

Spectroscopic studies on monomers and dimers of thiaporphyrins

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Abstract. Synthesis and spectroscopic properties of porphyrin macrocycles with sulphur as the heteroatom in the porphyrin core have been studied. Electronic absorption spectra of these macrocycles show porphyrin-like behaviour with a strong Soret band and weak *Q*-bands. Substitution of the -NH groups of tetraphenylporphyrin (TPPH₂) by sulphur causes a red shift of all the absorption bands and the magnitude of the red shift depends on the number of sulphur atoms substituted. Both the mono and dications of dithiaporphyrins (S₂TPP) show larger bathochromic shifts of *Q*-bands relative to TPPH₂ indicating a stronger resonance interaction with the phenyl groups. A positive shift for both oxidation and reduction potentials is observed upon substitution of sulphur atoms. ¹H NMR spectra of symmetrically substituted dithiaporphyrins show two sharp singlets for pyrrole protons and thiophene protons confirming the presence of a two-fold axis of symmetry. Only monothia derivatives (STPPH) form metal complexes [Ni(II), Cu(II)] and these metal complexes are five-coordinate with an apical chloride ligand.

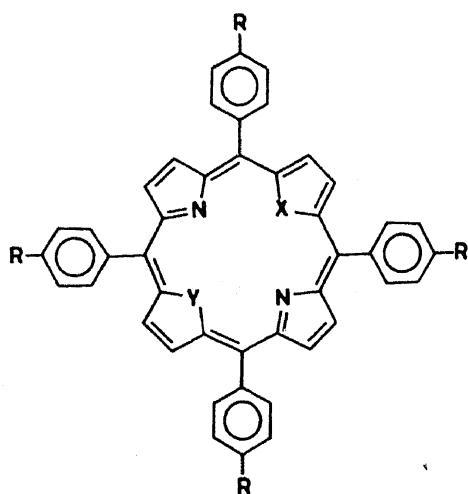
The water-soluble S₂TPPS, prepared from sulphonating the para positions of phenyl rings shows extensive aggregation at high concentrations (> 10⁻⁴ M). At low concentrations (≈ 10⁻⁶-10⁻⁷ M), dimerisation can be induced by the addition of cations (K⁺, NH₄⁺) and cation-crown ether complex. The induced red shifts upon dimerisation parallel findings reported for a variety of cofacial covalently linked porphyrin dimers.

Keywords. Thiaporphyrins; mono and dications and dimers; porphyrin macrocycles.

1. Introduction

Studies on the modifications of the porphyrin core by replacing one or more central nitrogens by other hetero atoms (S, O, Se) are receiving attention in recent years because of the interest in them as new complexing agents as well as their catalytic properties (Broadhurst *et al* 1971; Ulman and Manassen 1975; Ulman *et al* 1978; Hill *et al* 1982; Yamashita *et al* 1982; Vogel *et al* 1988). Recent X-ray studies by Grazynski *et al* (1987, 1989) on some of these systems have thrown light on the coordination abilities of the thiophene moiety, the geometric constraints imposed by the macrocycle as well as the multiplicity of possibilities (S-bound, C-bound or η⁵-bound) available for metal/thiophene coordination. Here we present the results of our systematic studies on the synthesis, characterization and spectroscopic properties of mono- and disubstituted porphyrins having sulphur as the heteroatom (figure 1). The water-soluble dithia tetra(*p*-sulphonatophenyl) porphyrin has been prepared for the first time and its spectroscopic properties are reported. Electronic and fluorescence spectral methods have been used to characterise the different thiaporphyrins and their

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1. X = S ; Y = NH ; R = H STPPH
2. X = S ; Y = S ; R = H S₂TPP
3. X = S ; Y = S ; R = CH₃ (CH₃)₄ S₂TPP
4. X = S ; Y = S ; R = OCH₃ (OCH₃)₄ S₂TPP
5. X = S ; Y = S ; R = SO₃[⊖] S₂TPPS

Figure 1. Structure of thiaporphyrins.

mono- and dications. NMR studies have been useful in arriving at the structures of thiaporphyrins while ESR studies are helpful in studying the metal coordination. Cyclic voltammetry has been used to follow the redox chemistry of the dithiaporphyrins.

2. Experimental

2.1 Synthesis of 2,5-bis (phenyl hydroxymethyl) thiophene

To a solution of N, N, N, N-tetramethyl ethylenediamine (6.906 g, 59.425 mmol, 9 ml) in hexane (90 ml), *n*-butyl lithium (3.806 g, 59.425 mmol, 37.1 ml) was added followed by thiophene (2 g, 23.7 mmol, 1.9 ml). The reaction mixture was stirred at room temperature for an hour and later refluxed for two hours. The reaction mixture was then allowed to attain room temperature. Benzaldehyde (6.2 g, 59.425 mmol, 6 ml) in THF (25 ml) was added dropwise to the ice-cooled reaction flask. After addition was over the reaction mixture was allowed to attain room temperature, saturated ammonium chloride solution was added and it was then extracted with ether or chloroform (50 ml × 3). The organic layers were combined and washed with brine and dried over anhydrous Na₂SO₄. The crude product, obtained on evaporation of the solvent was purified by flash chromatography over silica gel (ethyl acetate: petroleum ether 60–80°C, 4:6) and afforded the pure diol as a pale yellow solid (6.125 g, 87%), m.p.: 135°C.

