Covalently linked bisporphyrins bearing tetraphenylporphyrin and perbromoporphyrin units: Synthesis and their properties

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Abstract. A series of covalently linked bisporphyrins bearing *meso*-tetraphenylporphyrin (TPP) and octabromotetraphenylporphyrin (OBTPP) units have been synthesised and characterised. Electrochemical studies on these bisporphyrins showed an anodic shift (~ 30–60 mV) of the TPP unit and a cathodic shift (~ 40–80 mV) of OBTPP in redox potentials. Further, steady-state fluorescence studies on bisporphyrins indicated dramatic decrease in fluorescence quantum yields of the TPP moiety. Electrochemical redox and fluorescence data seem to suggest the possible existence of intramolecular interactions in these bisporphyrins.

Keywords. Bisporphyrins; brominated porphyrins; electrochemical redox; fluorescence studies.

1. Introduction

Bisporphyrins are of continued interest owing to their use as model compounds for energy and electron-transfer processes.[1–7] Notably, these have been employed as catalysts[8] and molecular hosts[9–11] for the selective encapsulation of guest molecules. Various groups have reported a wide variety of bisporphyrins with varying degree of fluxionality between the porphyrin units.[12–14] Direct conjugation between the porphyrin units in these systems showed interesting physico-chemical properties.[15] The majority of the bisporphyrins employed thus far bear similar porphyrin units. Syntheses of bisporphyrin with dissimilar units have been reported with interesting properties.[16–19]

Many perhaloporphyrins have been reported in the literature with unusual physico-chemical properties.[20] Furthermore, the high-valent metal complexes of perhaloporphyrins serve as robust catalysts for the oxidation of alkenes or alkanes in presence of oxygen donors.[21] The higher stability of metalloperhaloporphyrin catalysts is attributed to the stabilisation of the highest occupied molecular orbitals influenced by the inductive effect of the halogen substituents. Introduction of halogens at the meso-

phenyl groups in one of the porphyrin entities of the bisporphyrins shows interesting physico-chemical properties.[17,18] Bisporphyrins with perfluoroporphyrin and tetraphenylporphyrin shows electron transfer reactions.[19] Bisporphyrins with porphyrin and un-brominated porphyrin have been largely unexamined. The anodic shift of the reduction potentials and the large red-shifted absorption spectral features of perbrominated porphyrins could serve as acceptors for electron and energy transfer reactions.

In this article, we present the synthesis of bisporphyrins with meso-tetraphenylporphyrin (TPP) and octabromotetraphenylporphyrin (OBTPP), covalently linked through one of the meta or para-phenyl positions. The lengths and positions of the linkages (*m* or *p*) have been varied to probe the extent of interaction in these bisporphyrins. These compounds also display interesting physico-chemical properties.

2. Experimental section

2.1 *Materials*

The free base porphyrins, H_2TPP[22] and H_2OBTPP[23] were synthesized using the literature methods. Metal acetates, zinc (II) acetate dihydrate and copper (II) acetate monohydrate were procured from CDH, India and used as received. Aluminium oxide (neu-

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tral and basic) procured from Acmes (India) was used as received. 2,2-dibromodiethyl ether was prepared using the reported procedure.[24] All the solvents employed were purified prior to use by standard procedures.[25]

2.2 *Instrumentation*

Electronic absorption spectra were recorded on a Hitachi model U-3400 and Jasco V-530 UV-Visible absorption spectrophotometers using matched quartz cells of 1 cm path length at ambient temperature. The ^{1}H NMR spectra of samples were performed on a Bruker WH-270 MHz FT-NMR spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard at 298 K. Steady-state fluorescence measurements were carried out on a model MPF 44A, 650-60 fluorescence spectrophotometer in quartz cells of 10 mm path length at ambient temperature. Cyclic voltammetric measurements were performed on a BAS 100A electrochemical analyzer equipped with a video meter and an XY recorder. The electrochemical cell consists of three electrodes, Ag/AgCl as reference, platinum wire as counter and platinum button as the working electrode. All the measurements were carried out in CH_2Cl_2 medium using 0·1 M tetrabutylammonium perchlorate as the supporting electrolyte. Porphyrin concentrations were maintained at 0·5 mM. All the solutions were purged with argon gas prior to electrochemical measurements and all the experiments were performed at room temperature.

