature of the fluorescence emission bands of brominated free-base porphyrins are found to be complex. (5) Both the extent of red shifts and reduction in fluorescence yields are seen to be dependent on the nature of the substituents and it was more significant in the case of bromoporphyrins. (6) Zn(II) derivatives of nonbrominated porphyrins have a lower quantum yield compared to their free-base. (8) In contrast to the above, Zn(II) bromocompounds have a higher quantum yield than their free-base bromoderivatives.

The comparatively large quantum yield and significant red shift in the emission peaks of H_2TTpHP are commensurate with the absorption features of the compounds. All the tolyl derivatives of nonbrominated porphyrins manifest higher ϕf compared to the naphthyl derivatives, essentially due to lesser distortion in the former. We do not see any *meso*-aryl substituent dependency on ϕf in their bromoderivatives for the free-bases. Because of higher non-planarity of all the octabromoporphyrins, their quantum yields are expected to be less compared to the nonbrominated porphyrins which is in agreement with the observed data.

Generally nonbrominated zinc(II) porphyrins are reported to have quantum yields less than the nonbrominated free-base porphyrins [31]. The principal differences between the emission properties of free-base porphyrins and the emission properties of their metalloderivatives arise from: (1) the longer natural radiative life time kf^{-1} which is ~120 ns in the free-base compared to ~60 ns in the metalloderivatives and (2) the absence of any heavy atom effect in the free-base, which should reduce all the rates involved in the conversion from singlet to triplet to a minimum. However in the case of zinc(II) octabromotetraarylporphyrins, it is interesting to see that these porphyrins have a higher quantum yield compared to their corresponding free-base octabromoderivatives. This can be attributed to the fact that the free-base bromoporphyrins exhibit more distortional change due to the eight Br atoms and the general flexible character of the unfused central cavity. In the zinc(II) derivatives of the bromoporphyrins, even though there are heavy Br atom substituents as in the case of the free-bases, the central zinc(II) ion would make the porphyrin framework rigid because of four coordinate bonds and hence less it is distorted. As in the case of free-bases, Zn(II) bromocompounds have significantly red shifted emission bands compared to their nonbrominated forms. The feature is similar to that observed in optical absorption spectra and is caused by the shift noticed in both B and Q absorption bands for the species. It is seen that the presence of electron-withdrawing groups on pyrroles and nonplanarity of the porphyrins resulted in red shift of emission bands with reduction in intensity. As expected the nonbrominated zinc(II) compounds have higher quantum yields compared to their brominated ones. The heavy atom halogen substituents are known to quench fluorescence. The observed changes in photophysical properties of the porphyrins can be explained in terms of the simple spin–orbit coupling theory [32]. In accordance with the classical spin orbit coupling theory, incorporation of a halogen atom into the pyrrole ring is accompanied by a significant decrease in quantum yield and lifetime. The main effect of halogenation is in facilitating an intersystem crossing.

3.4. Electrochemical properties

Cyclic voltammetric properties of all the free-base porphyrins and their Zn(II) derivatives have been carried out to probe the effect of the various substituents in them. The measurements were carried out in CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBAF) as the supporting electrolyte. The cell assembly consists of a Pt button working electrode, Ag/AgCl as the reference electrode and Pt wire as the working electrode. The potentials were referenced to an internal ferrocene/ferrocenium redox couple. We find two oxidation steps for nonbrominated porphyrins with $E_{1/2}$ in the range of 0.97–1.08 V for the first and around 1.28 V for the second oxidation steps. A closer look at the data indicates that compared to $H_2TN\alpha HP$ and H_2TToHP the free-bases H_2TTmHP, H_2TTpHP and $H_2TN\beta HP$ undergo easier oxidation. We attribute this essentially to the possibility of having a moderate degree of conjugative interaction possible by tilt of the *meso*-aryl moieties in the latter category of porphyrins compared to the former. The Zn(II) derivatives of all these nonbrominated porphyrins also exhibit their characteristic oxidation features. We find that the Zn(II) metallation facilitates easier oxidation compared to their free base porphyrins which is expected from the modulating ability of this d^{10} ion.

As in the case of nonbrominated free-base porphyrins their brominated forms manifest two oxidation processes whose $E_{1/2}$ values are in the ranges of 0.97–1.12 V (for the I oxidation) and 1.35–1.38 (for the II oxidation). These values are at more positive potential than that of their corresponding nonbrominated derivatives. This indicates harder oxidation for all the brominated porphyrins. The electrochemical data obtained for oxidation and reduction of the octabromoderivatives are consolidated in Table 5. The ΔE_p values (ranging from 120 to 220 mV) indicate that almost all the oxidation steps are quasi-reversible in nature. There are two major factors which determine the magnitude of $E_{1/2}$ of the oxidation steps of the perbrominated porphyrins. They are the electron depleting ability of the Br atoms from the π-framework and the effect of distortion brought about by bulky Br substituents on the energy level ordering of the filled π orbitals. It has been shown by INDO/s calculations that puckering (to saddle type form) destabilises the π system of the macrocycle in such a way that the HOMO gets lifted in energy [28]. If this is the only factor that is operating, the oxidation of bromoporphyrins would have been easier. Our observation showing harder oxidation for the bromoporphyrins (which is contrary to the expected direction) indicates that this factor has only a minimal role in the $E_{1/2}$