IR (KBr) : 3320, 3080, 3050, 2910, 1605, 1495, 1455, 1200, 1040, 1020, 970 cm⁻¹.

¹H NMR (CDCl₃) : 1.17 (s, 2H), 5.14 (s, 2H), 6.06 (s, 2H), 6.75 (m, 10H).

This synthesis is as per the procedure of Ulman and Manassen (1975).

2.2 Synthesis of 2,5-bis (*p*-toluylhydroxy methyl) thiophene

Thiophene (2.0 g, 23.7 mmol, 1.9 ml), N, N, N, N-tetramethyl ethylenediamine (6.906 g, 59.425 mmol, 9 ml), and *p*-tolualdehyde (7.14 g, 59.425 mmol, 7 ml) under similar

reaction conditions as above (§2.1) afforded 2,5-bis(*p*-toluylhydroxy methyl) thiophene (6.263 g, 81.5%), m.p.: 83–85°C.

IR (KBr) : 3350, 3055, 2925, 1605, 1515, 1265, 1040, 1025, 1010 cm^{-1} .

$^1\text{H NMR}$ (CDCl_3) : 1.94 (*brs*, 2H), 2.35 (*s*, 6H), 5.90 (*s*, 2H), 6.68 (*s*, 2H), 7.2 (*q*, 8H).

2.3 Synthesis of 2,5-bis (*p*-anisyl hydroxymethyl) thiophene

Thiophene (2.0 g, 23.7 mmol, 1.9 ml) *N,N,N,N*-tetramethyl ethylenediamine (6.906 g, 59.425 mmol, 9 ml) and *p*-anisaldehyde (8.1 g, 59.425 mmol, 7.2 ml) under similar reaction conditions (see §2.1) afforded 2,5-bis(*p*-anisyl hydroxymethyl) thiophene (5.9 g, 70%), m.p. 152–4°C (lit. m.p.: 154°C, Ulman and Manassen 1979).

IR (KBr) : 3345, 3020, 2965, 2855, 1615, 1515, 1255, 1035, 1005 cm^{-1} .

$^1\text{H NMR}$ (CDCl_3) : 1.83 (*brs*, 2H), 3.84 (*s*, 6H), 5.94 (*s*, 2H), 6.71 (*s*, 2H), 6.87 (*d*, 4H, $J_{\text{AB}} = 8.3 \text{ Hz}$), 7.36 (*d*, 4H, $J_{\text{AB}} = 8.3 \text{ Hz}$).

2.4. Preparation of STPPH

2,5-bis(phenylhydroxymethyl) thiophene (0.7 g, 2.365 mmol), pyrrole (0.475 g, 7.095 mmol) and benzaldehyde (0.5 g, 2.365 mmol) were dissolved in freshly distilled propionic acid (250 ml). The reaction mixture was refluxed for an hour and left at room temperature for 24 h. The solvent was removed under reduced pressure. The crude product was dissolved in chloroform and washed with 25% ammonia solution followed by water and dried over anhydrous sodium sulphate. The solvent was removed and the crude product was purified by column chromatography over basic alumina (19:1, CCl_4 : CHCl_3 as eluent). The first fraction obtained was free TPPH₂ (pink), followed by STPPH (yellow) and traces of S₂TPP. Yield 4.5%. It was recrystallised from chloroform:*n*-hexane. (Grazynski *et al* 1987).

2.5 General procedure for the preparation of dithiatetraphenyl porphyrins

Substituted 2,5-bis(phenyl hydroxymethyl) thiophene (6 g, 20.3 mmol) and pyrrole (1.36 g, 20.3 mmol, 1.41 ml) were dissolved in freshly distilled propionic acid (500 ml) containing acetic anhydride 2% v/v. The reaction mixture was refluxed for an hour. When the reaction mixture attained room temperature, the solvent was removed under reduced pressure. The crude product so obtained was dissolved in chloroform and washed successively with 25% ammonia solution, water and dried over anhydrous sodium sulphate. The crude product obtained on evaporation of the solvent was purified by column chromatography over basic alumina (1:3, chloroform: benzene as eluent) to obtain S₂TPP (10%). The solid obtained was recrystallised from chloroform:*n*-hexane. (Ulman and Manassen 1975). $(\text{CH}_3)_4\text{S}_2\text{TPP}$: 10% yield; $(\text{OCH}_3)_4\text{S}_2\text{TPP}$: 10% yield.

Electronic absorption spectra were recorded with a Shimadzu-UV 160 spectrophotometer. $^1\text{H NMR}$ spectra were taken on a Bruker WP-80 spectrometer using TMS as an internal standard. Fluorescence spectra were recorded on a Spex Ramalog system with Spex photon counting and Spectra Physics Model 165 Ar laser (514.5 nm) as the excitation source. ESR measurements were made on a Varian E-109 spectrometer at liquid nitrogen temperature. Cyclic voltammetric experiments were conducted on a PAR Model 370 polarographic analyser utilizing the three electrode

configuration of a Pt (BAS) as the working electrode, a Pt mesh counter electrode, and a commercially available saturated calomel electrode (SCE) as the reference electrode. In RE 0074 Model X-Y recorder was used to record the current-voltage output. Half-wave potentials were measured as the average of the cathodic and anodic peak potentials.