2.3 *Methods*

The steady-state fluorescence spectra of the compounds were measured in CH_2Cl_2 at room temperature. The excitation wavelengths were kept at 515 and 417 nm of the unbrominated porphyrin (H_2TPP) unit. H_2OBTPP and ZnOBTPP absorb at the emission wavelength of the corresponding unbrominated porphyrin. The absorption correction was made by using the reported procedure.[26] Unbrominated MTPPs ($M = 2H$, Zn (II)) was employed as the reference standard. The singlet emission quantum yields (ϕ_f) of the bisporphyrins were calculated according to the literature method.[27]

$$(\phi_f)_s = (OD_r \times A_s \times \phi_{f(r)}]/(OD_s \times A_r), \qquad (1)$$

where ϕ_f refers to fluorescence quantum yield and subscripts r and s indicate the reference and sample

respectively. The area under the fluorescence band envelope is designated as A and OD indicates the absorbance value at the excitation wavelength, kept at 0·05 to 0·1. All the ϕ_f values obtained from Soret excitation wavelengths are similar to those obtained from 515 or 550 nm excitation wavelengths.

2.4 *Synthesis of bisporphyrins*

The precursor compounds 5-(3′ or 4′-hydroxyphenyl)-10,15,20-tetraphenylporphyrin, *m* or *p*-$H_2TPP(OH)$[28,29] and their 5-(3′ or 4′-(2-bromoethoxy/bisethylene-oxyphenyl))-10, 15, 20-triphenylporphyrin, *m* or *p*-H_2TPP-1-Br and *m*-H_2TPP-2-Br were synthesised using the reported procedures.[30]

2.4a *Synthesis of 2,3,7,8,12,13,17,18-octabromo-5-(3′ or 4′-(2-bromoethoxy phenyl)-10,15,20-triphenyl-porphyrin, m or p-H_2OBTPP-1-Br:* The perbrominated mono-functionalised free-base tetraphenylporphyrin was synthesised by the bromination reaction of the corresponding Cu (II) complex of the substituted porphyrin followed by acid demetallation reaction.

Cu (II) complex of the *m* or *p*-H_2TPP-1-Br was synthesised using the literature procedure[31], and the yield of the product being almost quantitative. Bromination of the *m* or *p*-$CuTPP$-1-Br was carried out using reported procedure with slight modifications.[23] The typical procedure for the synthesis of *m* or *p*-$CuOBTPP$-1-Br is as follows: Liquid bromine (0·6 ml, 11·6 mmol) in 25 ml of $CHCl_3$ is added dropwise to a stirred solution of *m* or *p*-$CuTPP$-1-Br (0·25 g, 0·31 mmol) in 100 ml of $CHCl_3$ over a period of 30 min at room temperature. The reaction mixture is stirred for 4 h. Then pyridine (1·5 ml) in 40 ml of $CHCl_3$ is added dropwise for 30 min. the solution is stirred for a further period of 12 h. Further, the reaction mixture is treated with 20% aqueous sodium metabisulphite solution. The organic layer is dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The green product is chromatographed on a silica gel column using $CHCl_3$ as the eluant. The yield of the product is about 0·36 g (70%).

The demetallation reaction is performed by the addition of conc. H_2SO_4 (0·5 ml) to a solution of *m* or *p*-$CuOBTPP$-**1**-Br (0·10 g, 0·07 mmol) in 50 ml of $CHCl_3$. The reaction mixture is then stirred for 30 min. It is cooled in an ice bath and 100 ml of distilled H_2O is added slowly. The organic layer is

separated and washed with saturated $NaHCO_3$ (50 ml) twice and dried over anhydrous Na_2SO_4. The organic layer is concentrated and chromatographed on to a silica gel column using $CHCl_3$ as the eluant. The yield of the product is about 0·90 g (90%). *m*-H_2OBTPP-**1**-Br: δ_H (270 MHz, $CDCl_3$, TMS): 8·20 (*m*, 6H, triphenyl H_o), 7·77 (*m*, 9H, triphenyl $H_{m,p}$), 7·47 (*m*, 4H, substituted phenyl-H), 4.56 (*t*, 2H, OCH_2), 3·81 (*t*, 2H, CH_2Br), −1·56 (*bs*, 2H, N–H). UV-visible spectrum of *m*-H_2OBTPP-1-Br in CH_2Cl_2, nm (logε): 367 (4·87), 469 (5·30), 589 (4·16), 625 (4·12), 742 (3·97). *p*-H_2OBTPP-1-Br: δ_H (270 MHz, $CDCl_3$, TMS): 8·21 (*m*, 6H, triphenyl H_o), 7·77 (*m*, 9H, triphenyl $H_{m,p}$), 7·33 (*d*, 2H, substituted phenyl H_m), 8·12 (*d*, 2H, substituted phenyl H_o), 4·58 (*t*, 2H, OCH_2), 3·84 (*t*, 2H, CH_2Br), −1·57 (*bs*, 2H, N–H). UV-visible in CH_2Cl_2 (logε): 364 (4·80), 469 (5·20), 586 (4·26), 623 (4·22), 741 (3·96).

