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Formation of Unusual Dithiaphlorins from Condensation of 2,5-Bis(arylhydroxymethyl)thiophene and Pyrrole

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Abstract

The first example of an unusual 21,23-dithiaphlorin containing, pyrrole and aryl groups at the sp^3 *meso* carbon that is present between pyrrole and thiophene rings were isolated from the condensation of 2,5-bis(arylhydroxymethyl) and pyrrole under mild acid catalyzed conditions. The crystal structure revealed that the macrocycle is significantly distorted because of the prescence of sp^3 *meso* carbon.

Keywords: Dithiaphlorin, dithiaporphyrin, thiophene dicarbinol, pyrrole, absorption properties.

Introduction

Ulman and Manassen reported[1] in 1974 that condensation of 2,5-bis(arylhydroxymethyl)thiophene with pyrrole under acid catalyzed conditions yielded 5,10,15,20-*meso*-tetraaryl-21,23-dithiaporphyrin **I**. Latos-Grazynski and co-workers found[2] that the condensation of bis(arylhydroxymethyl)thiophene with slight excess of pyrrole (2:3 molar ratio) in the presence of $BF_3.OEt_2$ (3 equivalents) resulted in the formation of minor amount of expanded porphyrin, 5,10,15,20-tetraaryl-26,28-dithiasapphyrin **II** (1.2%) in addition to major amount of **I** (Scheme 1). Chandrashekar and co-workers isolated[3] three macrocycles such as **I**, **II** and, 10,19,24-tetraaryl-30,33-dithiarubyrin **III** from condensation of 2,5-bis(arylhydroxymethyl)thiophene with pyrrole (1:2 molar ratio) in the presence of one equivalent of protic acid such as TFA, *p*-TsOH and HBr (Scheme 1). In 2001, Latos-Grazynski and co-workers isolated[4] 5,10,15,20-tetraaryl-2-aza-21-carba-22,24-dithiaporphyrin **IV** along with **I** when 2,5-bis(arylhydroxymethyl)thiophene and pyrrole (1:1) were condensed under $BF_3.OEt_2$ catalysed conditions. However, the same research group also isolated[4] 5,10,15,20-tetraaryl-25,27-dithiasapphyrin **V** in addition to **I** and **IV** when condensation of the same two substrates was carried out under CH_3SO_3H catalyzed conditions. Thus, the condensation of thiophene diol with pyrrole under slight variation in acid catalyzed reaction conditions resulted in the formation of five different types of macrocycles till date. Herein, we report the formation of unusual dithiapholrins by condensing 2,5-bis(arylhydroxymethyl)thiophenes with pyrrole (1:1.2 molar ratio) in the presence of dilute concentration of $BF_3.OEt_2$. The dithiaphlorins which were isolated in 4-5% yields contains one sp^3 *meso*-carbon having one pyrrole and one-tolyl group and three sp^2 *meso*-carbons containing aryl groups. This kind of dithiaphlorins cannot be obtained easily by adopting any rational approaches.[5,6] The reaction was tested by varying three different types 2,5-bis(arylhydroxymethyl)thiophenes and condensed with pyrrole

under acid catalyzed conditions to afford different *meso*-substituted dithiaphlorins (Scheme 2). The dithiaphlorins were characterized by HRMS, 1D, 2D NMR spectroscopy, absorption, and electrochemical techniques and obtained the crystal structure for one of the compound. Our preliminary studies indicated that dithiaphlorins sense various ions in their protonated form without specificity towards any particular anion.

Result and discussion

We carried out the reaction by condensing one equivalent of 2,5-bis(*p*-tolylhydroxymethyl)thiophene **1** with 1.5 equivalents of pyrrole in CH_2Cl_2 in the presence of $BF_3.OEt_2$ (3.3 mM) in 150 mL CH_2Cl_2 for 2.5 h followed by oxidation with 1.5 equivalents of *p*-chloranil for 3h at room temperature (Scheme 2). The TLC analysis showed the one major reddish brown spot which was followed closely by the green spot and other polar minor spots. The crude compound was subjected to silica gel column chromatographic purification and the major reddish brown spot corresponding to *meso*-tetra(*p*-tolyl)phenyl-21,23-dithiaporphyrin **1b** was collected and afforded in 14% yield. The green spot which followed the reddish brown spot of 21,23-dithiaporphyrin **1b** was subsequently collected and subjected further to two basic alumina column chromatographic purifications to afford pure green colored compound **1a**. The mass spectrum of green coloured compound showed a molecular ion peak at 772.28 which was matching with *meso*-tetraaryl dithiasapphyrin **II**. However, the ^{1}H NMR spectrum of compound **1a** showed signals only in 5.5 to 8 ppm region indicating that it was not the reported aromatic *meso*-tetraaryl dithiasapphyrin **II** but appears to be a macrocycle with disrupted π-electron delocalization. Fortunately, we obtained the single crystal structure of the green compound (vide infra) which confirmed that the green coloured compound was indeed 21,23-dithiaphlorin **1a** having one sp^3 and three sp^2 *meso*-carbon bridges. To confirm the formation of thiaphlorin **1a** under dilute acid catalyzed conditions, we condensed different 2,5-