3. Results and discussion

The electronic spectral data of different thiaporphyrins and their corresponding mono and dications are listed in table 1. For comparison the data of free base tetraphenylporphyrin (TPPH₂) and its dication are also included (Ulman and Manassen 1975). The observed effects upon substitution of nitrogen by sulphur are: (i) a red shift of the Soret band relative to TPPH₂, the magnitude of which depends on the number of pyrrole nitrogens replaced as well as on the parasubstituent of the phenyl ring, (ii) a red shift of the *Q*-bands; *Q*-bands I and II experience a larger shift relative to *Q*-bands III and IV, (iii) a large reduction in intensity of the Soret bands relative to free base TPP indicating a decrease in aromaticity, and (iv) the change in intensity pattern of *Q*-bands in which *Q*I is more intense than *Q*II in all thiaporphyrins. It is clear from table 1 that for all the thiaporphyrins the near UV Soret band is very strong and the visible *Q*-bands are one or two orders of magnitude less intense than the Soret band. These experimental results are in qualitative agreement with the predictions based on Gouterman's (1978) four-orbital model. According to the four-orbital model the Soret band can be assigned to excitation from the ground state to the *E* state and the *Q*-bands to the transitions to the *B* states in the porphyrin. The observed red shift of the Soret band and the *Q*-bands of thiaporphyrins relative

Table 1. Electronic spectral data of thiaporphyrins and their mono- and dications in CHCl₃.

Porphyrin	Soret band λ Max(nm)($\epsilon \times 10^{-4}$)	<i>Q</i> -bands, λ Max(nm)($\epsilon \times 10^{-3}$)			
		IV	III	II	I
S ₂ TPP	435(25)	514(26)	547(7.0)	633(2.2)	696(4.5)
S ₂ TPPH ⁺	449(14.4)		598(5.8)		697(7.0)
S ₂ TPPH ₂ ²⁺	463(28)		697(31.5)		735(29.7)
(CH ₃) ₄ S ₂ TPP	437(27)	516(26)	550(8.9)	634(1.9)	698(5.5)
(CH ₃) ₄ S ₂ TPPH ⁺	459(18)		609(11.8)		708(15.0)
(CH ₃) ₄ S ₂ TPPH ₂ ²⁺	468(26.5)		722(41.4)		760(40.2)
(OCH ₃) ₄ S ₂ TPP	440(25.1)	518(20.8)	555(11.3)	639(1.6)	703(5.8)
(OCH ₃) ₄ S ₂ TPPH ⁺	474(16)		772(36.7)		
(OCH ₃) ₄ S ₂ TPPH ₂ ²⁺	472(14.4)		783(55.7)		
STPPH	429(18.7)	513(17.1)	547(4.4)	618(1.9)	675(3.0)
^b STPPH ₃ ²⁺	456(19.0)		699(24)		
^c TPPH ₂	419(46.4)	515(18.7)	548(8.6)	592(5.5)	647(3.9)
^c TPPH ₂ ⁺	448(43.6)		608(9.0)		659(50.9)

^a Mono- and dications are generated by titrating a dilute solution of TFA in CHCl₃;

^b Monocation could not be generated in this case in CHCl₃;

^c Data taken from Ulman and Manassen (1975)

to TPPH₂ indicate the changes in the energy levels of *E* and *B* states upon substitution of sulphur. The sulphur atom being larger in size, the size of the porphyrin core is reduced and in disubstituted thiaporphyrins this decreased core size can induce bonding interaction between the two sulphur atoms (Abraham *et al* 1984). Indeed the MO energy calculations by Gouterman and coworkers on thiaporphyrins clearly provides evidence for the presence of bonding interactions between the heteroatoms, thus altering the energy levels of the porphyrin (Gouterman 1978; Hill *et al* 1982). Thus the observed red shifts can be accounted for in terms of changes in the energy levels of porphyrin upon substitution of sulphur.

The absorption spectra of (CH₃)₄S₂TPP and its mono- and dications generated by careful titration of dilute solutions of trifluoroacetic acid in CHCl₃ is shown in figure 2. The data for other thiaporphyrins are included in table 1. It was not possible to generate the monocation of STPPH in CHCl₃ probably due to very close pK values of mono- and dications. It is seen from the figure that upon protonation the four-banded *Q*-band structure is changed to a simple two-banded pattern. It was found that in all the dithiaporphyrins the absorption maxima of monocations are red-shifted relative to the neutral species and the formation of dications results in a further red shift of the *Q*-bands. A similar effect was observed for TPPH₂ and its dication derivative. It was shown by Stone and Fleischer (1968) that the red shift of the Soret and *Q*-bands observed in the formation of dications of TPPH₂ is due to greater resonance interaction with the phenyl groups with extension of conjugation in the dications. This was possible because of the reduced steric hindrance between the porphyrin plane and the phenyl rings in the dication, since the presence of two extra protons on nitrogens tilts the pyrrole rings out of the molecular plane. It can be expected that similar steric interactions are present in the thiaporphyrins because of similarities in the structures of the macrocycles. Also the magnitudes of the red shifts observed in the thiaporphyrins upon protonation is much larger (the *QI* band shifts 12 nm in TPPH₂ while the same band shifts 39, 62 and 80 nm for S₂TPP, (CH₃)₄S₂TPP and (OCH₃)₄S₂TPP, respectively, as compared to that in tetraphenylporphyrin indicating an increased resonance interaction with the phenyl groups. However, the magnitude of the red shift observed for the Soret band upon protonation

