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Nitrothienylporphyrins: Synthesis, crystal structure and, the effect of position and number of nitro groups on the spectral and electrochemical properties

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ABSTRACT

This article describes the investigation on the effect of orientation of the *meso* thienyl groups of porphyrins in deciding the site of nitration. The thienyl rings present at the *meso* position is found to be more susceptible for electrophilic nitration reaction than the pyrrole β-position in the molecules where there is a better conjugation between the thienyl rings and the porphyrin π-system. Signal corresponding to the imino hydrogens in the proton NMR spectrum of *meso* nitrothienylporphyrins get shifted to upfield with increase in the number of nitro groups on the porphyrin. This is also due to the extended conjugation of the porphyrins π-system with the *meso* thienyl rings. The above observations are also supported by the redox potentials of those compounds.

1. Introduction

Porphyrins are the class of compounds that have gained interest in research for decades owing to their existence in variety of biological systems and due to their application in the field of biomimetics, catalysis, medicine and sensors [1]. Thienylporphyrins, a type of heteroaromatic porphyrins, are of growing interest because they form ultra thin films [2,3] and also due to the electron and energy transfer properties [4] of their derivatives. Because of these remarkable electrical and optical properties, various research groups have investigated oligothiophene and polythiophene appended porphyrins [5,6]. *Meso* thienylporphyrins show attractive photophysical [7], structural [8–10], electrochemical [7,11] and magnetic [12] properties. Functionalization of the five membered thienyl ring, that can come in conjugation with the porphyrin π-system due to its small size [13,14], with groups of different electronic behavior can modulate the properties of the macrocycle. These groups may also act as the site for further reaction. Bromine is one such substituent which alters the electronic [15,16] as well as the stereochemical [16] properties of the porphyrins. Brominated porphyrins are good precursors in the synthesis of many highly functionalized and asymmetric porphyrins through Suzuki cross coupling, Sonogashira coupling and Heck reactions [17–19].

In an attempt to prepare the asymmetric thienylporphyrins for the synthesis of other highly functionalized and asymmetric porphyrins, we were successful in synthesizing β-nitrated 5-halo (chloro- or bromo-) thienylporphyrins [20]. Photophysical [21], catalytic [22] and nonlinear optical properties [23] together with the role of nitro group in nucleophilic substitution [24] and addition [25] reactions in the synthesis of other asymmetric porphyrinic molecules for therapeutic applications [26] make nitroporphyrins very attractive class of compounds in research. Cupric nitrate trihydrate, which is a mild nitrating agent, generally introduces the nitro group at the β-position of the porphyrin, especially when the central metal ion is Cu(II) or Ni(II) [27,28]. The hydrogen on the carbon next to sulfur in five membered heterocyclic compounds is prone to electrophilic substitution reactions. This led us to study, in the present work, the effect of cupric nitrate trihydrate on *meso* 5,10,15,20-tetrathienylporphyrinato nickel (II), NiThP, in which the site next to sulfur on the thienyl group is available for substitution. To investigate the position of nitration with conformation of the molecule, nickel derivative of *tetrakis*(5′-methylthien-2′-yl)porphyrin (Ni5MeThP) in which the fifth position on the thienyl ring is blocked and nickel derivative of *tetrakis*(3′-methylthien-2′-yl)porphyrin (Ni3MeThP) in which the fifth position on the thienyl ring is available for substitution, also have been nitrated under similar conditions. The molecular structure of various porphyrins synthesized in this study along with their abbreviation is given below (Fig. 1).

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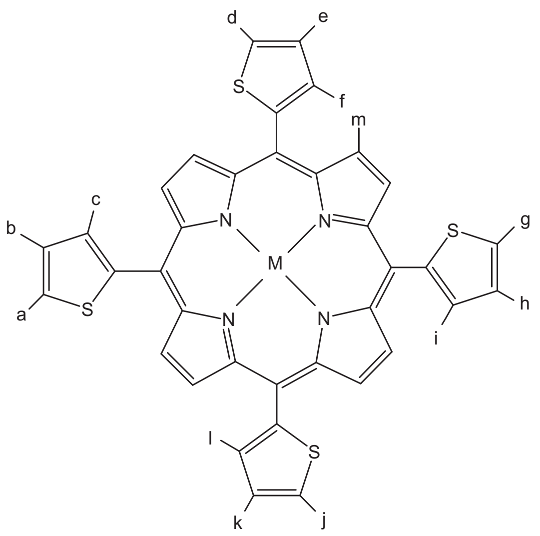

MThP :M = 2H or Ni(II); a,b,c,d,e,f,g,h,i,j,k,l,m = H
NiNThP :M = Ni(II); b,c,d,e,f,g,h,i,j,k,l,m = H; a = NO_2

M5MeThP :M = 2H or Ni(II); b,c,e,f,h,i,k,l, m = H; a,d,g,j = CH_3
Ni4N5MeThP :M = Ni(II); c,e,f,h,i,k,l,m = H; b = NO_2; a,d,g,j = CH_3

M3MeThP :M = 2H or Ni(II); a,b,d,e,g,h,j,k,m = H; c,f,i,l = CH_3
NiN3MeThP :M = Ni(II); a,b,d,e,g,h,j,k = H; m = NO_2; c,f,i,l = CH_3

MSNThP :M = 2H or Ni(II); b,c,d,e,f,g,h,i,j,k,l,m = H; a = NO_2
MTDNThP :M = 2H; b,c,d,e,f,h,i,j,k,l,m = H; a,g = NO_2
MCDNThP :M = 2H; b,c,e,f,g,h,i,j,k,l,m = H; a,d = NO_2
MTiNThP :M = 2H; b,c,e,f,h,i,j,k,l,m = H; a,d,g = NO_2
MTaNThP :M = 2H; b,c,e,f,h,i,k,l,m = H; a,d,g,j = NO_2

Fig. 1. Chemical structures of nitro substituted thienylporphyrins.