bis(arylhydroxymethyl)thiophenes **2** and **3** with pyrrole under identical reaction conditions and afforded pure green coloured 21,23-dithiaphlorins **2a** and **3a** in 4-5% yields along with 21,23-dithiaporphyrins **1b-3b** in 12-15% yields. To improve the yields of dithiaphlorins **1a-3a**, we carried out the reaction under different conditions. The increase of pyrrole equivalents in the condensation did not increase the yield of the desired dithiaphlorin **1a** but resulted in the formation of an additional macrocycle 10,19,24-tetraaryl-30,33-dithiarubyrin **III**. The change of oxidant from *p*-chloranil to different oxidizing agents such as DDQ, $KMnO_4$, Br_2, Ag_2O, CAN, $FeCl_3$ did not yield the dithiaphlorin. The formation of compounds **1a-3a** was confirmed by HRMS analysis and the crystal structure of compound **1a**. We propose the plausible mechanism for the formation of dithiaphlorins **1a-3a** as shown in Scheme 3. The dithiaporphyrinogen that is formed, while undergoing oxidation to form dithiaporphyrin in the presence of mild oxidizing agent like *p*-chloranil, is possibly attacked by pyrrole at one of the electrophilic meso-carbon followed by the usual sequential oxidation steps to form dithiaphlorin.

X-ray crystallography

We attempted to grow single crystals for compound **1a**, and fortunately we could get crystals suitable for X-Ray diffraction via slow diffusion of petroleum ether into CH_2Cl_2 over a period of one week. The X-ray crystal structure of compound **1a** (CCDC No. 1421852) is shown in Figure 1 and the relevant crystallographic parameters are presented in Table S1 (supporting information). The compound **1a** was crystallized in orthorhombic space group *Pbcn*. The crystal structure showed that the compound **1a** contains one sp^3 *meso*-carbon bearing one pyrrole and one-tolyl groups as substituents along with three *meso* sp^2 hybridized carbons having tolyl groups. The macrocycle is highly distorted due to presence of one sp^3 hybridized carbon which disrupts the π-delocalization of the molecule. The crystal structure of compound **1a** was compared with the reported crystal structure of 5,10-bis(*p*-chlorophenyl)-10,20-bisphenyl-21,23-

dithiaporphyrin **(4a)** that contain four sp^2 *meso* carbons.[7] The macrocycle **1a** was distorted compared to **4a** which was found to be almost planar. A close inspection of the crystal structure of compounds **1a** and **4a** indicated that in compound **4a**, the pyrrole and thiophene rings are almost in plane (~6.70° and 1.15° respectively) from the 24 atoms mean plane of the macrocycle. In compound **1a**, the pyrrole ring connected to sp^3 hybridized carbon center was significantly deviated by 44.14° from the mean plane of the macrocycle whereas, the thiophene ring that is connected to sp^3 hybridized carbon center was deviated by only 12.83°. However, the pyrrole and thiophene rings attached to sp^2 hybridized carbon center were not significantly deviated (9.83° and 8.56° respectively) from the mean plane of the macrocycle. Furthermore, the flexible sp^3 *meso* carbon was significantly deviated upward by 0.869 Å from the mean plane which is comparable to our recently reported 21-thiaisoporphyrin (of 0.996 Å)[8] and significantly higher than compound **4a** (in 0.013-0.139 Å). However, the deviation of three sp^2 *meso* carbon centres are almost in the same range (0.214, 0.141, 0.246 Å) from the mean plane. The S1 and S2 thiophene sulphurs of compound **4a** are essentially (0.034 Å) in the mean plane, whereas the N1 and N2 pyrrole nitrogens are slightly deviated (0.149 Å) from the mean plane of the macrocycle. In case of **1a**, the N1 of pyrrole and S1 of thiophene ring connected to sp^3 hybridised *meso* carbon centre are significantly deviated upward (0.462 and 0.295 Å), whereas the N2 of pyrrole and S2 of thiophene are almost in the plane of the macrocycle (0.027 and 0.029 Å respectively). The tolyl ring at sp^3 hybridized carbon center is almost perpendicular to the plane of the macrocycle. Thus, the crystal structure analysis reveal that compound **1a** is highly distorted as compared to compound **4a**, due to presence of sp^3 carbon center which induces flexibility in compound **1a**.