2.4b *Synthesis of 2,3,7,8,12,13,17,18-octabromo-5-(3′ or 4′-(2-bromo bisethylene oxyphenyl)-10,15, 20-triphenylporphyrin, m-H₂OBTPP-2-Br:*

This was prepared by the condensation of digol dibromide with *m*-H_2TPP(OH) using the literature method.[30] Further, the metallation of this derivative with Cu (II) followed by bromination of CuTPP-2-Br complex was carried out using the method described earlier (Yield: 65%). Its free-base derivative, H_2OBTPP-2-Br is obtained by adopting acid demetallation procedure as described above. The yield of the product is 90%. δ_H (270 MHz, $CDCl_3$, TMS): 8·07 (*m*, 6H, triphenyl H_o), 7·75 (*m*, 9H, triphenyl H_m), 7·57 (*m*, 4H, substituted phenyl-H), 4·42 (*t*, 2H, phenyl–O–CH_2), 4·01 (*m*, 4H, –CH_2–O–CH_2–), 3·61 (*t*, 2H, –CH_2Br), −1·55 (*bs*, 2H, N–H). UV-visible in CH_2Cl_2 (logε): 366 (4·75), 467 (5·25), 587 (4·30), 622 (4·25), 742 (3·93).

2.4c *Synthesis of ethoxy-bridged free base bisporphyrins:*

To a solution of dry DMF (100 ml) containing *m* or *p*-H_2TPP(OH) (0·10 g, 16 mmol) and *m* or *p*-H_2OBTPP-**1**-Br (0·22 g, 0·16 mmol), 0·5 g of anhydrous K_2CO_3 is added. The reaction mixture is stirred under anhydrous conditions at room temperature for 36 h. At the end of this period, the reaction mixture is filtered to remove K_2CO_3. The solvent, DMF, is evaporated under reduced pressure and chromatographed on an alumina column using $CHCl_3$/C_6H_{12} (1 : 3, *v/v*) solvent mixture as the eluant. The unreacted *m* or *p*-H_2OBTPP-**1**-Br is collected as the

first fraction followed by the desired free-base bisporphyrin, *m* or *p*-H_2TPP-1-H_2OBTPP. The yield of the product is 0·16 g (50%). *p*-H_2TPP–1–H_2OBTPP: δ_H (270 MHz, $CDCl_3$, TMS): 8·85 (*m*, 8H, β-H), 8·21 (*m*, 16H, phenyl H_o), 7·77 (*m*, 18H, phenyl $H_{m,p}$), 7·45 (*m*, 4H, bridging phenyl-H_m), 4·77 (*s*, 4H, bridging C_2H_4), −2·75 (*s*, 2H, N–H), −1·65 (*bs*, 2H, N–H). Elemental analysis calcd. for $C_{90}H_{54}N_8O_2Br_8$: C, 56·40; H, 2·73; N, 5·85%. Found: C, 56·10; H, 2·58; N, 5·93%. FAB mass spectrum (*m/z*): 1919·10 [$(M + H)^+$, 100%], 1839·20 [$(M + H)^+$ − Br, 11%]. *m*-H_2TPP-**1**-H_2OBTPP: δ_H (270 MHz, $CDCl_3$, TMS): 8·87 (*m*, 8H, β-H), 8·20 (*m*, 16H, phenyl H_o), 7·75 (*m*, 18H, phenyl $H_{m,p}$), 7·45 (*m*, 4H, bridging phenyl-$H_{m,p}$), 4·75 (*s*, 4H, bridging C_2H_4), −2·80 (*s*, 2H, N–H), −1·65 (*bs*, 2H, N–H). Elemental analysis calcd. for $C_{90}H_{54}N_8O_2Br_8$: C, 56·34; H, 2·84; N, 5·84%. Found: C, 56·10; H, 2·58; N, 5·93%.
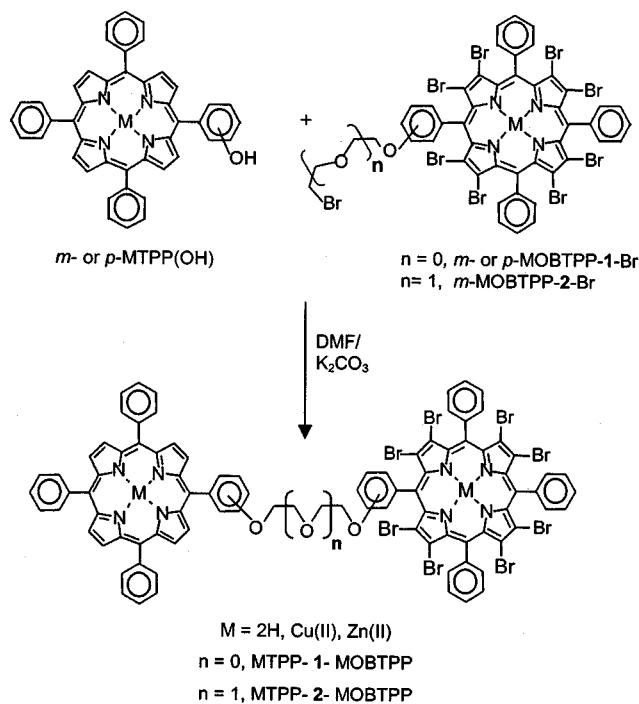
2.4d *Synthesis of metallated bisporphyrins, m or p-MTPP-1-MOBTPP (M = Zn (II), Cu (II)):*

