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Meso-tetrathienylporphyrins: electrochemical and axial ligation properties

P. Bhyrappa *, P. Bhavana

Department of Chemistry, Indian Institute of Technology, Chennai 600 036, India

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Abstract

5, 10, 15, 20-Tetrakis(2′- and 3′-thienyl)porphyrins [$H_2T(2'\text{-Thio})P$ and $H_2T(3'\text{-Thio})P$] and their metal [Zn(II) and Cu(II)] complexes were examined by electrochemical redox and axial ligation properties. A large anodic shift (100–150 mV) in reduction potentials was observed for MT(2′-Thio)Ps relative to MTPPs or MT(3′-Thio)Ps. MT(2′-Thio)Ps exhibited unusual redox behaviour and follows the trend in oxidation; $CuT(2'\text{-Thio})P > H_2T(2'\text{-Thio})P \geqslant ZnT(2'\text{-Thio})P$ in contrast to their corresponding MTPPs, $H_2TPP > CuTPP > ZnTPP$. It is reflected in the enhanced equilibrium constants (>60%) for the ligation of nitrogenous bases with ZnT(2′-Thio)P when compared to ZnTPP. This is interpreted in terms of increased electron deficient nature of the ZnT(2′-Thio)P in contrast to Zn(3′-Thio)P or ZnTPP. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The functionalised porphyrins are of considerable importance owing to their use as model compounds [1,2] and also for their interesting physico-chemical properties [3,4]. These properties can be altered by the introduction of appropriate substituents at the periphery of the porphyrin. The past decade has witnessed numerous reports on the synthesis and properties of highly substituted porphyrins [5]. The introduction of substituents at the *meso*- or at the β-pyrrole positions has dramatic influence over the electronic properties of the macrocycle [3,5]. By appending appropriate substituents (electron deficient or rich) at the peripheral positions, they serve as materials or compounds with unusual properties [6]. Further, high-valent metallotetraphenylporphyrins with bulky *ortho*-substitutents on the phenyl rings serve as robust catalysts for the oxidation of organic substrates [7,8].

The *meso*-tetraarylporphyrins were used as model compounds extensively owing to their ease of synthesis and facile functionalisation. In recent years, the *meso*-tetrathienylporphyrins are of growing interest due to their use as models for energy transfer reactions [9]. In addition, these oligomeric thienylporphyrins showed film-forming [10] and conductivity behaviour [11]. The physico-chemical studies on *meso*-thienylporphyrins have been largely unexamined. To delineate the effect of *meso*-thienyl groups on the electronic property of

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* Corresponding author. Fax: +91-44-235-0509.
E-mail address: bhyrappa@iitm.ac.in (P. Bhyrappa).

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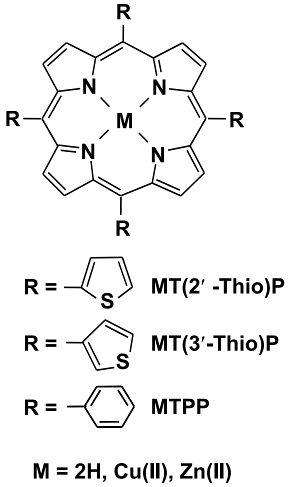

Fig. 1. Chemical structure of *meso*-tetraarylporphyrins.

the porphyrin π-system, electrochemical redox and axial ligation studies were performed on a series of thienylporphyrins (Fig. 1). These porphyrins exhibit interesting electrochemical and axial ligation properties.

2. Experimental

5, 10, 15, 20-Tetraphenylporphyrin, H_2TPP [12] and 5, 10, 15, 20-tetrakis(2′-thienyl)porphyrin and its metal [Cu(II) and Zn(II)] complexes were prepared using reported procedures [13,14]. The nitrogenous bases, pyridine, piperidine and morpholine were procured from Rankem (India) and purified before use [15]. Imidazole, 3-hydroxypyridine, 4-(dimethylamino)pyridine and 3-pyridinecarboxaldehyde purchased from Fluka (Switzerland) were used as received. Majority of the solvents employed were of reagent grade and purified [15] prior to use.