2. Experimental

2.1. Materials

CH_2Cl_2 (SD Fine Chemicals, India) was refluxed and distilled over CaH_2 and stored over 4 Å molecular sieves. Pyrrole, various thiophenecarboxaldehydes and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were procured from Sigma–Aldrich. Other required chemicals were purchased from SD Fine Chemicals, India. Free base *tetrakis*(2′-thienyl)porphyrin, H_2ThP [29] and its methyl derivatives, $H_2$5MeThP and $H_2$3MeThP [30] were prepared by following the procedure reported. The products were characterized by spectral methods and the data confirmed the formation of the compounds. For preparing Ni(II) derivatives of above porphyrins, nickel acetate in dimethylformamide was used as the metal ion carrier [31].

2.2. Measurements

^{1}H NMR spectra were recorded on a DRX-500 spectrometer in deuteriated chloroform using tetramethylsilane as the internal standard. Optical absorption spectra were recorded on a JASCO V-570 model UV/VIS/NIR spectrophotometer using quartz cells of 1 cm path length. BAS EPSILON model electrochemical system was employed for the cyclic voltammetric measurements. The electrochemical cell consists of three electrode cell assembly and the electrodes used were platinum working electrode, Ag/AgCl reference electrode and platinum wire auxiliary electrode. The concentrations of all the porphyrins employed were ~1 mM. All the measurements were performed in CH_2Cl_2 solution which was purged with nitrogen and 0.1 M $TBAPF_6$ was used as the supporting electrolyte. Electrospray mass spectra were recorded on a THERMO Finnigan LCQ Advantage max ion trap mass spectrometer.

2.3. Synthesis

2.3.1. Synthesis of 5-(5′-nitrothien-2′-yl)-10,15,20-tris(thien-2′-yl)porphyrinato nickel (II), NiNThP

Nitration of NiThP was carried out using cupric nitrate trihydrate [20] in acetic acid/acetic anhydride medium. To a solution of NiThP (0.17 g, 0.25 mmol) in 50 mL of chloroform and 3 mL of acetic acid, a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.06 g, 0.25 mmol) in 15 mL of acetic anhydride was added dropwise over a period of 20 min. The reaction mixture was stirred under refluxing conditions for 25 min. At the end of this period, the reaction mixture was treated with water (3 times) followed by 100 mL of 20% aqueous $NaHCO_3$ (2 times) and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by distillation and the product was purified by column chromatography using 3:2 chloroform and hexanes as the eluent. Unreacted NiThP, which was present in trace amounts and eluted first on the column, was collected separately. The yield of NiNThP was 70% (0.13 g). The compound was characterized by UV–vis, ^{1}H NMR and mass spectral techniques. UV–vis and ^{1}H NMR spectral details are given in Tables 1 and 2, respectively. ESI-MS for NiNThP: m/z $[M]^+$ Calcd. 740.52. Found: 740.9.

2.3.2. Synthesis of 5-(4′-nitro-5′-methylthien-2′-yl)-10,15,20-tris(5′-methylthien-2′-yl)porphyrinato nickel (II), Ni4N5MeThP

Nitration of Ni5MeThP was carried out using cupric nitrate trihydrate as given in the case of NiNThP. The reaction mixture was refluxed for 30 min after the addition of nitrating agent. The yield was 77%. The compounds were characterized by UV–vis, ^{1}H NMR and mass spectral techniques. UV–vis and ^{1}H NMR spectral details are given in Tables 1 and 2, respectively. ESI-MS for Ni4N5MeThP: m/z $[M]^+$ Calcd. 796.63. Found: 797.1.

2.3.3. Synthesis of 2-nitro-5,10,15,20-tetrakis(3′-methylthien-2′-yl)porphyrinato nickel (II), NiN3MeThP

Nitration of Ni3MeThP was carried out using cupric nitrate trihydrate as given in the case of NiNThP. The reaction mixture was refluxed for 20 min after the addition of nitrating agent. The yield was 71%. The compounds were characterized by UV–vis, ^{1}H NMR and mass spectral techniques. UV–vis and ^{1}H NMR spectral details are given in Tables 1 and 2, respectively. ESI-MS for NiN3MeThP: m/z $[M]^+$ Calcd. 796.63. Found: 796.9.

2.3.4. Synthesis of 5-(5′-nitrothien-2′-yl)-10,15,20-tris(thien-2′-yl)porphyrin, H_2SNThP

This porphyrin was synthesized using a mixture of thienylaldehydes by following the procedure by Lindsey et al. with modifications in it [32]. To a mixture of 5-nitro-2-thiophenecarboxaldehyde (0.6 g, 3.82 mmol) and thiophene-2-carboxaldehyde (1.08 mL, 11.4 mmol) in the ratio 1:3 in 600 mL of dichloromethane, pyrrole (1 mL, 15.2 mmol) was added under N_2 atmosphere. To this, BF_3 etherate (0.62 mL, 5.06 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. At the end of the period, *p*-chloranil (3.73 g, 15.2 mmol) was added and stirring was continued for another half an hour. Following this, triethylamine (0.7 mL, 5.06 mmol) was added and stirred for another 1 h. The reaction mixture was then adsorbed on 200 g of silica gel (230–400 mesh) and the mixture of porphyrins was eluted using chloroform. The solution was then concentrated

Table 1
UV–vis absorption spectral data[a] of nitro substituted thien-2-ylporphyrins in CH_2Cl_2.

