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Novel nitrothien-2-ylporphyrins: Spectroscopic and electrochemical investigation on the role of conformation of porphyrins in their reactions

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ABSTRACT

An efficient and facile methodology for the regioselective nitration of two series of thien-2-ylporphyrins, 5,10,15,20-*tetrakis*(thien-2-yl)porphyrinato nickel(II) and 5,10,15,20-*tetrakis*(5-methylthien-2-yl)porphyrinato nickel(II) is presented. X-ray crystal structures of a few of the synthesized compounds are given. The effect of relative orientation of *meso* thien-2-yl rings with the porphyrin central π-system in determining the site of electrophilic substitution on these molecules is explained through electronic spectroscopy and cyclic voltammetry. The results indicate the important role of conformation of the porphyrin in their subsequent reactions.

1. Introduction

The high versatility of the stable porphyrin framework to allow for further functionalisation and the ease of accommodation of various metal ions of different size and coordination properties, along with unusual physicochemical properties, has increased interest in porphyrins in various fields like biomimetics [1], catalysis [2], sensors [3,4] and supramolecular chemistry [5]. Further, as porphyrins and their derivatives are also one of the most important classes of compounds found in many biological systems, research directed towards functionalising porphyrins for use in the fields of medicine, catalysis, organoelectronics, etc. continues to attract attention. In particular, the facile ability to synthesize a large number of functionalized derivatives makes the simplest *meso* tetraphenylporphyrin highly interesting [6]. Functionalisation can be carried out on the various *meso* phenyl positions, at the pyrrolyl β-position or even on the nitrogen of the N–H group at the core of the molecule [7]. Compared to that exerted at the β-position, the influence of substituents on the *meso* phenyl rings has less impact on the electronic properties of the porphyrin framework. This is expected due to the near perpendicular orientation of the phenyl ring with respect to the porphyrin core in the energy preferred form which limits the conjugation between the two π-systems. It is possible to append other aromatic systems to the *meso* position, especially groups smaller than phenyl rings. Thus, there are reports in literature describing porphyrins with five-membered heteroaryl groups such as furyl [8], pyrazolyl [9], imidazolyl [10], pyrrolyl [11] etc. In these compounds, along with the smaller size of the *meso* substituent, the presence of heteroatom also imparts specific properties to the porphyrin, e.g. in their self- assembling properties [12]. Major on-going work in this field revolves around various derivatives of *meso* thienylporphyrins as they are relatively easy to synthesize and are comparatively stable [13]. The presence of the thienyl group in many photovoltaic systems enhances research into thienylporphyrins [14]. Thus, various thien-2-yl- and thien-3-yl-porphyrin derivatives have been widely studied for their energy- and electron-transfer properties [15], for ultra thin film formation [16,17], in electrocatalysis [18], for the detection of explosives [19], as biosensors [20] and in the study on the structural factors determining the morphology of different nano structures [21].

Porphyrins are generally functionalized at their periphery with nitro [22,23], formyl [24] and bromo [25,26] groups for subsequent utilization in the synthesis of asymmetric and highly functionalized derivatives. Other than the nucleophilic substitution [27] and addition [28] reactions, a nitro group on porphyrins can be reduced to amine for subsequent reactions [29]. For the synthesis of nitroporphyrins, there are different nitrating agents employed for

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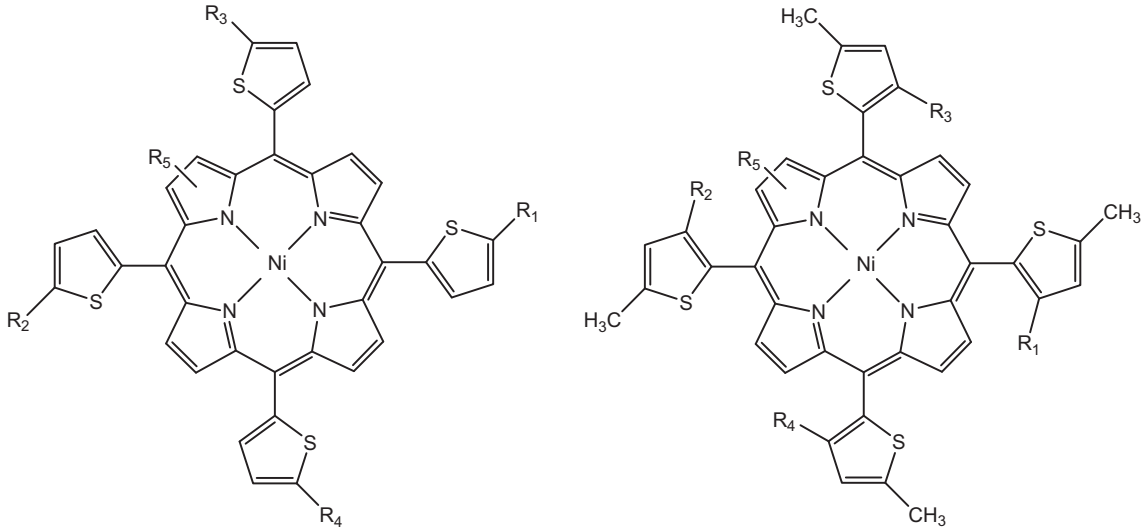