2.1. Synthesis of 5,10,15,20-tetrakis(3′-thienyl)porphyrin, $H_2T(3'$-Thio)P

To a refluxing propionic acid (200 ml), thiophene-3-carboxaldehyde (3 ml, 34 mM) and pyrrole (2.3 ml, 34 mM) were added. The reaction mixture was refluxed for 45 min. Then it was allowed to cool to room temperature and filtered. The purple crystals were washed with methanol and recrystallised from chloroform/methanol mixture. The yield of the porphyrin was found to be 0.73 g (14%). The synthesised porphyrins were characterised by ^1H NMR, UV–visible and mass spectroscopic methods. ^1H NMR of $H_2T(3'$-Thio)P ($CDCl_3$, 400 MHz): δ 8.97 (s, 8H, pyrrole β-H), 8.02 (d, 4H, thienyl 2′-H), 7.99 (d, 4H, thienyl 5′-H), 7.74 (q, 4H, thienyl 4′-H), −2.72 (s, 2H, imino-H). FAB mass spectrum (*m/z*): 639 (calcd. 638.84). MT(3′-Thio)Ps (M = Cu(II) and Zn(II)) were prepared using the reported procedures [16]. The yield of the metal complexes was almost quantitative.

The ^1H NMR measurements were performed on a 400 MHz Brucker FT-NMR spectrometer using $CDCl_3$ as the solvent at ambient temperature. UV–visible spectral measurements were carried out on a JASCO V-550 series spectrophotometer using matched quartz cells of 1 cm path length. Cyclic voltammograms were obtained from Bioanalytical System (BAS 100A, USA) provided with a three-electrode cell assembly, videometer and electrochemical analyzer. The cell assembly consists of a platinum button (2 mm), Ag/AgCl and platinum wire as working, reference and counter electrodes, respectively. All the electrochemical studies were performed in CH_2Cl_2 solvent under N_2 atmosphere using 0.1 M tetrabutylammonium hexafluorophosphate, TBAHFP as the supporting electrolyte. The concentrations of the porphyrins employed were ~0.4 mM. The axial ligation of nitrogenous bases to Zn(II)-porphyrins were carried out in toluene at 25 °C using a thermostat cell holder. The equilibrium constants, K_{eq} were evaluated using literature procedure [17,18] and calculated at four different wavelengths. The average of four K_{eq} values was taken for data analysis. K_{eq} values at different wavelengths were found to be within 13% error.

3. Results and discussion

The various thienylporphyrins were examined to determine the effect of position of the *meso*-thienyl-S substituent on the electrochemical and

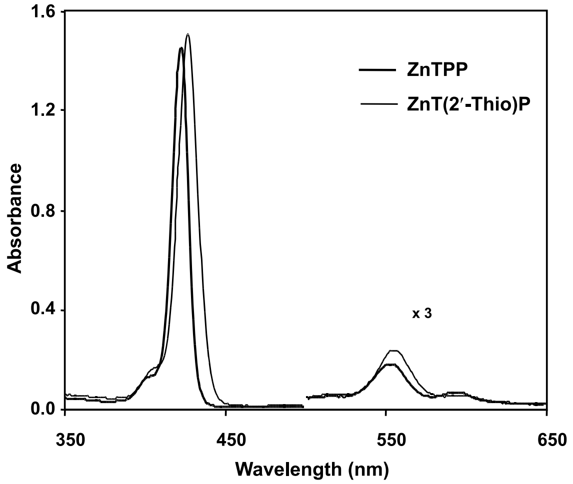

Fig. 2. Electronic absorption spectra of ZnT(2′-Thio)P and ZnTPP in CH_2Cl_2 at ambient temperature.