Porphyrin	Soret band (nm)	Q bands (nm)	FWHM (nm)
H_2ThP	426 (5.59)	523 (4.30), 560 (4.02), 597 (3.88), 661 (3.86)	16.56
H_2SNThP	426 (5.51)	522 (4.30), 562 (4.02), 596 (3.90), 658 (3.48)	21.46
H_2TDNThP	428 (5.43)	523 (4.30), 563 (4.05), 596 (3.90), 658 (3.55)	26.11
H_2CDNThP	429 (5.43)	523 (4.35), 562 (4.08), 596 (3.99), 658 (3.54)	26.77
H_2TiNThP	431 (5.42)	523 (4.34), 562 (4.04), 596 (3.95), 658 (3.39)	29.45
H_2TaNThP	432 (5.50)	522 (4.45), 560 (4.12), 596 (4.05), 656 (3.46)	30.73
NiThP	423 (5.26)	537 (4.12), 628 (3.03)	26.73
NiNThP	423 (5.29)	538 (4.27)	33.30
Ni5MeThP	428 (5.44)	540 (4.34), 628 (3.64)	28.22
Ni4N5MeThP	428 (5.29)	540 (4.27)	31.67
Ni3MeThP	420 (5.55)	534 (4.38), 626 (3.45)	24.34
NiN3MeThP	434 (5.46)	546 (4.39), 588 (4.20)	35.43

[a] The values in parenthesis refer to logε values, ε in dm^3 mol^{-1} cm^{-1}.

by rotary evaporation and the porphyrins were separated by column chromatography using chloroform containing 0.5–3% of methanol as the eluent for various nitro derivatives. The yield of the required product H_2SNThP was 202 mg (7.8%). Other porphyrins isolated from the reaction mixture were obtained in the following yield: H_2ThP (92 mg, 5.1%), H_2TDNThP (39 mg, 2.8%), H_2CDNThP (36 mg, 2.6%), H_2TiNThP (20 mg, 2.1%) and H_2TaNThP (4 mg, 0.5%). The compounds were characterized by UV–vis, ^{1}H NMR and mass spectral techniques. UV–vis and ^{1}H NMR spectral data are given in Tables 1 and 2, respectively. ESI-MS: *m*/*z* $[M]^+$ H_2SNThP (Calcd. 683.84. Found: 684.3), H_2TDNThP (Calcd. 728.84. Found: 729.2), H_2CDNThP (Calcd. 728.84. Found: 729.2), H_2TiNThP (Calcd. 773.84. Found: 774.1), H_2TaNThP (Calcd. 818.84. Found: 819.1).

Table 2
^{1}H NMR spectral data[a,b] of nitroporphyrins in deuteriated $CHCl_3$ (ppm).

Porphyrin	Imino H	Pyrrole β-H	Thienyl H	Methyl H
H_2ThP	−2.64, s, 2H	9.07, s, 8H	7.51, dd, 4H (b,e,h,k) 7.86, d, 4H (a,d,g,j) 7.92, d, 4H (c,f,i,l)	–
NiNThP	–	8.884–9.005, sm, 8H	7.410–7.437, asm, 3H (e,h,k) 7.672–7.682, d, 1H (b) 7.734–7.745, d, 3H (d,g,j) 7.764–7.785, d, 3H (f,i,l) 8.223–8.233, d, 1H (c)	–
$H_2$5MeThP	−2.61, s, 2H	9.09, s, 8H	7.14–7.15, d, 4H (b,e,h,k) 7.66–7.67, d, 4H (c,f,i,l)	2.81, s, 12H
Ni4N5MeThP	–	8.704–8.716, d, 2H 8.996–9.023, asm, 6H	7.044–7.052, asm, 3H (e,h,k) 7.468–7.486, asm, 3H (f,i,l) 7.702–7.704, s, 1H (c)	2.728–2.737, asm, 12H
$H_2$3MeThP	−2.62, s, 2H	8.91–9.09, m, 8H	7.30–7.32, dd, 4H (b,e,h,k) 7.71–7.72, dd, 4H (a,d,g,j)	2.09–2.17, m, 12H
NiN3MeThP	–	8.737–9.06, asm, 7H	7.146–7.226, asm, 4H (b,e,h,k) 7.651–7.66, asm, 4H (a,d,g,j)	2.169, s, 12H
H_2SNThP	−2.658, s, 2H	9.005–9.111, sm, 8H	7.511–7.53, asm, 3H (e,h,k) 7.866–7.887, asm, 4H (b,d,g,j) 7.926–7.934, d, 3H (f,i,l) 8.32–8.33, d, 1H (c)	–
H_2TDNThP	−2.704, s, 2H	9.02–9.13, sm, 8H	7.52–7.54, dd, 2H (e,k) 7.87–7.88, d, 2H (b,h) 7.89–7.91, dd, 2H (d,j) 7.93–7.95, dd, 2H (f,l) 8.33–8.34, d, 2H (c,i)	–
H_2CDNThP	−2.692, s, 2H	9.02–9.13, sm, 8H	7.52–7.54, dd, 2H (h,k) 7.87–7.88, d, 2H (b,e) 7.89–7.90, dd, 2H (g,j) 7.93–7.94, dd, 2H (i,l) 8.33–8.34, d, 2H (c,f)	–
H_2TiNThP	−2.743, s, 2H	9.04–9.15, sm, 8H	7.554–7.563, dd, 1H (k) 7.892–7.905, asm, 3H (b,e,h) 7.92–7.936, dd, 1H (j) 7.953–7.964, dd, 1H (l) 8.34–8.36, asm, 3H (c,f,i)	–
H_2TaNThP	−2.82, s, 2H	9.12, s, 8H	7.91, d, 4H (b,e,h,k) 8.39, d, 4H (c,f,i,l)	–

[a] sm, symmetric multiplet like; asm, asymmetric multiplet like; s, singlet; d, doublet; dd, doublet of doublet; m, multiplet.