ThP	$R_1 = R_2 = R_3 = R_4 = R_5 = H$
$(N)_1$ThP	$R_1 = NO_2$, $R_2 = R_3 = R_4 = R_5 = H$
***t*-$(N)_2$ThP**	$R_1 = R_2 = NO_2$, $R_3 = R_4 = R_5 = H$
***c*-$(N)_2$ThP**	$R_1 = R_3 = NO_2$, $R_2 = R_4 = R_5 = H$
$(N)_3$ThP	$R_1 = R_2 = R_3 = NO_2$, $R_4 = R_5 = H$
$(N)_3(\beta\text{-}N)_1$ThP	$R_1 = R_2 = R_3 = R_5 = NO_2$, $R_4 = H$

5MeThP	$R_1 = R_2 = R_3 = R_4 = R_5 = H$
5Me$(N)_1$ThP	$R_1 = NO_2$, $R_2 = R_3 = R_4 = R_5 = H$
5Me$(N)_2$ThP	$R_1 = R_2 = NO_2$, $R_3 = R_4 = R_5 = H$
5Me$(N)_3$ThP	$R_1 = R_2 = R_3 = NO_2$, $R_4 = R_5 = H$
5Me$(N)_4$ThP	$R_1 = R_2 = R_3 = R_4 = NO_2$, $R_5 = H$
5Me$(N)_2(\beta\text{-}N)_1$ThP	$R_1 = R_2 = R_5 = NO_2$, $R_3 = R_4 = H$
5Me$(N)_3(\beta\text{-}N)_1$ThP	$R_1 = R_2 = R_3 = R_5 = NO_2$, $R_4 = H$

Fig. 1. Chemical structures of nitro-substituted thien-2-ylporphyrins.

regiospecific nitration reactions. Examples of nitrating agents include NO_2 [30], N_2O_4 [31], fuming nitric acid [23], $AgNO_2/I_2$ [32], nitrating mixture [33], $[NO_2]BF_4$ [34], $NOBF_4$ [35], $NaNO_2$ [36] and cupric nitrate [37]. Cupric nitrate trihydrate is a very attractive nitrating agent as it is readily available, easy to handle, and known to introduce the nitro group at the pyrrolyl β-position of tetraphenylporphyrin, especially when the central metal ion is Cu(II) or Ni(II) [38].

In our recent report on the synthesis of asymmetric 5-bromo- and 5-chloro-*meso* thien-2-ylporphyrins, with a nitro group at the β-position, the porphyrin precursor was nitrated with cupric nitrate [39]. As the central metal ion was Cu(II) and as the *meso* groups are electron-withdrawing owing to the presence of bromo- and chloro- groups on the thien-2-yl ring, β-nitration was observed, as expected. In addition, the normally most susceptible position for electrophilic substitution on the heterocyclic ring, i.e. the fifth position, was blocked which also directed the nitration to the β-position. In order to find out the exact reason which dictates the site of nitration, i.e. whether it is the non-availability of the fifth position on the thien-2-yl ring or it relates to the electronic nature of the ligand, we performed similar nitration reactions on two isomeric compounds, *meso*-3-methylthien-2-yl- and *meso*-5-methylthien-2-yl-porphyrins [40]. The results obtained in that study illustrated the role of extended conjugation of the porphyrin π-system with the *meso* thien-2-yl rings in determining the site of nitration. To gain further insight into this aspect of thien-2-yl-porphyrin chemistry, in the present work, we have carried out a series of nitration (mono- to poly-nitration) reactions on two related molecules. Our first aim was to carry out mono-, di- and tri-nitration of thien-2-yl-porphyrin in good yields so that the resulting porphyrins can be used as precursors for further functionalisation due to their potential stability and efficiency in dye-sensitized solar cells. Complementing this aim was the motivation to explore the effect of the relative orientation of the thien-2-yl ring attached to the porphyrin core in dictating the site of electrophilic substitution. The chemical structures of the compounds investigated in the present study, namely 5,10,15,20-*tetrakis*(thien-2-yl)porphyrinato nickel(II), hereafter ThP, and 5,10,15,20-*tetrakis*(5-methylthien-2-yl)porphyrinato nickel(II), 5MeThP, and the various products formed during the nitration are given in Fig. 1.

2. Experimental

2.1. Materials

Dichloromethane (SD Fine Chemicals, India) was refluxed and distilled over CaH_2 and stored over 4 Å molecular sieves. Pyrrole, thiophene-2-carboxaldehyde, 5-methylthiophene-2-carboxaldehyde and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were procured from Sigma–Aldrich. Other chemicals were purchased from SD Fine Chemicals, India. Both *meso tetrakis*(thien-2-yl)porphyrin [41] and *meso tetrakis*(5-methylthien-2-yl)porphyrin [42] were prepared by following the reported procedures. The products were confirmed by spectroscopy. The Ni(II) complexes were prepared by reacting a stoichiometric amount of nickel acetate tetrahydrate with these free bases in dimethylformamide [43].

2.2. Methods

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in deuterated 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. A BAS EPSILON model electrochemical system was employed for the cyclic voltammetric measurements. The electrochemical cell comprises a three electrode cell assembly with a platinum working electrode, an Ag/AgCl reference electrode and a platinum wire auxiliary electrode. The concentrations of all the porphyrins employed were ~1 mM. All measurements were performed in CH_2Cl_2 solution which was purged with nitrogen, and