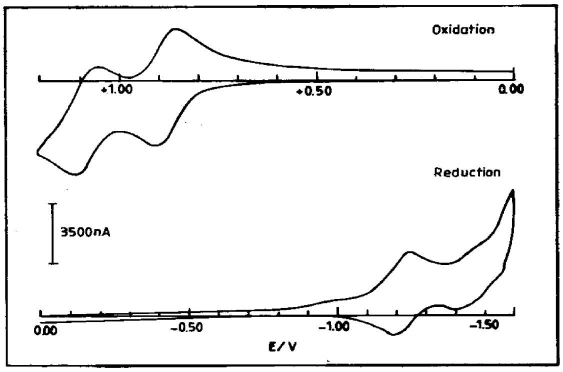

Fig. 3. Cyclic voltammograms of ZnT(2′-Thio)P in CH_2Cl_2 with 0.1 M TBAHFP as the supporting electrolyte at a scan rate of 100 mV/s at ambient temperature.

axial ligation properties. Fig. 2 shows the optical absorption spectra of representative ZnT(2′-Thio)P along with ZnTPP and the spectral data are summarised in Table 1. In general, thienylporphyrins show a red shift of absorption bands relative to their corresponding MTPPs. The observed number of bands and spectral pattern of MT(2′ or 3′-Thio)Ps are quite similar to MTPPs. Further, the molar absorption coefficients of thienylporphyrins are not significantly different from that of MTPPs [19]. For a smaller thienyl ring, one would anticipate a possible co-planarity of the ring with the porphyrin macrocycle. However, the dihedral angle formed between the porphyrin plane and the thienyl ring in ZnT(2′-Thio)P (67–70°) [14] is found to be greater than that observed for ZnTPP (60–63°) [20]. This indicates that the extent of conjugation of the thienyl group with the porphyrin ring is less favourable. An increase in red shift of the absorption spectral features is possibly due to inductive effect of the thienyl groups.

The electrochemical studies were performed on thienylporphyrins to elucidate the effect of thienyl groups on the electron deficiency of the porphyrin macrocycle. A representative cyclic voltammogram of ZnT(2′-Thio)P is shown in Fig. 3 and the redox data of the complexes are shown in Table 2. All the porphyrins showed two successive one-electron oxidation and two one-electron reduction potentials. For comparison, MTPPs were also examined under similar conditions and the data are

Table 1
UV–visible absorption spectral data[a] of tetrathienylporphyrins in CH_2Cl_2 at 25 °C

Porphyrin	B band (nm)	Q bands (nm)
$H_2T(2'\text{-Thio})P$	426(5.59)	523(4.30), 560(4.02), 597(3.88), 661(3.86)
$H_2T(3'\text{-Thio})P$	421(5.67)	519(4.29), 555(4.09), 595(3.85), 653(3.85)
H_2TPP	417(5.72)	514(4.36), 548(4.03), 590(3.90), 647(3.86)
CuT(2′-Thio)P	421(5.62)	546(4.37), 582(sh)
CuT(3′-Thio)P	418(5.67)	542(4.31), 577(sh)
CuTPP	415(5.80)	539(4.45), 571(sh)
ZnT(2′-Thio)P	427(5.67)	555(4.40), 595(3.79)
ZnT(3′-Thio)P	422(5.71)	551(4.36), 591(3.92)
ZnTPP	422(5.79)	553(4.41), 595(4.00)

[a] The values in parentheses refer to log ε values, ε in $dm^3/mol/cm$.

Table 2
Half-wave redox potentials[a,b] (mV) of thienylporphyrins in CH_2Cl_2 using 0.1 M TBAHFP at 25 °C

Porphyrin	Oxidation		Reduction	
	I	II	I	II
$H_2T(2'\text{-Thio})P$	890	1130	−1090	−1420
$H_2T(3'\text{-Thio})P$	950	1205	−1225	−1525
H_2TPP	1000	1335	−1230	−1540
CuT(2′-Thio)P	990	1350	−1190	−1577
CuT(3′-Thio)P	920	1300	−1345	−1750[c]
CuTPP	970	1350	−1325	–
ZnT(2′-Thio)P	885	1085	−1225	−1425
ZnT(3′-Thio)P	805	1090	−1385	−1695
ZnTPP	825	1235	−1360	−1710[c]

[a] Vs Ag/AgCl electrode.
[b] Error in redox potentials is within ±15 mV.
[c] Data from differential pulse voltammetry.

summarised in Table 2. The observed potentials of MTPPs are quite similar to the literature values [4]. MTPPs were chosen to delineate the effect of *meso*-phenyl groups versus the thienyl groups at the *meso*-carbons on the electronic properties of the porphyrin π-system.