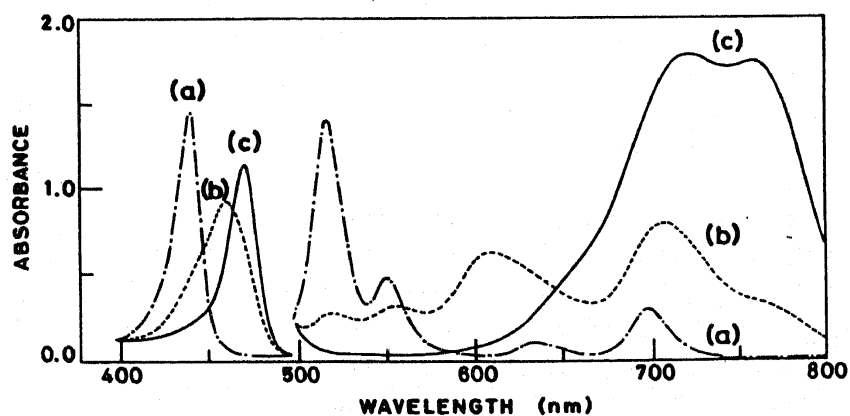


Figure 2. Electronic spectra of (a) (CH₃)₄S₂TPP, (b) (CH₃)₄S₂TPPH⁺, and (c) (CH₃)₄S₂TPPH₂²⁺ in CHCl₃. Concentrations for the *Q*-bands $\approx 10^{-5}$ M and for the Soret band $\approx 10^{-6}$ M.

Table 2. Emission data of the thiaporphyrins in CHCl_3 .

Porphyrin	$Q(0,0)$ (nm)	$Q(0,1)$ (nm)	τ^a (ns)
STPPH	678	760	
S_2TPP	706	781	$1.30 + 0.05$
$(\text{CH}_3)_4\text{S}_2\text{TPP}$	712	790	
$(\text{OCH}_3)_4\text{S}_2\text{TPP}$	720	—	
H_2TPP^b	652	718	$9.5 + 0.5$

^aFrom Hill *et al* (1982); ^bFrom Quimby and Longo (1975)

in TPPH_2 and thiaporphyrins remains more or less constant: (29 nm for TPPH_2 , 27, 31 and 32 nm for S_2TPP , $(\text{CH}_3)_4\text{S}_2\text{TPP}$ and $(\text{OCH}_3)_4\text{S}_2\text{TPP}$, respectively). Thus, one must await X-ray structural studies on the dication of thiaporphyrin to prove the presence of greater resonance interaction with the phenyl groups.

The room temperature fluorescence spectral data of free base thiaporphyrins are listed in table 2. The fluorescence spectra were recorded using the Argon laser (514.5 nm) by exciting the Q_{IV} absorption band at 515 nm. Comparison of the data in the table indicates: (i) a decrease in fluorescence life-time upon going from H_2TPP to S_2TPP , (ii) both the $Q(0,0)$ and $Q(0,1)$ (Ner and Alder 1975; Quimby and Longo 1975) bands of thiaporphyrins are red-shifted relative to free base TPPH_2 . The magnitude of these red shifts is directly proportional to the number of sulphur atoms present in the porphyrin core. The para-substituents on the phenyl rings of S_2TPP seem to have a significant effect on the red shift of the emission bands. This observation is in marked contrast to what is observed for para-substituted TPPH_2 derivatives. Substitution of phenyl rings of TPPH_2 at the para-position by methyl, fluoro, chloro and bromo ligands hardly shifts the emission bands. This lack of interaction between the "para phenyl" substituents and the porphyrin π -system was attributed to the large dihedral angle between the planes of the phenyl and porphyrin systems (Ner and Alder 1975; Quimby and Longo 1975). Ortho substitution on the other hand significantly reduced the intensity of the $Q(0,0)$ band. The observed red shifts of the emission bands upon para-substitution in the present study probably indicate a weak interaction between the para substituent and the porphyrin plane thereby indicating a decreased dihedral angle between the phenyl rings and the porphyrin plane.

Redox chemistry of thiaporphyrins was followed by cyclic voltammetry. Typical cyclic voltograms of $(\text{CH}_3)_4\text{S}_2\text{TPP}$ and $(\text{OCH}_3)_4\text{S}_2\text{TPP}$ in methylene chloride are shown in figure 3. Both S_2TPP and $(\text{CH}_3)_4\text{S}_2\text{TPP}$ show one peak for the oxidation and two peaks for the reduction process. Further oxidation was accompanied by decomposition in these two cases. However in the case of $(\text{OCH}_3)_4\text{S}_2\text{TPP}$ the second oxidation was achieved in the potential range scanned. The monosulphur derivative $(\text{CH}_3)_4\text{STPPH}$ showed only one oxidation and one reduction peak and the electron transfer process is reversible (Lisowski 1989). Table 3 lists all the half-wave potentials for the oxidation and reduction processes of thiaporphyrins along with the data for TPPH_2 . The oxidation reduction processes observed in the present study did not show the characteristics (Weissberger and Rossiter 1971) (anodic-cathodic peak separation and the ratio of peak currents) of reversible electron transfer. An inspection of table 3 indicates the following effects upon replacement of NH by a sulphur atom: (i) a slight positive shift of the oxidation potentials relative to TPPH_2 indicating that