Table 5
Oxidation–reduction features of free-base octabromoporphyrins and their Zn(II) derivatives (V against Ag/AgCl)

Porphyrin	$E_{1/2}$		
	I oxidation (V)	II oxidation (V)	I reduction (V)
H_2TToBP	1.07	1.37	−1.02
H_2TTmBP	0.99	1.36	−1.04
H_2TTpBP	0.97	1.35	−1.03
$H_2TN\beta BP$	1.03	1.36	−1.05
$H_2TN\alpha BP$	1.13	1.38	−0.98
ZnTToBP	0.88	1.11	−0.94
ZnTTmBP	0.85	1.08	−1.03
ZnTTpBP	0.83	1.10	−1.04
ZnTNβBP	0.86	1.09	−0.96
ZnTNαBP	0.92	1.15	−0.89

variation noticed. Accordingly, we attribute harder oxidation of these porphyrins to the cumulative electron withdrawing ability of the eight Br atoms which is significant in nature and enough to offset the effect due to distortion that would lower the HOMO level. It has been generally known that the nature and extent of porphyrin frame distortion is determined more by the bulkiness of the β substituents than the nature of the *meso*-aryl moieties [22,28]. This is expected because all the eight Br atoms are on adjacent β carbons while the aryl moieties are on the four *meso* positions which can stay orthogonal to the macrocycle plane avoiding any steric interaction. So we can tacitly assume that the extent of distortion is the same in all the octabromoporphyrins under study. The variation observed in the $E_{1/2}$ values for the octabromoderivatives for the oxidation step which are positive compared to the corresponding nonbrominated porphyrins can, therefore, be essentially due to the effect of various *meso*-aryl groups which can conjugatively interact with the macrocyclic π-framework to varying degrees depending on their nature, by adjusting their relative orientations. Among the brominated free-base porphyrins we find that the H_2TTpBP is the easiest to oxidise and H_2TNαBP the hardest. As H_2TTpBP and H_2TTmBP will have a lower rotation barrier for the *meso*-aryl moieties [25], the tolyl groups in them can have a better conjugative interaction than H_2TToBP making the oxidation of the former two porphyrins easier, which is in agreement with the experimental data. The higher $E_{1/2}$ observed for H_2TNαBP is indicative of the expected less conjugative interaction of the α-naphthyl moieties because of its steric constraints.

The second oxidation potential has almost the same $E_{1/2}$ values for the brominated free-base porphyrins as their nonbrominated analogues indicating that removal of the second electron from the porphyrin cation radical is independent of the *meso*-substituent in both categories of porphyrins. For the Zn(II) bromoderivatives we also find a two-step oxidation processes. The $E_{1/2}$ values for these are in the ranges of 0.83–0.92 V for the I oxidation and 1.08–1.15 V for the II oxidation. Just as in the case of nonbrominated porphyrins the metallation of the bromoderivatives by Zn(II) is seen to make the oxidation of the π system easier. The trend in $E_{1/2}$ seen for various *meso*-aryl forms is found to be similar to their corresponding nonbrominated analogues. The difference noticed among themselves was, however, very marginal. The electrochemical reduction of all the porphyrins were carried out in the range from 0 to −1.5 V at a constant scan rate of 100 mV/s. The reduction features for all the brominated derivatives are summarised again in Table 5.

It is seen that the reduction features are poorly manifested in voltammograms. Varying the scan rates also did not seem to improve the CV features. A two-step reduction is seen in most cases but some of them are found to be irreversible. The quasi-reversible reduction processes have ΔE_p values in the range 90–200 mV. The nonbrominated free-base porphyrins have the $E_{1/2}$ values around −1.22 V but in the case of brominated porphyrins the first reduction step occurs at a more positive potential indicating easier reduction for the latter. It is known that the saddle type distortion would lower the energy of the LUMO while lifting that of the HOMO level. Besides this distortion dependent lowering, the LUMO would get lowered further in energy because of the electronegative nature of the Br atoms. Consequently the reduction would get highly facilitated which is very much in agreement with the experimental data. While the free-bases of tolyl substituted octabromoporphyrins have almost similar $E_{1/2}$ values for the reduction, H_2TNαBP is seen to undergo easier reduction. The metallation of bromoporphyrins with Zn(II) does not seem to affect the $E_{1/2}$ of the reduction processes significantly as all the redox processes are porphyrin-centered. The trend observed in $E_{1/2}$ for the Zn(II) derivatives is also seen to be the same as that for the free-bases of the bromporphyrins.

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