[b] Position of proton in parenthesis, refer Fig. 1.

Table 3
Summary of crystallographic details of NiN3MeThP.

Empirical formula	$C_{40}H_{27}N_5NiO_2S_4$	
Formula weight	796.62	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	$a = 24.7587(9)$ Å $b = 11.4258(4)$ Å $c = 12.6142(4)$ Å	$\alpha = 90^\circ$ $\beta = 96.575(3)^\circ$ $\gamma = 90^\circ$
Volume	3544.9(2) Å3	
Z	4	
Density (calculated)	1.493 Mg/m3	
Absorption coefficient	3.354 mm−1	
$F(000)$	1640	
Crystal size	0.52 mm × 0.35 mm × 0.12 mm	
Theta range for data collection	5.24–75.46°	
Index ranges	$-31 \le h \le 29$, $-14 \le k <= 9$, $-15 \le l <= 13$	
Reflections collected	13468	
Independent reflections	7108 [R(int) = 0.0472]	
Completeness to theta = 67.50°	100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.26805	
Refinement method	Full-matrix least-squares on $F2$	
Data/restraints/parameters	7108/130/513	
Goodness-of-fit on $F2$	1.073	
Final R indices [$I > 2$ sigma(I)]	R1 = 0.0763, wR2 = 0.2076	
R indices (all data)	R1 = 0.0942, wR2 = 0.2226	
Largest diff. peak and hole	0.653 and −0.517 e Å−3	

2.4. *X-ray crystallography*

The dark brown colored irregular plate shaped single crystals of NiN3MeThP suitable for the X-ray structure analysis was obtained by the diffusion of methanol into a solution of the compound in chloroform. X-ray diffraction results were obtained with an Oxford Diffraction Gemini-R diffractometer equipped with graphite-monochromated Mo Kα radiation. The structure was solved by the direct method and refined by full-matrix least-squares analysis using anisotropic thermal parameters for nonhydrogen atoms with the SHELXL-97 program [33,34]. Details of the crystal parameters, data collection, and refinements are summarized in Table 3. The crystallographic data of NiN3MeThP was deposited with the Cambridge Crystallographic Data Centre and supplementary publication number is CCDC 840586.

3. Results and discussion

As the a_{2u} orbital has electron density contribution from imino nitrogen and *meso* carbon, and a_{1u} has the same from β-carbon, it is found that nitration of the Cu(II) and Ni(II) derivatives of porphyrin using cupric nitrate generally ensures nitration at the pyrrole β-position [27,28]. In the case of *meso* 2′-thienylporphyrins, susceptibility for β-nitration is even higher owing to the presence of electron withdrawing thienyl groups at the *meso* position which can further lift the degeneracy of the HOMO [35]. The same was observed in the nitration of *meso tetrakis*(5′-halothien-2′-yl)porphyrins [20]. In the present work, in an effort to understand the position of nitration on the thienylporphyrins, the compound NiThP (in which the carbon next to sulfur on the thienyl group can be substituted) has been nitrated using one equivalent of cupric nitrate trihydrate in acetic anhydride. The reagent was added dropwise over a period of 20 min and the nitration took place only under refluxing conditions. The reaction was monitored by thin layer chromatography (TLC) and the formation of the product was indicated by the appearance of red colored band on the TLC plate. The reaction was quenched by adding water when it indicated completion on the TLC plate and the product was purified by column chromatography.

The UV–vis spectrum of the above nitrated porphyrin did not show any shift in the Soret band compared to that of parent compound, NiThP (Table 1). However, on mononitration using cupric nitrate, tetrabromothienyl- and tetrachlorothienyl-porphyrins showed a shift of ∼14 nm of the Soret band [20] of the porphyrin (β-nitration took place). This led us to synthesize H_2SNThP, for a comparison, by following a variant of the procedure reported by Lindsey et al. using a mixture of aldehydes; thiophene-2-carboxaldehyde and 5-nitrothiophene-2-carboxaldehyde [32]. H_2SNThP (second fraction from the reaction mixture eluted on the column) showed a similar UV–vis pattern as that of H_2ThP. Also, the nickel incorporated H_2SNThP (i.e. NiSNThP) showed similar spectral pattern as that of the mononitrated sample using cupric nitrate. This shows that the nitration has taken place on the *meso* thienyl ring (NiNThP) and not at the generally expected pyrrole β-position while using $Cu(NO_3)_2$ as the nitrating agent. In order to confirm the position of nitration, ^{1}H NMR spectra were recorded for both H_2SNThP (modified Lindsey procedure) and the nitrated sample, NiNThP (Fig. 2). Both spectra showed similar spectral pattern (with metallated sample showing relatively upfielded signals). This indicated the formation of *meso* 5-(5′-nitrothien-2′-yl)-10,15,20-*tris*(thien-2′-yl)porphyrinato nickel (II), NiNThP on nitrating NiThP with $Cu(NO_3)_2$ (Table 2). i.e. it is found that NiSNThP and NiNThP obtained from different synthetic routes are the same.