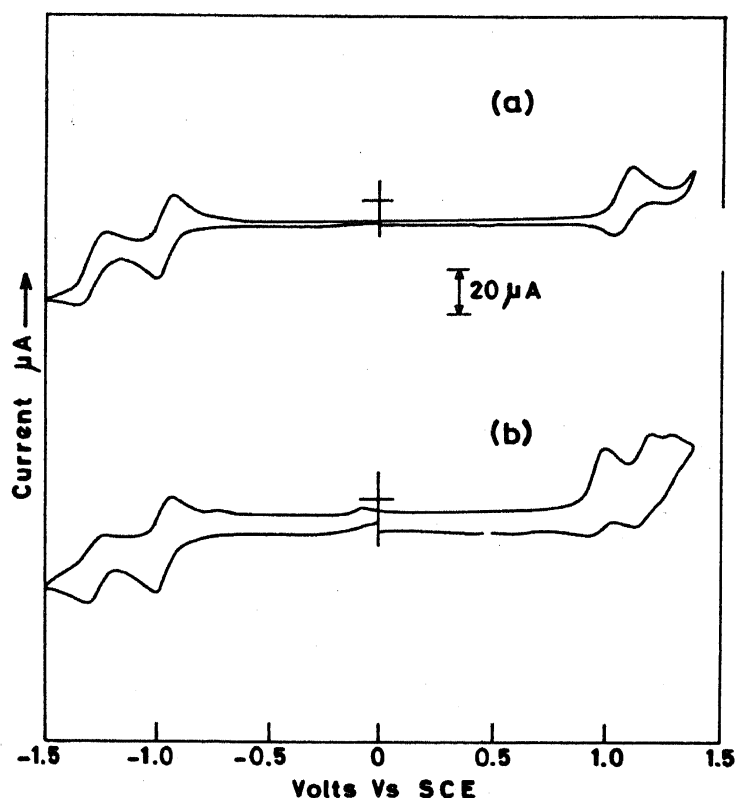


Figure 3. Cyclic voltammogram of (a) $(\text{CH}_3)_4\text{S}_2\text{TPP}$, and (b) $(\text{OCH}_3)_4\text{S}_2\text{TPP}$, in CH_2Cl_2 and 0.1 M TBAP. The scan rate for (a) is 50 mV/s and for (b) is 100 mV/s. The concentration of porphyrin used is $\approx 10^{-3}$ M.

Table 3. Half-wave potentials of thiaporphyrins in CH_2Cl_2 ($E_{1/2}$ in V vs SCE).

Porphyrin	I Ox.*	II Ox.	I Red.	II Red.	Δ redox
S_2TPP	1.17	—	-0.94	-1.23	2.11
$(\text{CH}_3)_4\text{S}_2\text{TPP}$	1.09	—	-0.95	-1.27	2.04
$(\text{OCH}_3)_4\text{S}_2\text{TPP}$	0.98	1.17	-0.97	-1.28	1.95
$(\text{CH}_3)_4\text{STPPH}^b$	1.035	—	-1.065	—	2.10
TPPH_2	1.03	—	-1.23	-1.55	2.26

Δ redox = $E_{1/2}(\text{I ox}) - E_{1/2}(\text{I red.})$;

*Data from Kadish and Morrison (1976); ^bData from Lisowski *et al* (1989);

*Ox - oxidation; Red - reduction.

the thiaporphyrins are harder to oxidise with the exception of $(\text{OCH}_3)_4\text{S}_2\text{TPP}$, (ii) a slight positive shift of both the reduction potentials indicating the ease of reduction relative to TPPH_2 , (iii) electron-donating groups at the para positions of the phenyl rings of S_2TPP shift the oxidation potentials to less positive values while slightly more negative shifts are observed for reduction potentials exactly in contrast to what is observed for TPPH_2 (Kadish and Morrison 1976, 1977), (iv) a linear decrease of Δ redox upon the substitution of a sulphur atom. These shifts in the $E_{1/2}$ values of thiaporphyrins indicate the changes in the energies of HOMO and LUMO. Indeed

Kadish *et al* (1976) have shown that in heterosubstituted porphyrins, both the HOMO and LUMO are stabilised by different mechanisms. An inductive effect suggested for the stabilisation of LUMO accounts for the observed positive shifts of reduction potential while participation of the *d*-orbitals of the sulphur atom was found to stabilise the HOMO resulting in bonding interactions between sulphur atoms. This accounts for the positive shift observed for the oxidation potential.

The ^1H NMR spectra of thiaporphyrins were recorded in CDCl_3 and the dications were generated by addition of appropriate amounts of TFA to the CDCl_3 solution. Figure 4 shows the ^1H NMR spectra of $(\text{CH}_3)_4\text{S}_2\text{TPP}$ and its dication derivative. All the proton chemical shifts and coupling constants are collected in table 4. The proton NMR spectra of all the dithiaporphyrins show two sharp singlets for the pyrrole and the thiophene protons. The phenyl protons in unsubstituted S_2TPP (Ulman and Manassen 1979) appear as two multiplets centered around 8.26 and 7.84 ppm due to ortho, meta and para protons respectively. The phenyl protons in para-substituted S_2TPP appear as an AB system. The appearance of two sharp singlets for the thiophene and pyrrole protons indicate that the presence of a two-fold axis of symmetry in dithiaporphyrins is in accordance with the structure. A comparison of the chemical shifts of both the pyrrole and the phenyl protons of TPPH_2 with that of the dithiaporphyrin indicates only marginal changes upon substitution of sulphur atoms.