Notably, $H_2T(2'\text{-Thio})P$ shows a cathodic shift in first oxidation (60–100 mV) and anodic shift in first reduction (>100 mV) relative to $H_2T(3'\text{-Thio})P$ or H_2TPP. From Table 2 it can be seen that the redox potentials of thienylporphyrins indicates an ease of oxidation and reduction in $H_2T(2'\text{-Thio})P$ relative to $H_2T(3'\text{-Thio})P$ or H_2TPP. The free-base porphyrins examined in this study follows the trend, $H_2T(2'\text{-Thio})P < H_2T(3'\text{-Thio})P < H_2TPP$ in first oxidation and $H_2T(2'\text{-Thio})P < H_2T(3'\text{-Thio})P \approx H_2TPP$ in reduction. For Zn(II)-porphyrins, ZnT(2′-Thio)P showed almost similar first oxidation potential relative to $H_2T(2'\text{-Thio})P$ where as its first reduction potential is cathodic by about 130 mV relative to $H_2T(2'\text{-Thio})P$. The redox potentials of CuT(2′-Thio)P complex are more anodic relative to CuT(3′-Thio)P or CuTPP. The shift is more pronounced in reduction potentials (>120 mV) in contrast to oxidation potentials. The observed redox potentials of CuT(2′-Thio)P are consistent with the literature values [13]. The general trend in first oxidation potentials for thienylporphyrins follow the order: $CuT(2'\text{-Thio})P > H_2T(2'\text{-Thio})P \geqslant ZnT(2'\text{-Thio})P$ in contrast to MTPPs, $H_2TPP > CuTPP > ZnTPP$. However, the observed trend in reduction is quite similar to that of MTPPs. MT(3′-Thio)P compounds follow similar redox behaviour to that of MTPPs. The anodic shift in redox potentials of MT(2′-Thio)Ps relative to MT(3′-Thio)Ps can be ascribed to the enhanced electron deficient nature of the porphyrin macrocycle induced by the 2-thienyl groups relative to 3-thienyl groups. As reported earlier, the *ortho*-phenyl substitutents in MTPPs have significant

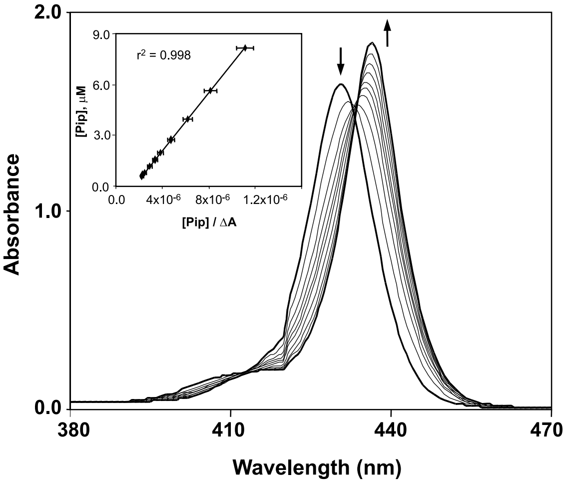

Fig. 4. Optical absorption spectral features for the Soret region of ZnT(2′-Thio)P in presence of increasing addition of piperidine in toluene at 25 °C. Inset shows the plot of concentration of piperidine [Pip] against [Pip]/Δ*A*. For explanation of terms, see [25].