In order to see the effect of orientation of the thienyl rings at the *meso* position on the site of nitration, 5′- and 3′-methyl derivatives of tetrathienylporphyrins, Ni5MeThP and Ni3MeThP have been mononitrated under similar conditions using cupric nitrate. We had expected β-nitration on Ni5MeThP as the fifth position on the thienyl ring is blocked in this molecule. At the same time, nitration at the fifth position of the thienyl ring in Ni3MeThP was expected as this position is available. Also, this position is prone to electrophilic substitution reactions in five membered heterocyclic compounds. Therefore, a high red shift of the Soret band for Ni5MeThP and no significant shift of the same for Ni3MeThP were expected on mononitration. Interestingly, UV visible spectral data showed a different result. There was a significant red shift of Soret band (14 nm) on introducing a nitro group on Ni3MeThP whereas no shift for the same in Ni5MeThP (Table 1). The electronic spectral behavior of Ni5MeThP on mononitration is similar to that of NiThP where there was no shift of Soret band on introducing the nitro group on the thienyl ring. The electronic communication [36] due to the nitro group is more for Ni3MeThP as evidenced from full width at half maximum (FWHM) values.

The above electronic spectral results can be explained on comparing the ^{1}H NMR spectra of the synthesized compounds. From the ^{1}H NMR spectrum, it is found that in Ni3MeThP (in which the methyl groups are pointing towards the porphyrin core and also hindering the thienyl groups to come in conjugation with the porphyrin π-system), the nitration has taken place at the pyrrole β-position (Table 2). But in the case of Ni5MeThP (in which the methyl groups are pointing away from the porphyrin core and not hindering the thienyl rings to come in conjugation with the porphyrin π-system), the ^{1}H NMR spectrum (Fig. 3 and Table 2) indicated that the mononitration has taken place on one of the thienyl rings (at the 4′-position). These results show that the orientation of the thienyl ring is the deciding factor of position of nitration. In the case where no extended conjugation is possible for the thienyl ring with the porphyrin π-system, nitration has taken place at the pyrrole β-position (NiN3MeThP). But in Ni5MeThP, where better conjugation is possible both due to the absence of hindering group at the

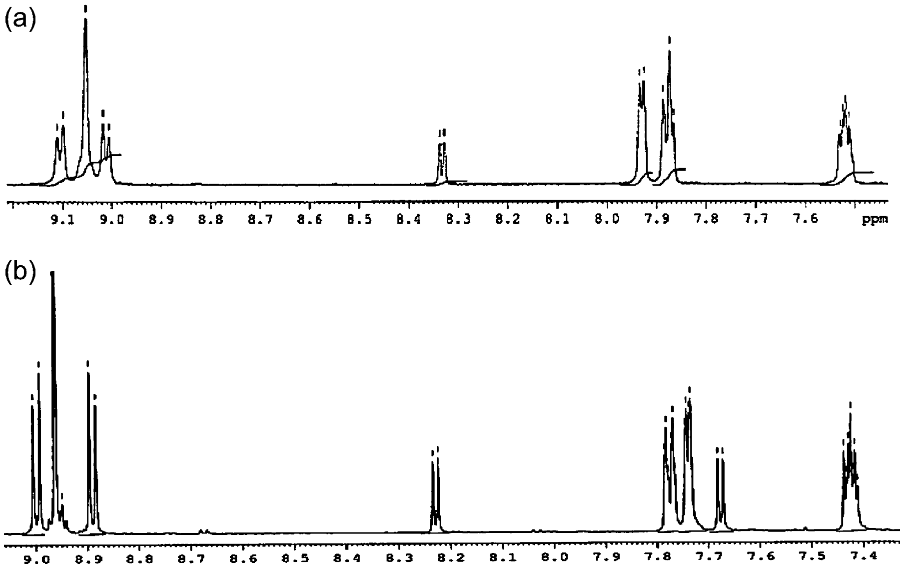

Fig. 2. ^{1}H NMR spectra of (a) *meso* mononitrothienylporphyrin, H2SNThP (modified Lindsey method) and (b) nickel derivative of mononitrated *meso* nitrothienylporphyrin, NiNThP (this work).

3′-position of thienyl ring and due to the smaller size of the thienyl ring (compared to that of phenyl group in tetraphenylporphyrin), the nitration had taken place at the 4′-position of one of the thienyl rings (Ni4N5MeThP). This shows that the electronic requirement for the electrophilic substitution by nitro group on thienyl ring is satisfied in Ni5MeThP due to its relatively better conjugation with porphyrin core when compared to that in Ni3MeThP. The effect due to the methyl groups is expected to be the same on both compounds.

To confirm the site of nitration by X-Ray diffraction technique, we tried to crystallize the compounds. We were successful in solving the crystal structure of NiN3MeThP. In the structure of NiN3MeThP, the usual ruffling of the saddle type [37–39] as indicated by the deviations of C5, C10, C15 and C20 from the NiN_4 plane [C5 (0.481 Å), C10 (−0.485 Å), C15 (0.496 Å), C20 (−0.497 Å)] was observed (Fig. 4). Ni-N bond lengths are in the normal range for low spin Ni(II) porphyrins ranging from 1.918(3) Å to 1.934(3) Å [40]. While the structure contains two disordered thiophene rings (as is typically found for such substituents [41,42]), there is no disorder in the rest of the molecule and the position of the nitro substituent in the molecule is clearly established.