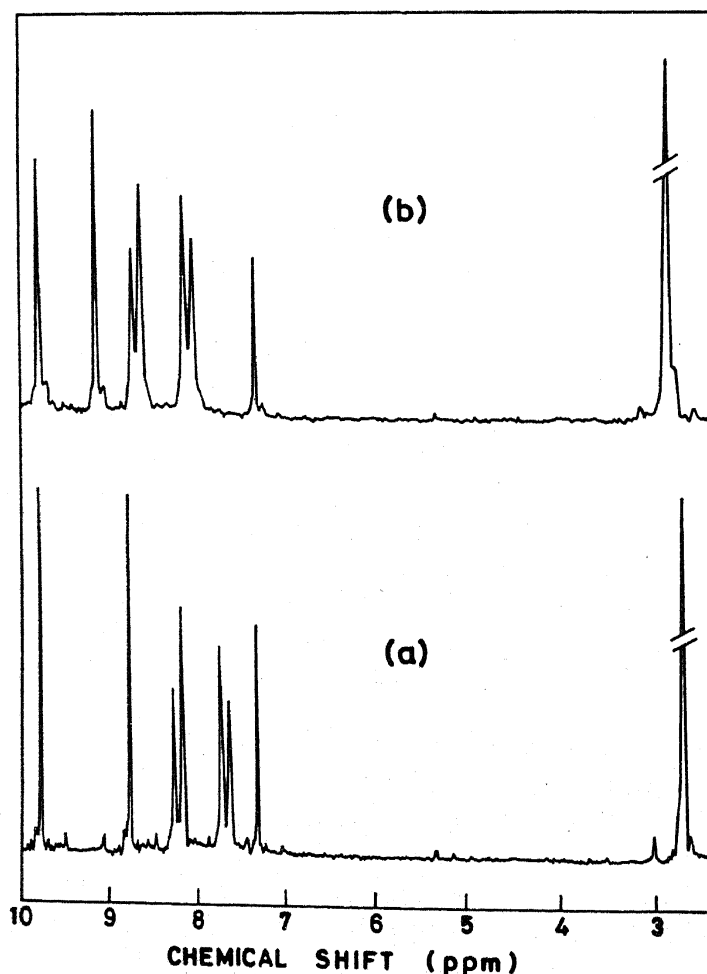


Figure 4. ^1H NMR spectra of (a) $(\text{CH}_3)_4\text{S}_2\text{TPP}$, and (b) $(\text{CH}_3)_4\text{S}_2\text{TPPH}_2^+$, in CDCl_3 .

Table 4. ^1H NMR of thiaporphyrins and their dications* in CDCl_3 .

Porphyrin	Pyrrole	Thiophene	Phenyl		p-Substituent
S_2TPP	8.69(s)	9.61(s)	8.26(o)(M)	7.84(m, p)(M)	—
$\text{S}_2\text{TPPH}_2^+$	9.08(s)	9.74(s)	8.64(o)(M)	8.16(m, p)(M)	—
$(\text{CH}_3)_4\text{S}_2\text{TPP}$	8.78(s)	9.80(s)	8.23(o)d	7.68(m)d	2.75(s)
			$J_{\text{AB}} 7.5 \text{ Hz}$	$J_{\text{AB}} 7.5 \text{ Hz}$	
$(\text{CH}_3)_4\text{S}_2\text{TPPH}_2^+$	9.13(s)	9.77(s)	8.64(o)d	8.05(m)d	2.91(s)
			$J_{\text{AB}} 8.8 \text{ Hz}$	$J_{\text{AB}} 8.8 \text{ Hz}$	
$(\text{OCH}_3)_4\text{S}_2\text{TPP}$	8.72(s)	9.72(s)	8.21(o, d)	7.42(m, d)	4.12(s)
			$J_{\text{AB}} 8.8 \text{ Hz}$	$J_{\text{AB}} 8.8 \text{ Hz}$	
$(\text{OCH}_3)_4\text{S}_2\text{TPPH}_2^+$	8.95(s)	9.58(s)	8.68(o, d)	7.76(m, d)	4.31(s)
			$J_{\text{AB}} 8.8 \text{ Hz}$	$J_{\text{AB}} 8.8 \text{ Hz}$	
TPPH_2^a	8.72(s)	—	8.30(o, M)	7.80(m, p, M)	
TPPH_4^+	8.67(s)	—	8.59(o, M)	8.01(m, p, M)	

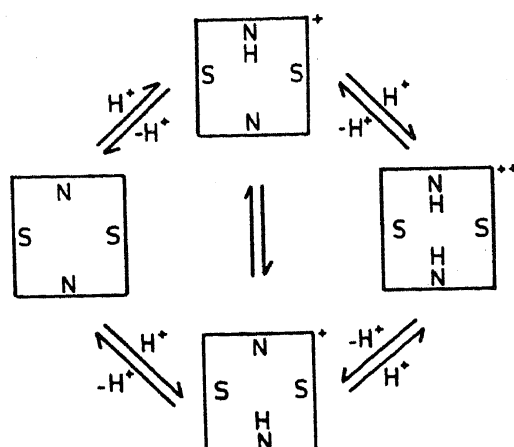
* Dications are generated by titrating appropriate amounts of TFA to CDCl_3 solution; s, d, M refers to singlet, doublet and multiplet;

o, p, m refers to ortho, meta and para protons of phenyl rings;

^a Data taken from Abraham *et al* (1974).

