



Role of conformational and electronic effects on various thienylporphyrinic ionophores in the detection of metal ions – A potentiometric investigation



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ARTICLE INFO

Article history:

Received 24 March 2017

Received in revised form

25 August 2017

Accepted 26 August 2017

Available online 28 August 2017

Keywords:

Conformation

Extended conjugation

Substituent

Potentiometry

Solid contact ion selective electrode

Ionophore

ABSTRACT

An attempt of correlating the conformation of the derivatives of free base *meso*-thien-2-ylporphyrin with their performance as ionophores in sensing metal ions (potentiometric investigation) is made in the present work. The porphyrins were synthesized by following the condensation of pyrrole with corresponding aldehyde in Lewis acidic medium. The orientation of the 3- or 5- substituted (bromo- or methyl-) thien-2-yl- group at the *meso*-position of the porphyrin dictates their conformation. The molecule with a better electron delocalization due to the near planarity of the *meso*-ring has showed better activity as ionophore (porphyrin with 5-bromothien-2-yl- vs 3-bromothien-2-yl-). The role of the position of the substituent is investigated by comparing the results obtained for porphyrins with 5-bromothien-2-yl- and 4-bromothien-2-yl- at the *meso*-positions. The importance of resonance due to the electron delocalization from the substituent to the porphyrin core is evident on comparing the results obtained for porphyrin with 5-bromothien-2-yl and 5-methylthien-2-yl groups.

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1. Introduction

The attractiveness of porphyrins in research comes from their ease of synthesis, versatile functionalisation, feasibility of incorporating variety of metal ions of different coordination number and oxidation state and, presence of imino hydrogens (-NH) in the free base form which are very prone to interact with different species in neutral condition, on acidification of the core and/or on making the molecule nonplanar. Many of the properties of the porphyrins and related molecules in biology are dictated by their conformation [1]. Conformation of the core has a high influence also on the properties of man-made systems (like in catalysis and NLO properties). However, the aspect of conformation of porphyrins is not explored in the field of ion selectivity.

Stripping voltammetry using modified electrodes is a widely used electrochemical technique for the detection and quantification of metal ions [2,3]. Compared to stripping voltammetry, potentiometry using ion selective electrodes (ISEs) is a relatively simple technique which also is often employed for sensing metal

ions and anions [4]. The success of molecules as ionophores in ISE depends mainly on its lipophilicity and its extent of interaction with the analyte. Present days, more attention is given to solid contact ion selective electrodes (SCISE) than the conventional liquid membrane ISE which is relatively difficult to handle [5,6].

Conformation of the porphyrin is dictated by size of the metal ion at the centre and the size and/or shape of the substituents (leading to steric crowding) at the periphery. The effect of the type of substituents on the porphyrin and their size in the potentiometric sensing is reported by Chaniotakis et al. [7]. Shamsipur et al. has employed perbromoporphyrin (porphyrin with nonplanar core due to the crowding of sterically bulky groups) for detection of thiocyanate ion [8]. The article by Seo et al. has used a sterically crowded tetraphenylporphyrins (with *o*-phenyl- substitution) for the sensing of thiocyanate [9].

The number of articles on sensing of metal ions using porphyrins as ionophores is very limited in literature and to the best of our knowledge, there is no article on the conformational dependence of potential variations in the sensing of cations. One of the main reasons for employing porphyrins as candidates for ionophores in the sensing of metal ions is the availability of their core which is known for accommodating varieties of metals ions of different size and coordination numbers. Gupta et al. has reported the sensing of

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Zn(II) based on the ionophores protoporphyrin IX [10] and protoporphyrin IX dimethyl ester [11]. Jain et al. has reported Zn(II) sensing using hematoporphyrin IX as the ionophore [12]. Sensing of Zn(II) ion using free base tetraphenylporphyrin was reported by the members in the above mentioned two research groups [13]. Gupta et al. has also reported a Cu(II) sensor. The porphyrin is in free base form in this case with silicon containing group on the phenyl ring at the *meso*-position [14]. Singh and Bhatnagar have reported carboxylated and methylated porphine based Ni(II) sensor [15]. Other Ni(II) sensing based on free base porphyrins are using tolyl- and 4-[tris-(4-allyldimethylsilyl-phenyl)-silyl]-phenyl- containing porphyrins [16,17]. Other reports found in literature are for Pb(II) [18], Ag(I) [19], Cu(II) [20], Fe(III) [21,22] ions and for Ag(I), Pb(II) and Cu(II) ions together [23].

The interaction between the heavy metal ions and functional groups containing soft base centres like N, S, Se and P are known for decades. Ionophores with these atoms are employed in the detection of heavy metal ions. A few of the recent reports on sulfur containing molecules which acted as ionophores (with a possible interaction with the metal ion under investigation) are for Cu(II) [24], Hg(II) [25], Ag(I) [26] and Ho(III) [27] ions. However, to the best of our knowledge, none of the porphyrin based ionophore having sulfur interacting with metal ion is reported. The sulfur atom of the thienyl group can have a favorable interaction with heavy metal ions like cadmium, mercury and lead.