Metal complexes of the bisporphyrins are prepared using the appropriate metal carrier. A typical procedure for the synthesis of the metallation reaction is as follows: Metal acetate (0·10 g) in 15 ml of methanol is added to a stirred solution of free-base porphyrin in $CHCl_3$ (0·10 g, 0·052 mmol), and the reaction mixture was stirred at ambient temperature for 30 min. The solvent is removed by distillation and the residue thus obtained is dissolved in $CHCl_3$ and washed with distilled water. Bimetallic bisporphyrins are obtained by silica gel column chromatography using $CHCl_3$ as the eluant. The yield of the product is almost quantitative. *m*-CuTPP–1–CuOBTPP: FAB mass spectrum (*m/z*): 2041·8 [$(M + H)^+$, 100%], 1963·9 [$(M + H)^+$ –Br, 10%]. *m*-ZnTPP–1–ZnOBTPP: δ_H (270 MHz, $CDCl_3$, TMS) 8·91 (*m*, 8H, β-H), 8·09 (*m*, 16H, phenyl H_o), 7·69 (*m*, 22H, phenyl $H_{m,p}$), 4·58 (*s*, 4H, bridging C_2H_4).

2.4e *Synthesis of bisethylene oxide bridged bisporphyrins, (m-H₂TPP-2-H₂OBTPP):*

Free-base bisporphyrin bearing bisethylene oxide spacer group is prepared by the condensation of *m*-H_2TPP(OH) with the functionalised brominated *m*-H_2OBTPP-2-Br using the procedure employed for the synthesis of ethylene oxide-bridged bisporphyrins with slight modifications. The product is purified by alumina column using cyclohexane/chloroform (1 : 6, *v/v*) solvent mixture as the eluant. The yield of the prod-

uct is about 45%. Elemental analysis calcd for $C_{92}H_{58}N_8O_3Br_8$: C, 56·30; H, 2·98; N, 5·71%. Found: C, 55·96, H, 2·82, N, 5·55%. FAB mass spectrum (m/z): 1963·6 [$(M + H)^+$, 100%)], 1883·5 [$(M + H)^+$ −Br, 9%]. δ_H (270 MHz, CDCl$_3$, TMS): 8·85 (m, 8H, β-H), 8·18 (m, 16H, phenyl H$_o$), 7·67 (m, 18H, phenyl H$_{m,p}$), 7·40 (m, 4H, bridging phenyl H$_{m,p}$), 4·43 [s, 4H, (ph–O–CH$_2$)$_2$)], 4·12 (s, 4H, (–CH$_2$–O–CH$_2$–)), −2·81 (s, 2H, N–H), −1·65 (bs, 2H, N-H). m-MTPP-2-MOBTPP (M = Cu (II) and Zn (II)) is prepared using the procedure employed for the synthesis of ethylene oxide-bridged porphyrins. The yield of the porphyrin is almost quantitative. m-ZnTPP-**2**-ZnOBTPP: ^{1}H NMR in CDCl$_3$: 8·88 (m, 8H, β-pyrrole-H), 8·08 (m, 16H, phenyl-o-H), 7·63 (m, 18H, phenyl H$_{m,p}$), 7·40 (m, 4H, bridging phenyl H$_{m,p}$), 4·11 [s, 4H, (ph–O–CH$_2$)$_2$)], 3·73 [s, 4H, (–CH$_2$–O–CH$_2$–)]. m-CuTPP-2-CuOBTPP: FAB mass spectrum (m/z): 2085·8 (($M + H)^+$, 100%), 2006·6 [$(M + H)^+$−Br, 9%].

3. Results and discussion

Bisporphyrins were synthesized as described in scheme 1. They are crystalline in nature and soluble in a variety of organic solvents. Integrity of the bisporphyrins was checked by UV-visible, ^{1}H NMR,