The formation of dications of thiaporphyrins results in a large downfield shift of the pyrrole protons while the thiophene protons experience a negligible shift (figure 4). In fact, in case of $(\text{OCH}_3)_4\text{S}_2\text{TPP}$ the thiophene protons experience a small upfield shift. All the phenyl protons experience a considerable downfield shift with coupling constants remaining unaltered. The fact that the pyrrole protons in all the dithiaporphyrins experience a large deshielding effect [0.39 for S_2TPP , 0.35 for $(\text{CH}_3)_4\text{S}_2\text{TPP}$ and 0.26 ppm for $(\text{OCH}_3)_4\text{S}_2\text{TPP}$] relative to the thiophene protons [0.13 for S_2TPP , -0.03 for $(\text{CH}_3)_4\text{S}_2\text{TPP}$ and -0.14 ppm for $(\text{OCH}_3)_4\text{S}_2\text{TPP}$] indicates that protonation occurs at the pyrrole nitrogen and not at the thiophene sulphur atom (Ulman *et al* 1979). The observed downfield shift of the pyrrole protons upon protonation can be ascribed to the following two effects: (i) the introduction of two extra positive charges into the porphyrin core, and (ii) the nonplanarity of the dications leading to release of repulsive interactions between the ortho hydrogen of the phenyl and the pyrrole hydrogen facilitating greater resonance interaction with the phenyl rings (Janson and Katz 1979; Abraham *et al* 1974). Based on the data obtained from optical and NMR studies, scheme 1, similar to that proposed for the protonation of $(\text{CH}_3)_4\text{STPPH}$ (Lisowski *et al* 1989), is suggested for dithiaporphyrins.

Metal complexes of $(\text{Ni}^{+2}, \text{Cu}^{+2})$ of the monothia derivative have been prepared. The Cu complex gave an axially symmetric ESR at liquid nitrogen temperature ($g_{\parallel} = 2.217$, $g_{\perp} = 2.0637$, $A_{\parallel}^{\text{Cu}} = 164 \text{ G}$). While this work was in progress in our laboratory, Balch and coworkers reported the X-ray structure of Fe(II), Ni(II) and Cu(II) complexes of monothia derivative (Grazynski *et al* 1987, 1989). The X-ray structure indicates that the complexes have a basic 5-coordinate structure with approximately square pyramidal geometry and an apical chloride ligand. The thiophene ring is bent from the plane of the STPP ligand core and is η^1 -bound to the metal through a pyramidal sulphur. The Ni(II) derivative was found to be a high spin complex. Attempts to synthesize the metal derivatives of dithia porphyrins have not yet succeeded.



Scheme 1. Protonation scheme for dithiaporphyrins.

Table 5. Monomer and dimer absorption data of S_2 TPPS in water.

Porphyrin	Soret band $\lambda_{\max}(\text{nm})$	Q-bands $\lambda_{\max}(\text{nm})$	V (cm^{-1})
S_2 TPPS	431	516, 547(<i>sh</i>) [†] , 629, 695	
S_2 TPPS + 18C6 + K^+	433	521, 557(<i>sh</i>), 640, 703	^a 656, 306
H_2 TPPS*	414	516, 552, 580, 635	
H_2 TPPS + 18C6 + K^+	415	524, 565, 598, 657	^b 834, 1055

*Calculated for 547, 695 nm bands; ^bcalculated for 552, 635 nm bands; *data taken from Chandrashekar *et al* (1984); [†](*sh*) represents shoulder.

The water-soluble S_2 TPPS, prepared from sulphonation of the para position of S_2 TTP, shows extensive aggregation in the concentration range (10^{-3} – 10^{-4} M) (unpublished results). However, in dilute solutions it exists as a monomer. The effect of sulphonation at the para-position shows very little effect on the absorption spectrum. A small blue shift of the Soret band and a small red shift of the QIV and QII bands are observed upon sulphonation. A comparison with the absorption spectrum (table 5) of water-soluble tetra(*p*-sulphonatophenyl) porphyrin (H_2 TPPS) (Chandrashekar and Willigen 1983) indicates a considerable red shift of the Soret band as well as the QII and QI bands upon introduction of sulphur in the porphyrin core.

Addition of cations (K^+ , NH_4^+) and 18-crown-6 to a dilute solution ($\approx 10^{-5}$ M) of S_2 TPPS in water results in the red shift of all Q-bands accompanied by a reduction in intensity of the Soret band. Figure 5 shows the spectrum of S_2 TPPS in water before and after the addition of 18-crown-6 and K^+ ions. A similar effect was observed in the case of H_2 TPPS upon addition of K^+ and 18-crown-6 which was interpreted as due to formation of a cofacial dimer in solution (Chandrashekar and Willigen 1983; Chandrashekar *et al* 1984, 1985). The dimerization is dependent upon the ionic strength and an increase in ionic strength favours the formation of the dimer. The dimerization induced shifts of both S_2 TPPS and H_2 TPPS are listed in table 5. It is seen from table 5 that the dimerization-induced shifts for S_2 TPPS upon addition of cation and crown ether are smaller than those of H_2 TPPS. These