The ^{1}H NMR spectra of the nitrothienylporphyrins obtained from the synthesis using mixture of thiophenealdehydes were also compared to see the effect of number of nitro groups on the electronic properties of the molecules. A downfield shift of NH resonance was expected with the increase in the number of nitrothienyl rings at the porphyrin periphery (*meso* position). Interestingly, the imino hydrogen signals of the thienylporphyrins are shifted towards the shielded region with increase in the number of nitrothienyl groups (Table 2). This indicates that, as the number of nitro groups increases, there is an increased ring current (possibly due to the lesser dihedral angle of the thienyl groups with the porphyrin core) that makes the NH to resonate at a higher field. This chemical shift is nearly linear with respect to the number of nitrothienyl groups (Fig. 5). The NH signals of *cis* and *trans* did not show a noticeable difference in their spectrum. The signal corresponding to the β-pyrrole protons of the mono- (Fig. 2a), di- [both *trans*- (Fig. 6a) and *cis*- (Fig. 6b)] and tri- (Fig. 6c) *meso* nitrothienyl substituted compounds were symmetric multiplet like in nature which indicated the symmetry in the molecule. Free base of all *meso* nitrothienylporphyrins showed typical porphyrinic UV–vis spectrum comprising of four Q bands with decreasing order of intensity and an intense Soret band. There is a gradual increase in the

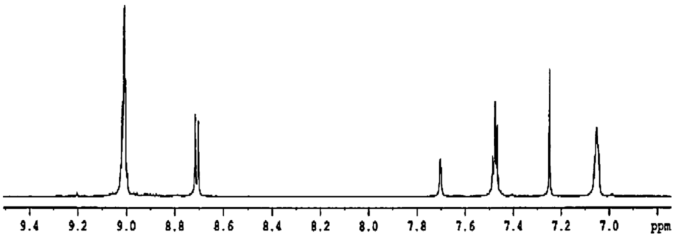

Fig. 3. Aromatic region in the ^{1}H NMR spectrum of Ni4N5MeThP recorded in deuteriated $CHCl_3$.

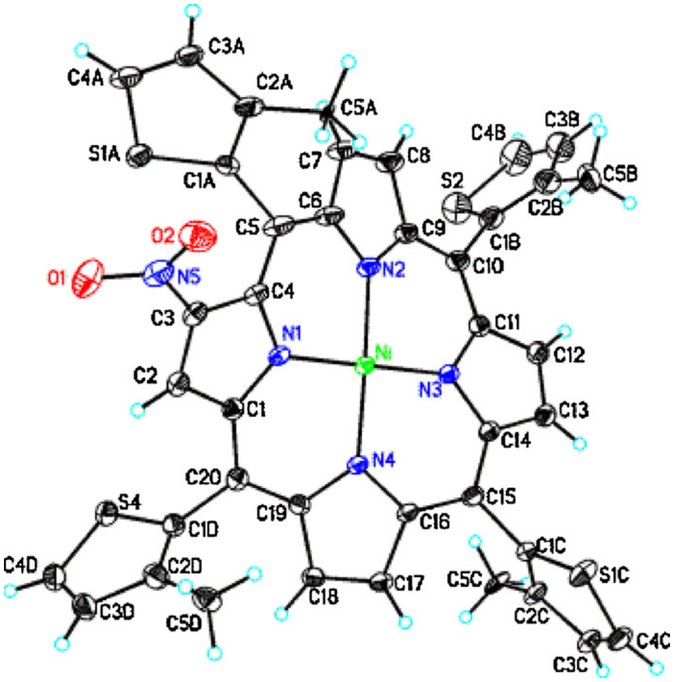

Fig. 4. Molecular structure of NiN3MeThP at 50% thermal ellipsoidal probability.

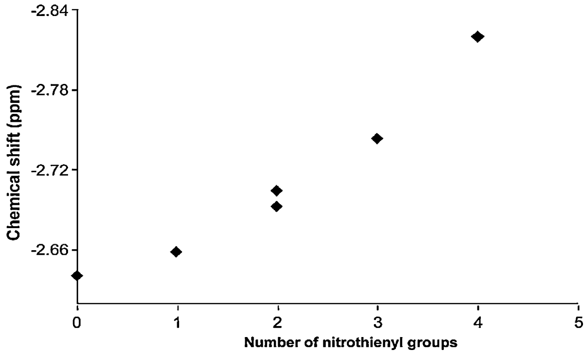

Fig. 5. Plot of variation of the chemical shift of imino hydrogens in the ^{1}H NMR spectra *vs* number of nitrothienyl groups present on *meso* nitrothienylporphyrins.

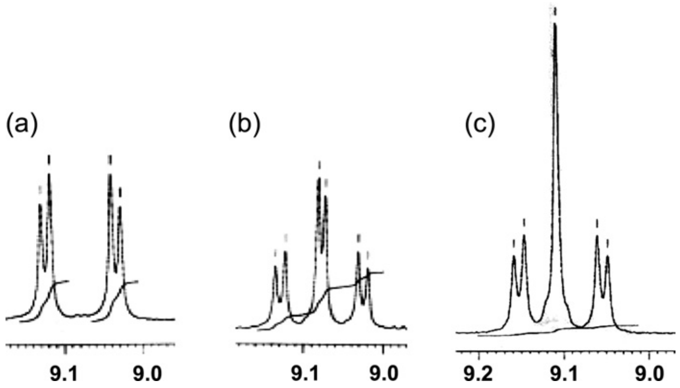

Fig. 6. ^{1}H NMR signal of pyrrole β-protons of (a) $H_2TDNThP$, (b) $H_2CDNThP$, and (c) $H_2TiNThP$.

wavelength of the Soret band absorption on increasing the number of nitrothienyl groups, with isomers $H_2TDNThP$ and $H_2CDNThP$ absorbing at nearly same wavelength. The electronic communication was also found to be increasing with increasing the number of nitrothienyl groups at the *meso* position.