mass spectroscopies and also by elemental analysis. Optical absorption spectra of bisporphyrins were examined to probe the extent of intramolecular interactions in these bisporphyrins. Electronic absorption spectra of a representative bisporphyrins are shown in figure 1. A comparison is made with the absorption spectra of 1:1 synthetic mixtures of the individual components. Absorption spectral data of the bisporphyrins are shown in table 1. Bisporphyrins reveal characteristic Soret bands around 460–475 nm arising from the OBTPP moiety and in the range 410–425 nm region for unbrominated porphyrin TPP. It can be seen from the figure that ab-
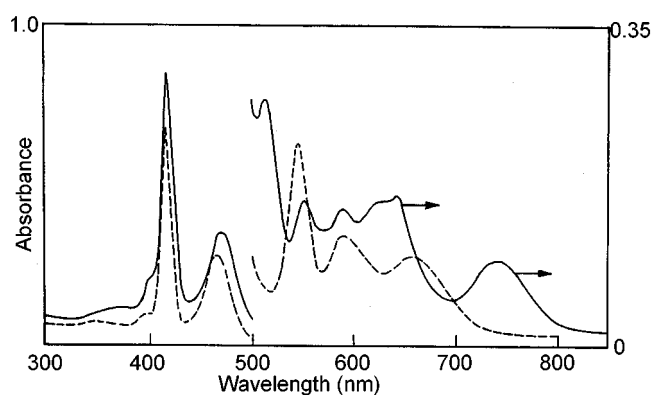
Figure 1. Electronic absorption spectra of m-H$_2$TPP-2-H$_2$OBTPP (——) and m-ZnTPP-2-ZnOBTPP (----) in CH$_2$Cl$_2$ at 298 K. Arrows indicate the absorbance for magnified Q bands on the y-axis.

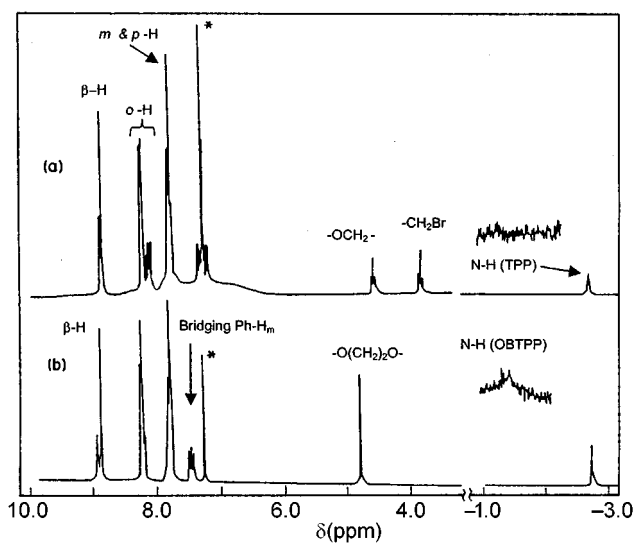**Figure 2.** ^{1}H NMR spectrum of (**a**) 1:1 synthetic mixture of p-H$_2$TPP(OH) and p-H$_2$OBTPP-1-Br and (**b**) bisporphyrin p-H$_2$TPP-1-H$_2$OBTPP in CDCl$_3$ at 298 K. *Denotes the solvent peak.

Scheme 1. Synthetic route for bisporphyrins.

Table 1. Electronic absorption spectral data[a,b] of bisporphyrins in CH_2Cl_2 at 298 K.

Compound	*B* bands (nm)	*Q* bands (nm)
m-H$_2$TPP-1-H$_2$OBTPP	357 (4·65), 418 (5·68) 469 (5·3)	514 (4·38), 550 (4·17) 589 (4·15), 629 (*sh*) 644 (4·01), 739 (3·92)
m-CuTPP-1-CuOBTPP	361 (4·72), 415 (5·75) 449 (*sh*), 465 (5·17)	538 (4·44), 579 (4·34) 623 (3·86)
m-ZnTPP-1-ZnOBTPP	352 (4·78), 419 (5·80) 470 (5·17)	548 (4·42), 594 (4·13) 664 (4·13)
p-H$_2$TPP-1-H$_2$OBTPP	376 (4·76), 419 (5·68) 472 (5·31)	514 (4·39), 551 (4·19) 590 (4·13), 628 (*sh*) 644 (4·24), 748 (3·94)
p-CuTPP-1-CuOBTPP	364 (4·65), 416 (5·73) 450 (*sh*), 469 (5·22)	539 (4·46), 581 (4·30) 625 (3·94)
p-ZnTPP-1-ZnOBTPP	351 (4·69), 420 (5·80) 471 (5·48)	549 (4·45), 592 (4·16) 667 (4·18)
m-H$_2$TPP-2-H$_2$OBTPP	372 (4·85), 418 (5·72) 469 (5·33)	513 (4·42), 551 (4·18) 631 (*sh*), 642 (4·20)
m-CuTPP-2-CuOBTPP	363 (4·75), 415 (5·73) 446 (*sh*), 466 (5·17)	538 (4·42), 579 (4·30) 624 (*sh*)
m-ZnTPP-2-ZnOBTPP	351 (4·78), 419 (5·74) 468 (5·36)	548 (4·34), 591 (4·07) 658 (3·98)
1 : 1, H$_2$OBTPP/H$_2$TPP	367 (4·87), 417 (5·68) 469 (5·30)	514 (4·38), 550 (4·19) 589 (4·16), 629 (*sh*) 644 (4·23), 742 (3·97)
1 : 1, CuOBTPP/CuTPP	360 (4·71), 415 (5·75) 448 (*sh*), 464 (5·16)	538 (4·47), 579 (4·31) 623 (3·92)
1 : 1, ZnOBTPP/ZnTPP	353 (4·74), 419 (5·81) 466 (5·40)	548 (4·43), 590 (4·17) 655 (4·05)