Table 3
Equilibrium constants (K_{eq})[a] for the ligation of various nitrogeneous bases with Zn(II)-thienylporphyrins in toluene at 25 °C

Base	$K_{eq} \times 10^{-3}$			
	ZnT(2′-Thio)P	ZnT(3′-Thio)P	ZnTPP	pK_a
Piperidine	87.10	55.38	53.57	11.22
4-(Dimethylamino)pyridine	159.41	113.43	90.26	9.70
Morpholine	34.22	28.68	25.02	8.33
Imidazole	56.72	33.62	29.43	6.95
Pyridine	5.42	4.16	3.26	5.23
3-Hydroxypyridine	4.86	3.71	2.84	4.86
3-Pyridinecarboxaldehyde	1.69	1.36	1.08	4.77

[a] Within the error ±13%.

influence over the redox potentials relative to *meta*- or *para*-substitution [4,21]. The greater anodic shift in redox potentials is possibly due to the inductive effect in 2-thienyl relative to 3-thienyl group.

In an effort to understand the unusual electrochemical behaviour of thienyl porphyrins, axial ligation of various nitrogenous bases with ZnT(2′- and 3′-Thio)P were carried out in toluene to elucidate the effect of position of the thienyl-S group on the extent of electron deficient nature of the porphyrin π-system. Zn(II)-porphyrins were chosen for their simple well established five coordination behaviour. A typical absorption spectral features of ZnT(2′-Thio)P with the increasing addition of piperidine is shown in Fig. 4. The observed optical absorption spectral behaviour of Zn(II)-thienylporphyrins in presence of bases is similar to that reported for Zn(II)-porphyrins [22,23]. The stoichiometry of the complexation was analysed by Hill method [24]. In all cases, ligation of Zn(II)-thienylporphyrin with base (L) showed 1:1 complexation Eq. (1).

$$\begin{aligned} &\mathrm{Zn(2'\text{- or }3'\text{-Thio})P + L} \\ &\quad \rightleftharpoons \mathrm{ZnT(2'\text{- or }3'\text{-Thio})P(L)} \end{aligned} \tag{1}$$

The data were analysed using available reported procedures [17,18,25]. K_{eq} values for the thienylporphyrins are given in Table 3. For comparison, ZnTPP complexation with all the bases were also carried out under similar conditions and the data are shown in Table 3. The observed K_{eq} values for ZnTPP are quite similar to that of reported values [26]. It can be seen that the ZnT(2′-Thio)P shows about > 60% higher binding constants relative to ZnT(3′-Thio)P or ZnTPP. However, ZnT(3′-Thio)P showed a marginal increment of about 20–30% in K_{eq} values relative to ZnTPP. The enhanced K_{eq} values of ZnT(2′-Thio)P relative to ZnT(3′-Thio)P can be ascribed to greater inductive effect of the 2-thienyl-S group.

4. Conclusions

The present work demonstrates the interesting electrochemical redox and axial ligation properties of *meso*-tetrathienylporphyrins. Upon variation of S-group from 2- to 3-position on the thienyl groups, thienylporphyrins showed an unusual shift of redox potentials of MT(2′-Thio)Ps relative to the corresponding MTPPs or MT(3′-Thio)Ps. Of the two porphyrins, MT(2′-Thio)Ps showed a marginal anodic shift of oxidation potential and a pronounced anodic shift in reduction potentials were observed in contrast to the corresponding MT(3′-Thio)Ps. This was further supported by the increased equilibrium constants for the axial ligation of bases with Zn(II)-porphyrins and thus follow the order: ZnT(2′-Thio)P > ZnT(3′-*Thio*)P ⩾ ZnTPP.

Acknowledgements

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[25] [Pip] denotes the concentration of the piperidine added for a given concentration of ZnT(2′-Thio)P in toluene. ΔA represents the difference in absorbance between ZnT(2′-Thio)P and ZnT(2′-Thio)P(Pip) complexes in toluene solution at a particular wavelength. The binding constants were evaluated using procedures from [17] and [18].

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