For delineating the effect of number as well as the position of nitro groups on the electronic properties of thienylporphyrins, cyclic voltammetric studies had been carried out and the data is summarized in Table 4. For comparison, the data of the half wave redox potentials of MThP is also given. Porphyrins generally show two, one electron oxidations and two, one electron reductions which are reversible and ligand based in nature. In nitrated thienylporphyrins, the redox potentials are either irreversible or quasireversible in nature. As the number of nitrothienyl groups at the *meso* position of porphyrin increases, the oxidation potential also increases. The magnitude of the reduction potentials was decreased with the increase in the number of nitrothienyl groups; for $H_2TDNThP$, $H_2TiNThP$ and $H_2TaNThP$, the first reduction was irreversible. As for NiThP, electron deficiency of the porphyrin core due to the presence of Ni (II) is reflected in the difference in redox potentials of H_2SNThP (modified Lindsey's procedure) and NiNThP (nitration by cupric nitrate).

Table 4
Half-wave redox potentials[a] (mV) of nitro substituted tetrathienylporphyins in CH_2Cl_2 using 0.1 M $TBAPF_6$ at 25 °C.

Porphyrin	III	II	I	I	II	III
H_2ThP		1130	890	−1090	−1420	
NiThP		1280	1058	-1083^{i}	−1231	
NiNThP		1361	1168	−818		
Ni5MeThP		1082	939	-1132^{i}	−1243	
Ni4N5MeThP		1218	1063	−1063		
Ni3MeThP		1353	1102	−1196		
NiN3MeThP			1369	−874	−1173	-1775^{i}
H_2SNThP	1508^{i}	1330^{i}	1057^{i}	−853	-1536^{b}	
$H_2TDNThP$		1493^{i}	1210^{i}	-943^{i}	−1133	−1427
$H_2CDNThP$		1584^{i}	1254^{i}	−777	−921	−1109
$H_2TiNThP$		1570^{i}	1335^{i}	-837^{i}	-1185^{i}	−1379
$H_2TaNThP$			1442^{i}	-675^{i}	−843	-1340^{i}

i, irreversible.
[a] *Vs* Ag/AgCl electrode.
[b] Values from differential pulse voltammetry.

From Table 4, it is clear that among Ni3MeThP and Ni5MeThP, oxidation of Ni5MeThP is easier. This can be due to the enhanced conjugation of the 5′-methylthienyl rings with the porphyrin core. Reduction potentials also supported the same reason. The nitration at the 4′-position of the thienyl ring (which is generally not the preferred position in the electrophilic substitution reactions of five membered heterocyclic rings) can be ascribed to this electronic conjugation which satisfied the electronic requirement of nitration. Though the number of nitro group is same on the molecules, the electronic nature of Ni4N5MeThP and NiN3MeThP is very different. The presence of electron withdrawing nitro group at the pyrrole β-position made NiN3MeThP very electron deficient. The difference in the oxidation potentials of NiN3MeThP and Ni4N5MeThP is 306 mV. Compared to the respective parent compounds, the influence of nitration is more on the properties of NiN3MeThP (267 mV) than on Ni4N5MeThP (124 mV). The higher electron deficiency of the porphyrin core of NiN3MeThP can be due to the combined effect of the position of the nitro group (at pyrrole β-) and the lack of conjugation of the thienyl ring due to the hindering nature of methyl groups at the 3′-position. Effect of conjugation on the electronic properties was also evident from the NMR study that as the number of 5′-nitrothienyl groups at the *meso* position increases, there was an upfield shift in the imino hydrogen signals.

4. Conclusions

As a part of the study on the properties of unsymmetrical and highly functionalized tetrathienylporphyrins, various nitro substituted thienylporphyrins have been synthesized and their properties have been investigated electrochemically and spectrophotometrically. The method adopted in the present study is a convenient method for the synthesis of *meso* nitrothienylporphyins in high yield, compared to the conventional method of condensing pyrrole with a mixture of aldehydes. The redox potentials of Ni3MeThP and Ni5MeThP showed the role of π-conjugation in deciding the site of electrophilic substitution on the porphyrin. An X-ray crystal structure has clearly established the position of nitro substitution in NiN3MeThP. NMR study also indicated the role of π-conjugation in explaining the observed upfield shift of the imino hydrogen signal with the increase in number of nitrothienyl rings. These results show the potential use of nitrothienylporphyrins in the synthesis of materials for nonlinear optical applications. The study of functionalizing the *meso* thienyl groups with various synthetically potential substituents other than nitro groups is in progress in our laboratory.

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References

[1] K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 6, Academic Press, San Diego, 2000, pp. 133–256.