[a]Values in parentheses refer to log ε; [b]error in $\lambda_{max} = \pm 1\cdot0$ nm

sorption bands in the visible region (500–800 nm) overlap considerably. The position of the absorption spectral bands of the bisporphyrins bears close resemblance to the spectra obtained for 1 : 1 synthetic mixtures with comparable molar absorption coefficients. A variation in position of the attachment (para or meta) or the length of the linkage group (ethylene oxide and bisethylene oxide) in these bisporphyrins do not show any significant differences in their absorption spectral features.

^{1}H NMR spectra of the bisporphyrins are very useful in characterization of the compounds. Figure 2 shows the ^{1}H NMR spectrum of bisporphyrin *p*-H$_2$TPP-1-H$_2$OBTPP along with that of the synthetic mixture of the monomeric entities. The bisporphyrins exhibit proton resonances characteristic of β-pyrrole, unsubstituted meso-phenyl groups, sub-

stituted meso-phenyl and bridging alkyl ether protons. The integrated intensities of the proton resonances have been useful in identifying the number of protons in the respective bisporphyrins. In the case of bisporphyrins, the imino protons resonate around –1·65 ppm, characteristic of brominated porphyrin, while the resonance at –2·80 ppm arises from the unbrominated porphyrin unit. The presence of covalent linkages in the bisporphyrin systems is shown by comparison of the ^{1}H NMR spectra of the bisporphyrins with that of the 1 : 1 synthetic mixture of the constituents. It can be seen that the ether protons in the intermolecular mixtures resonate as two triplets centred at 3·73 ppm (CH$_2$Br) and 4·48 ppm (OCH$_2$) (*J* ~ 4 Hz) in the *p*-H$_2$OBTPP-1-Br compound while it appears as a singlet at 4·77 ppm in the bisporphyrin (*p*-H$_2$TPP-1-H$_2$OBTPP) owing to

the symmetric disposition of the ethylene oxide protons between the porphyrin units. The dimetallic bisporphyrin, *p* or *m*-ZnTPP-1-ZnOBTPP shows resonances not significantly different from those of the free-base bisporphyrin except for the absence of the imino proton resonances. The bisethylene oxide-bridged bisporphyrin, *m*-H$_2$TPP-2-H$_2$OBTPP shows resonances quite similar to that the *m*-H$_2$TPP-1-H$_2$OBTPP complex with two singlets for the bridging bisethylene oxide group at 4·43 ppm (–O–CH$_2$) and 4·12 ppm (CH$_2$–O–CH$_2$) groups, whereas the synthetic mixture shows two triplets at 4·42 ppm (OCH$_2$) and 3·77 ppm (CH$_2$Br), and a multiplet centred at 4·01 ppm (–CH$_2$–O–CH$_2$–). The ^{1}H NMR spectrum of the bisporphyrins does not show direct evidence for the existence of any strong intramolecular interactions in bisporphyrins.

Cyclic voltammetric studies were performed to determine the electrochemical redox potentials of bisporphyrins to examine the possible presence of intermolecular interactions. A representative voltammogram of *m*-CuTPP-1-CuOBTPP is shown in figure 3 and the data of all the bisporphyrins are summarised in table 2. The majority of the bisporphyrins exhibit reversible potentials involve a one-electron process. In some cases, the potentials overlap with one another and the differential pulse voltammetry is indicative of more than one electron transfer process. Under similar conditions, the redox
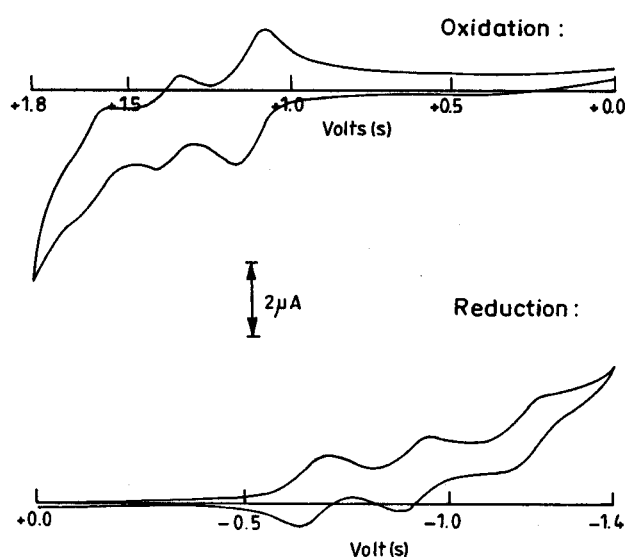