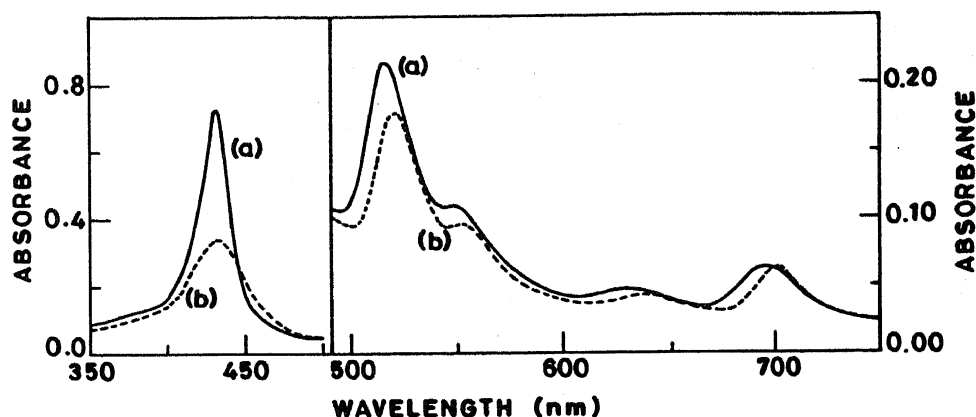


Figure 5. Electronic spectra of (a) S_2 TPPS, and (b) S_2 TPPS + 18-crown-6 + K^+ , in water.

dimerization-induced shifts could be accounted for in terms of exciton theory (Kasha *et al* 1965) which involves dipole-dipole interactions between the transition moments associated with the optical transitions in the dimer constituents. This exciton theory has been satisfactorily used by several workers to relate absorption band shifts to the dimer structures of several covalently linked diporphyrins (Chang 1977, 1979). The exciton splitting parameter V calculated for the dimers of S_2 TPPS and H_2 TPPS are also listed in table 5. These values are comparable to those found recently for the dimerization of crowned phthalocyanines (770 – 1600 cm^{-1}) (Kobayashi and Lever 1987). Further work is in progress to deduce the solution structure of these dimers.

Acknowledgements

Financial assistance from the Council of Scientific and Industrial Research to TKC and DR is gratefully acknowledged.

References

- Abraham R J, Hawkes G E and Smith K M 1974 *Tetrahedron Lett.* 1483
 Abraham R J, Leonard P and Ulman A 1984 *Org. Magn. Reson.* **22** 561
 Broadhurst M J, Grigg R and Johnson A W 1971 *J. Chem. Soc. C* 3681
 Chandrashekar T K and Willigen H V 1983 *J. Am. Chem. Soc.* **105** 6323
 Chandrashekar T K, Willigen H V and Ebersole M H 1984 *J. Phys. Chem.* **88** 4326
 Chandrashekar T K, Willigen H V and Ebersole M H 1985 *J. Phys. Chem.* **89** 3453
 Chang C K 1977 *J. Heterocyclic Chem.* **14** 1285
 Chang C K 1979 *Adv. Chem. Ser.* **173** 162
 Gouterman M 1978 in *The porphyrins* (ed.) D Dolphin (New York: Academic Press) vol. 3, p. 1
 Grazynski L L, Lisowski J, Olmstead M M and Balch A L 1987 *J. Am. Chem. Soc.* **109** 4428
 Grazynski L L, Lisowski J, Olmstead M M and Balch A L 1989 *Inorg. Chem.* **28** 1183
 Hill R L, Gouterman M and Ulman A 1982 *Inorg. Chem.* **21** 1450
 Janson T R and Katz J J 1979 in *The porphyrins* (ed.) D Dolphin (New York: Academic Press) vol. 4, p. 1
 Kadish K M and Morrison M M 1976 *J. Am. Chem. Soc.* **98** 3326
 Kadish K M and Morrison M M 1977 *Bio. Inorg. Chem.* **7** 107
 Kasha M, Rawls H R and El-Bayoumi M 1965 *Pure Appl. Chem.* **11** 371
 Kobayashi N and Lever A B P 1987 *J. Am. Chem. Soc.* **109** 7433
 Lisowski J, Grzeszczuk M and Grazynski L L 1989 *Inorg. Chim. Acta* **161** 153

- Ner M M and Alder A D 1975 *J. Am. Chem. Soc.* **97** 5107
Quimby D J and Longo F 1975 *J. Am. Chem. Soc.* **97** 5111
Stone A and Fleischer E B 1968 *J. Am. Chem. Soc.* **90** 2735
Ulman A and Manassen J 1975 *J. Am. Chem. Soc.* **97** 6540
Ulman A and Manassen J 1979 *J. Chem. Soc., Perkin 1* 1066
Ulman A, Manassen J, Frolow F and Rabinovich D 1978 *Tetrahedron Lett.* 167
Ulman A, Manassen J, Frolow F and Rabinovich D 1978 *Tetrahedron Lett.* 1885
Ulman A, Manassen J, Frolow F and Rabinovich D 1979 *J. Am. Chem. Soc.* **101** 7055
Ulman A, Manassen J, Frolow F and Rabinovich D 1981 *Inorg. Chem.* **20** 1987
Vogel E, Haas W, Knipp B, Lex J and Schmickler H 1988 *Angew. Chem., Int. Ed. Engl.* **27** 406
Weissberger A and Rossiter B W 1971 *Electrochemical methods* (New York: Wiley) part 2A, p. 536
Yamashita K, Yamamoto T, Shimidzu H and Suzuki H 1982 *Chem. Lett.* 807