[2] H. Maruyama, H. Segawa, S. Sotoda, T. Sato, N. Kosai, S. Sagisaka, T. Shimidzu, K. Tanaka, Synth. Met. 96 (1998) 141–149.
[3] R. Friedlein, F. von Kieseritzky, S. Braun, C. Linde, W. Osikowicz, J. Hellberg, W.R. Salaneck, Chem. Commun. (2005) 1974–1976.
[4] N.M. Boyle, J. Rochford, M.T. Pryce, Coord. Chem. Rev. 254 (2010) 77–102 (and the references cited therein).
[5] N. Xiang, Y. Liu, W. Zhou, H. Huang, X. Guo, Z. Tan, B. Zhao, P. Shen, S. Tan, Eur. Polym. J. 46 (2010) 1084–1092.
[6] J. Fortage, J. Boixel, E. Blart, H.C. Becker, F. Odobel, Inorg. Chem. 48 (2009) 518–526.
[7] J. Rochford, S. Botchway, J.J. McGarvey, A.D. Rooney, M.T. Pryce, J. Phys. Chem. A 112 (2008) 11611–11618.
[8] P. Bhyrappa, M. Sankar, B. Varghese, P. Bhavana, J. Chem. Sci. 118 (2006) 393–397.
[9] M. Ghazzali, M.A.M. Abu-Youssef, K. Larsson, Ö. Hansson, A. Amer, T. Tamm, L. Öhrström, Inorg. Chem. Commun. 11 (2008) 1019–1022.
[10] C.O. Paul-Roth, J. Letessier, S. Juillard, G. Simonneaux, T. Roisnel, J. Rault-Berthelot, J. Mol. Struct. 872 (2008) 105–112.
[11] P. Bhyrappa, P. Bhavana, Chem. Phys. Lett. 349 (2001) 399–404.
[12] M. Kelemen, C. Wachter, H. Winter, E. Dormann, R. Gompper, D. Hermann, Mol. Phys. 90 (1997) 407–413.
[13] C. Brückner, P.C.D. Foss, J.O. Sullivan, R. Pelto, M. Zeller, R.R. Birge, G. Crundwell, Phys. Chem. Chem. Phys. 8 (2006) 2402–2412.
[14] A. Ghosh, S.M. Mobin, R. Fröhlich, R.J. Butcher, D.K. Maity, M. Ravikanth, Inorg. Chem. 49 (2010) 8287–8297.
[15] K.M. Kadish, F. D'Souza, A. Villard, M. Autret, E.V. Caemelbecke, P. Bianco, A. Antonini, P. Tagliatesta, Inorg. Chem. 33 (1994) 5169–5170.
[16] P. Bhyrappa, V. Krishnan, Inorg. Chem. 30 (1991) 239–245.
[17] M.K. Tse, Z.-Y. Zhou, T.C.W. Mak, K.S. Chan, Tetrahedron 56 (2000) 7779–7783.
[18] J.-P. Tremblay-Morin, H. Ali, J.E. van Lier, Tetrahedron Lett. 46 (2005) 6999–7002.
[19] O.B. Locos, D.P. Arnold, Org. Biomol. Chem. 4 (2006) 902–916.
[20] R. Prasath, P. Bhavana, J. Heterocycl. Chem., in press, doi:00923.
[21] V.S. Chirvony, A. van Hoek, T.J. Schaafsma, P.P. Pershukevich, I.V. Filatov, I.V. Avilov, S.I. Shishporenok, S.N. Terekhov, V.L. Malinovskii, J. Phys. Chem. B 102 (1998) 9714–9724.
[22] J.F. Bartoli, O. Mansuy, B.-O. Le, K.L.B. Ozette, M. Palacio, D. Mansuy, J. Chem. Soc. Chem. Commun. 82 (2000) 7–828.
[23] A. Sen, V. Krishnan, Tetrahedron Lett. 37 (1996) 5421–5424.
[24] M.J. Crossley, M.M. Harding, C.W. Tansey, J. Org. Chem. 59 (1994) 4433–4437.
[25] M.J. Crossely, L.G. King, J. Org. Chem. 58 (1993) 4370–4375.
[26] E. Fagadar-Cosma, L. Cseh, V. Badea, G. Fagadar-Cosma, D. Vlascici, Comb. Chem. High Throughput Screen. 10 (2007) 466–472.
[27] A. Giraudeau, H.J. Callot, J. Jordan, I. Ezahr, M. Gross, J. Am. Chem. Soc. 101 (1979) 3857–3862.
[28] H.K. Hombrecher, V.M. Gherdan, S. Ohm, J.A.S. Cavaleiro, M. Graca, P.M.S. Neves, M.F. Condesso, Tetrahedron 49 (1993) 8569–8577.
[29] P. Bhavana, B. Varghese, P. Bhyrappa, Acta Crystallogr. C C57 (2001) 252–253.
[30] X. Sun, J. Zhang, B. He, J. Photochem. Photobiol. A: Chem. 172 (2005) 283–288.
[31] M.S. Chorghade, D. Dolphin, D. Dupre, D.R. Hill, E.C. Lee, T.P. Wijesekara, Synthesis (1996) 1320–1324.
[32] J.S. Lindsey, I.C. Schreiman, H.C. Hsu, P.C. Kearney, A.M. Marguerettaz, J. Org. Chem. 52 (1987) 827–836.
[33] G.M. Sheldrick, SHELXS-97, Program for Crystal Structures Solution, University of Göttingen, Göttingen, Germany, 1997.
[34] G.M. Sheldrick, SHELXL-97, Program for Crystal Structures Refinement, University of Göttingen, Göttingen, Germany, 1997.
[35] A. Wickramasinghe, L. Jaquinod, D. Nurco, K.M. Smith, Tetrahedron 57 (2001) 4261–4269.
[36] P. Bhyrappa, K.S. Suslick, J. Porphyr. Phthalocyanines 2 (1998) 391–396.
[37] J.L. Hoard, in: K.M. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1975, pp. 317–380.
[38] L.D. Sparks, C.J. Medforth, M.S. Park, J.R. Chamberlain, M.R. Ondrias, M.O. Senge, K.M. Smith, J.A. Shelnutt, J. Am. Chem. Soc. 115 (1993) 581–592.
[39] J.A. Shelnutt, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 7, Academic Press, New York, 2000, pp. 167–223.
[40] Y. Song, R.E. Haddad, S.-L. Jia, S. Hok, M.M. Olmstead, D.J. Nurco, N.E. Schore, J. Zhang, J.-G. Ma, K.M. Smith, S. Gazeau, J. Pecaut, J.-C. Marchon, C.J. Medforth, J.A. Shelnutt, J. Am. Chem. Soc. 127 (2005) 1179–1192.
[41] P. Wagner, D.L. Officer, M. Kubicki, Acta Crystallogr. E63 (2007) o3054–o3055.
[42] P. Wagner, D.L. Officer, M. Kubicki, Acta Crystallogr. C63 (2007) o400–o404.