Figure 3. Cyclic voltammograms of *m*-CuTPP-1-CuOBTPP in CH$_2$Cl$_2$ with 0·1 M TBAHFP at 298 K with a scan rate of 100 mV/s.

potentials of the 1 : 1 synthetic mixtures of TPP and OBTPP were also determined and are listed in table 2. The observed redox data of the individual porphyrins (TPPs[32] and OBTPPs[23]) are fairly similar to that of the literature values. It is reported earlier that the MOBTPPs show a marginal anodic shift of the oxidation potentials with a substantial anodic shift in the reduction potentials of the ring-centred redox potentials relative to that of the corresponding MTPPs. The intramolecular interactions in these bisporphyrins would shift redox potentials cathodically for OBTPP centre while it is anodic shift in redox potentials for MTPPs. It can be seen from the data that generally in bisporphyrins, the first redox potentials of OBTPP are shifted cathodically by 40–80 mV, while that of TPP moieties show an anodic shift (30–60 mV). In some cases, especially for the di-zinc bisporphyrins, the oxidation potentials overlap considerably due to the close proximity of the potentials. The cathodic shift of redox potentials of OBTPP and the anodic shift of TPP potentials indicate minimal intramolecular interactions in these bisporphyrins.

In order to probe the possible existence of intramolecular electron or energy transfer (singlet–singlet) reactions in these bisporphyrins, steady state fluorescence spectra were obtained in CH$_2$Cl$_2$. A typical fluorescence spectrum of bisporphyrin is shown in figure 4. The fluorescence spectra of bisporphyrins are compared with the spectra of the corresponding 1 : 1 synthetic mixture of their constituents. For all the compounds, the excitation wavelength was kept at 419 nm. For comparison, fluorescence quantum yields of the TPP derivatives (H$_2$TPP and ZnTPP) were also determined and are listed in table 3. Observed data for MTPPs (M = 2H, Zn (II)) are similar to reported values.[33] The singlet emission bands of H$_2$TPP (651, 714 nm) overlap considerably with the absorption spectra of H$_2$OBTPP (626, 743 nm). Similarly, the emission bands of ZnTPP (596, 646 nm) overlap with the absorption spectra of ZnOBTPP (594, 656 nm). It can be seen that the positions of the emission bands of bisporphyrins are not altered significantly. However, the values of the quantum yields decrease dramatically relative to those of their 1 : 1 synthetic mixtures. Quantum yields of the synthetic mixtures (H$_2$TPP/H$_2$OBTPP and ZnTPP/ZnOBTPP) show a marginal decrease relative to the corresponding H$_2$TPP and ZnTPP units. The unbrominated porphyrin (TPP) unit is expected to act as a donor, while the brominated

Table 2. Half-wave potentials[a] (vs Ag/AgCl, V) of bisporphyrins in CH_2Cl_2 using 0·1 M $TBAPF_6$ as the supporting electrolyte at 298 K.

Bisporphyrin	Oxidation				Reduction			
	I	II	III	IV	I	II	III	IV
m-H$_2$TPP-1-H$_2$OBTPP	1·05[b]	1·18	1·40[b]	–	–0·62	–1·04	–1·40	–
m-ZnTPP-1-ZnOBTPP	0·93	1·19	–	–	–0·86	–1·36[b]	–	–
m-CuTPP-1-CuOBTPP	1·17[b]	1·42	1·63	–	–0·63	–0·88	–1·14	–1·53[c]
m-H$_2$TPP-2-H$_2$OBTPP	1·08[b]	1·19	1·40	–	–0·57	–1·01	–1·33	–
m-ZnTPP-2-ZnOBTPP	0·94	1·21	–	–	–0·92	–1·23	–1·41	–
m-CuTPP-2-CuOBTPP	1·17	1·37	1·58	–	–0·67	–0·91	–1·18	–1·52[c]
p-ZnTPP-1-ZnOBTPP	0·98	1·25	–	–	–0·91	–1·30	–1·65	–
p-CuTPP-1-CuOBTPP	1·10	1·40	1·62	–	–0·63	–0·90	–1·03	–1·40
1 : 1, H$_2$TPP/H$_2$OBTPP	1·00	1·14	1·35	–	–0·57	–0·92	–1·10	–1·35
1 : 1, ZnTPP/ZnOBTPP	0·81	0·96	1·19	–	–0·93	–1·33	–	–
1 : 1, CuTPP/CuOBTPP	1·01	1·35	1·55	–	–0·59	–0·85	–1·09	–1·59[c]