Though polarity of the porphyrin will increase on changing the *meso*-phenyl group with heteroaryl groups like thienyl, imidazolyl, pyrazolyl, pyrrolyl etc., the role of conformation is expected to favourably influence the interaction of metal ions with these porphyrins. There is enhanced and favorable electron delocalization present in these porphyrin owing to the less hindrance felt at the *meso*-position(s) by the smaller rings (i.e., the five-membered heteroaryl compared to phenyl). Studies have shown that there is a considerable influence of conformation of the porphyrin as a whole [1] as well as the orientation of the *meso*-group with respect to the central macrocycle [28–31] in dictating the properties. Nitration reaction of many conformationally different thienyl-substituted porphyrins have been investigated by the author and is found that conformation has a very important role in deciding the site of electrophilic substitution [32–34]. No report is present in literature on the performance of thienyl- or other five-membered heteroaryl-substituted porphyrin in the detection and quantification of metal ions. Many of the molecular recognition reported are based on the electrostatic (especially hydrogen bonding) interaction of the analyte with the host molecule. Though there is no specific hetero atom present on the phenyl ring to make it suitable for interacting with metal ion, phenylporphyrin is found to act as good ionophore.

In the present work, an attempt is made to correlate the potentiometric sensing activity (using solid contact electrode) of derivatives of thien-2-ylporphyrins with their conformation. The chemical structures of the compounds under investigation are given in Fig. 1.

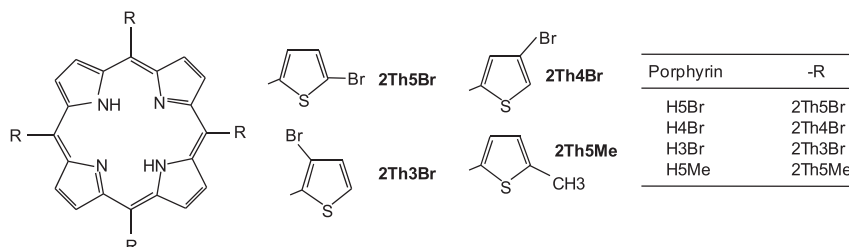


Fig. 1. Chemical structure of the free base porphyrins.

Table 1
UV visible absorption spectral data^a (in nm) of various porphyrins in CH₂Cl₂.

Porphyrin	Soret Band	Q Bands
H5Br	429 (5.55)	524 (4.23), 562 (3.91), 597 (3.76), 658 (3.22)
H4Br	425 (5.39)	520 (4.26), 558 (3.95), 595 (3.61), 655 (3.23)
H3Br	424 (5.26)	518 (4.18), 550 (3.89), 594 (3.71), 649 (3.19)
H5Me	431 (5.50)	526 (4.14), 567 (3.98), 597 (3.77), 662 (3.49)

^a The values in parenthesis refer to log_e values, ϵ in dm³mol⁻¹cm⁻¹.

2. Experimental

2.1. Materials and methods

Pyrrole, 3-bromo-2-thiophenecarboxaldehyde, 4-bromo-2-thiophenecarboxaldehyde, 5-bromo-2-thiophenecarboxaldehyde, 5-methyl-2-thiophenecarboxaldehyde, triethylamine, dichlorodicyanobenzoquinone (DDQ), hexamine, sodium tetraphenylborate (NaTPB), tetraoctylammonium bromide (TOABr), PVC (high molecular weight) and *o*-nitrophenylether (*o*-NPOE) were procured from Sigma–Aldrich. Other required chemicals were purchased from Merck and *sd* fine chemicals. All the commercial compounds are of high purity.

¹H NMR spectra were recorded on a Bruker Avance (400 MHz) in deuteriated chloroform (CDCl₃) using tetramethylsilane as the internal standard. Optical absorption spectra were recorded (in dichloromethane) on a JASCO V-770 model UV–Vis/NIR spectrophotometer using quartz cells of 1 cm path length. Electrospray mass spectra were recorded on a 410 Prostar Binary LC with 500 MS IT PDA Detectors, Varian Inc, USA mass spectrometer.

The potentiometric measurements were carried out using BAS Epsilon model electrochemical work station. The reference electrode used is Ag/AgCl electrode and the electrode used for preparing solid contact electrode is glassy carbon electrode. pH measurements were done using ELICO LI -120 pH meter. Nitrate salt of the metal ions was used for the measurements. Hexamine and HNO₃ were used for adjusting the pH of aqueous solution of different metal nitrates.

2.2. Synthesis

The procedure for the synthesis of H3Br is given below. Similar procedure is followed for the synthesis of other porphyrins using the corresponding aldehyde and is reported [30,35]. UV visible spectral details of all the porphyrins in Table 1.

Synthesis of 5,10,15,20-tetrakis (3-bromothien-2-yl)porphyrin, H3Br:

To a mixture of 3-bromo-2-thiophenecarboxaldehyde (0.57 mL, 5.2 mmol) in 300 mL of dichloromethane, pyrrole (0.36 mL, 5.2 mmol) was added under N₂ atmosphere. To this, BF₃ etherate (0.22 mL, 1.7 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. At the end of the period, DDQ (1.18 g, 5.2 mmol) was added and the stirring was continued for

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