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Electronic and conformational features of *meso*-5-aminothien-2-ylporphyrins and its ferrocene coupled dyad and triads

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ABSTRACT

The role of conformation of the linker groups at the *meso*-position of *meso*-(5-aminothien-2-yl)porphyrins and its ferrocene coupled dyad and triads on the electronic, electrochemical and photophysical properties has been investigated. An efficient and facile methodology is adopted for the synthesis of 5-aminothien-2-ylporphyrins and their ferrocene appended dyad and triads. The possible nearly in-plane arrangement of the thien-2-yl ring with the porphyrin π-system influences the role of ferrocene moiety on the fluorescence behaviour of porphyrin macrocycle. The present study supports the presence of interaction between ferrocene and porphyrin units in their thien-2-yl bridged conjugates.

1. Introduction

Synthesis of porphyrins containing redox active sites is an important area in research owing to the application of these types of porphyrins in the field of sensors and biomimetics [1]. One of the important classes of redox active site is ferrocene [2–6] due to the presence of electrochemically active iron in it. Ferrocene containing BODIPY and pyrazabole are extensively studied for donor–acceptor properties [7,8]. In the reported porphyrin – ferrocene conjugates, it is found that ferrocene moiety got connected to the porphyrin central π-system at pyrrole β-position through spacers like ethynyl and ethynylphenyl groups [9,10], directly at the *meso*-position [11–19], through ether group in between *meso*-phenyl and ferrocene [20] etc. Also found reports on ferrocenyl group bound to the central metal ion of porphyrin axially [21] as well as on porphyrin dimer linked through ferrocenyl moiety [22]. These ferrocene appended porphyrins are found to be potential candidates as sensors [23,24].

The choice of linker groups is important more in the case of porphyrins where the ferrocenyl group is appended indirectly at the *meso*-position. This is because the interaction between the porphyrin macrocycle and the redox active site should be very significant if it has to be used as redox switches. Appending groups on the phenyl rings at the *meso*-position has been studied by many research groups [25,26]. Studies have shown that a group which is sterically less demanding than a phenyl group can be a good candidate to be present at the *meso*-position to bring a good electronic interaction between the redox centre and porphyrin core [27]. In view of this, there are reports on ethynyl moiety as the linking group between the porphyrin centre and the redox site [25]. Another class of linker group can be five membered heterocyclic rings as they can be in-plane with the porphyrin core to a larger extent compared to that of nearly perpendicularly oriented (with the porphyrin core) phenyl group [28–30]. Porphyrins with thienyl ring at the *meso*-position can be good candidates for better electronic communication within the molecule owing to smaller size of thienyl ring and ease of synthesis [31].

In our previous reports, we have explained the role of the size of the groups at the *meso*-position in deciding the site of nitration reaction [32–34]. In the present work the high synthetic versatility of nitro group on the thein-2-yl rings at the *meso*-position of the porphyrin is explored by converting it into amino group. The presence of amino group has made it easy to append a ferrocenyl group on the thien-2-ylporphyrin by condensing it with ferrocenecarboxaldehyde. Compared to introducing ethynyl moiety on the thien-2-yl ring [30] of the porphyrin, this method is relatively an easier one to maintain the electron delocalisation between the porphyrin core and the ferrocenyl group (through thien-2-yl group

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and azomethine bridge). The coupled dyad and triads shows fluorescence on–off switching properties. The chemical structure of the porphyrins in the study is given in Fig. 1.

2. Experimental

2.1. Materials

Pyrrole, 2-thiophenecarboxaldehyde and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were procured from Sigma–Aldrich. Ceric ammonium nitrate (CAN) and all other required chemicals were purchased from *sd* fine chemicals, India. Synthesis of different *meso*-5-nitrothien-2-yl- containing porphyrins is carried out by following the reported methods [32,33]. The products were characterised by different spectral techniques. The Ni(II) and Cu(II) complexes were prepared from the free base porphyrin using nickel acetate tetrahydrate [35] or cupric acetate monohydrate [36] as the metal ion carrier in solvent dimethylformamide and chloroform, respectively.

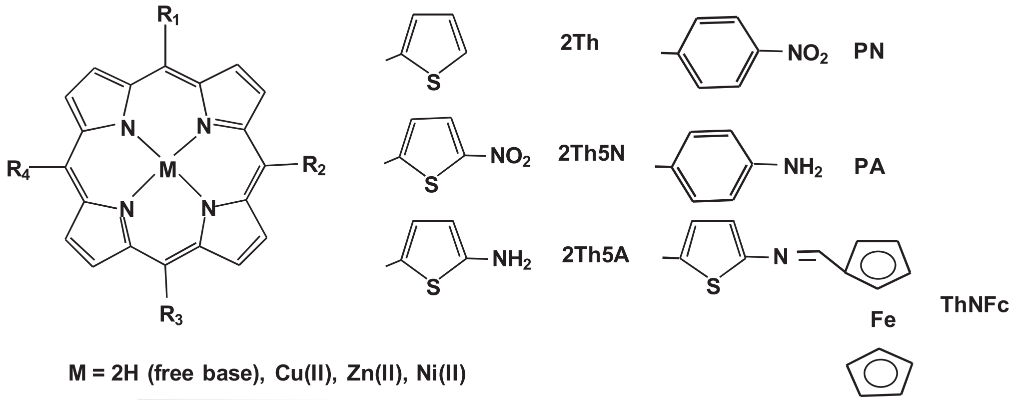
2.2. Measurements

^{1}H NMR spectra were recorded on a Bruker 400 MHz 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. 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, a 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 0.1 M $TBAPF_6$ was used as the supporting electrolyte. Fluorescence spectra were recorded on a JASCO FP-6300 spectrofluorometer. Mass spectra were recorded on 410 Prostar Varian Inc, USA mass spectrometer. Elemental analysis was carried out using Elementar Analysensysteme GmbH; vario MICRO cube.

2.3. Synthesis

2.3.1. Synthesis of nickel(II) derivatives of porphyrins containing both thien-2-yl and 4-nitrophenyl groups at the meso-position

The mixture of free base porphyrins were synthesized by using a mixture of thiophene-2-carboxaldehyde and 4-nitrophenyl carboxaldehyde by following the procedure by Lindsey et al. with



Porphyrin	-R$_1$	-R$_2$	-R$_3$	-R$_4$
MTh2P	2Th	2Th	2Th	2Th
M5NThP	2Th5N	2Th	2Th	2Th
NiT5NThP	2Th5N	2Th	2Th5N	2Th
NiC5NThP	2Th5N	2Th5N	2Th	2Th
M5AThP	2Th5A	2Th	2Th	2Th
NiT5AThP	2Th5A	2Th	2Th5A	2Th
NiC5AThP	2Th5A	2Th5A	2Th	2Th
NiSNPhP	PN	2Th	2Th	2Th
NiTNPhP	PN	2Th	PN	2Th
NiCNPhP	PN	PN	2Th	2Th
NiSAPhP	PA	2Th	2Th	2Th
NiTAPhP	PA	2Th	PA	2Th
NiCAPhP	PA	PA	2Th	2Th
MSThNFcP	ThNFc	2Th	2Th	2Th
NiTThNFcP	ThNFc	2Th	ThNFc	2Th
NiCThNFcP	ThNFc	ThNFc	2Th	2Th

Fig. 1. Chemical structures of derivatives of thien-2-ylporphyrins.