[a]Error ± 15 mV; [b]quasireversible; [c]data from differential pulse voltammetry
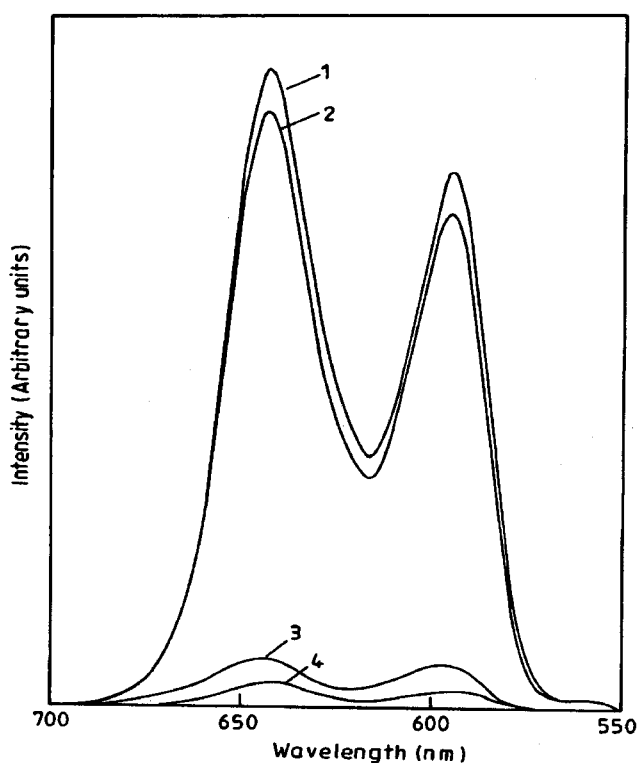

Figure 4. Fluorescence spectra of (1) ZnTPP, (2) 1 : 1 synthetic mixture of ZnTPP and ZnOBTPP, (3) *m*-ZnTPP-2-ZnOBTPP and (4) *m*-ZnTPP-1-ZnOBTPP in CH_2Cl_2 at 298 K. The excitation wavelength is at 419 nm.

Table 3. Steady-state singlet emission data of bisporphyrins in CH_2Cl_2 at 298 K.

Compound	λ_{em} (nm)	ϕ_f[a]	η_{ss}
m-H$_2$TPP-1-H$_2$OBTPP	652, 713	0·0019	98·52
m-ZnTPP-1-ZnOBTPP	596, 645	0·0007	99·80
p-H$_2$TPP-1-H$_2$OBTPP	650, 715	0·0032	97·60
p-ZnTPP-1-ZnOBTPP	598, 644	0·0027	91·88
m-H$_2$TPP-2-H$_2$OBTPP	651, 716	0·0015	98·82
m-ZnTPP-2-ZnOBTPP	597, 646	0·0011	96·72
H$_2$TPP/H$_2$OBTPP	652, 715	0·124	
ZnTPP/ZnOBTPP	597, 645	0·029	
H$_2$TPP	651, 714	0·130	
ZnTPP	596, 646	0·033	

[a]Uncertainty in values, ± 8%

H_2OBTPP) and H_2TPP respectively. An examination of the data in table 3 shows that the singlet emission of the TPP entity is quenched very efficiently in all the bisporphyrins and less so, if the two units are mixed intermolecularly. Interestingly, the emission spectrum of the TPP overlaps with the absorption spectrum of the OBTPP indicative of the possible existence of energy transfer from the TPP unit to the non-radiative OBTPP unit.

The electron transfer process from the donor (TPP) to acceptor (OBTPP) can be calculated from the expression, $\Delta G_{et} = E_{ct} - E_s$ where ΔG_{et} represents the free-energy change accompanied by the excited state electron transfer process in bisporphyrins. E_{ct} is the energy of the charge transfer state calculated from the difference between the first oxidation and first reduction potentials of TPP and OBTPP units respectively. E_s refers to the energy of the singlet-

porphyrin acts as an acceptor. Steady-state fluorescence quantum yields obtained in this study permit us to calculate[34] the efficiency of quenching, $\eta_{ss} = (1 - \phi_{DA}/\phi_D) \times 100$ where ϕ_{DA} and ϕ_D are the quantum yields of the bisporphyrin (*m* or *p*-H$_2$TPP–1–

excited state of the TPP entity. The electrochemical redox data shown in table 2 indicate that the ΔG_{et} is exergonic. The fluorescence spectrum of the bisporphyrins may afford a large local concentration of the brominated porphyrin in the neighbourhood of the unbrominated porphyrin (H_2TPP or ZnTPP) resulting in the possible efficient quenching of fluorescence of the unbrominated TPP entity.

4. Summary

Synthesis and characterization of a new class of bisporphyrins, bearing electron-deficient (OBTPP) and electron-rich (TPP) units have been presented. The electrochemical redox properties of free-base and bimetallic complexes of bisporphyrins show weak intramolecular interactions. Steady-state singlet emission studies on the bisporphyrins show a dramatic decrease in quantum yields with high efficiency of singlet-state quenching of the TPP unit in the bisporphyrins. Electrochemical redox and fluorescence studies show possible intramolecular interactions in these bisporphyrins.

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