NMR studies

The dithiaphlorins **1a-3a** were freely soluble in common organic solvents and characterized in detail by 1D and 2D NMR studies. The dithiaphlorins **1a-3a** were characterized in detail by 1D and 2D NMR studies. The resonances were identified based on integration, coupling constant and proton-proton correlations observed in 1D and 2D NMR spectra. The ^{1}H, ^{1}H-^{1}H COSY and NOESY NMR spectra of dithiaphorin **1a** are shown in Figure 2. The close inspection of ^{1}H NMR spectrum showed one broad signal at 7.93 ppm (*type r*) corresponding to inner NH proton and one relatively sharp signal at 8.05 ppm (*type q*) corresponding to NH proton of pyrrole present at the sp^{3} *meso*-carbon. In ^{1}H-^{1}H COSY, the *type q* NH signal at 8.05 ppm showed cross-peak correlation with a signal present at the 6.73 ppm which we identified as *type a* proton of pyrrole present at the sp^{3} *meso*-carbon. The *type a* proton showed a cross peak connectivity with a signal at 6.14 ppm which we assigned as *type b* proton which in turn showed correlation with a signal at 5.75 ppm corresponding to *type c* pyrrole proton present at the sp^{3} *meso*-carbon. Furthermore, the eight protons corresponding to four thiophene and four pyrrole protons appeared as eight sets of signals in 6.00-7.40 ppm region. In NOESY spectrum, the *q-type* NH proton at 8.05 ppm showed a cross-peak correlation with the doublet at 6.75 ppm which we identified as *type d* pyrrole proton. The *type d* pyrrole proton showed cross-peak correlation in COSY spectrum with a signal at 7.35 ppm which was assigned as *type e* pyrrole proton. To identify the *type f* and *g* protons of thiophene, we followed the NOE correlations of methyl group of *p*-tolyl present at the sp^{3} *meso*-carbon. The ^{1}H NMR spectrum showed four singlets at 2.30, 2.44, 2.45 and 2.48 ppm corresponding to three protons each. The signal at 2.30 ppm was identified as *type **I*** methyl signal of tolyl group present at the sp^{3} *meso*-carbon. The signals at 2.44, 2.45 and 2.48 ppm corresponding to three protons each were identified as *type **II***, *type **III*** and *type **IV*** methyl protons of *meso*-tolyl groups present at the sp^{2} carbons. The *type **I*** methyl

signal at 2.30 ppm showed NOE correlation with a signal at 7.03 ppm which we identified as *type m* protons of *meso*-aryl group present at the sp^3 carbon. The signal at 6.90 ppm was identified as *type l* proton as it was showing cross peak correlation with *type m* proton. The *type l* proton at 6.90 ppm showed NOE correlation with a signal at 7.12 ppm which we assigned as *type f* proton of thiophene ring. The *type f* proton at 7.12 ppm in turn showed cross-peak correlation with a signal at 7.29 ppm which was identified as *type g* proton of thiophene. To identify the *type h* and *i* protons of pyrrole as well as *type k* and *j* protons of thiophene, we followed the NOE correlations observed between *type II, III* and *IV* methyl protons signals with *meso*-aryl protons signals. However, the *meso*-aryl protons appeared as two sets of signals at 7.48 and 7.25-7.36 ppm corresponding to four and eight protons respectively and these protons were difficult to assign to particular type of *meso*-aryl protons. But the close inspection of Figure 2 clearly showed that the set of *meso*-aryl signals appeared at 7.48 ppm showed cross peak correlation with a signals at 6.40 and 7.12 ppm. We assigned the signal at 6.40 ppm to *type i* pyrrole proton and a signal at 7.12 ppm to the *type j* proton of thiophene. The *type i* pyrrole proton at 6.40 ppm showed a cross-peak correlation with a doublet at 6.01 ppm which we identified as *type h* pyrrole proton. Similarly, the *type J* thiophene proton appeared at 7.12 ppm showed cross-peak correlation with a signal at 6.73 ppm which we identified as *type k* thiophene proton. Thus, NMR studies helped in identifying all protons of thiophene and pyrrole rings, NH protons and some selected *meso*-aryl protons. Thus, NMR studies helped in identifying all protons of thiophene and pyrrole rings, NH protons and some selected *meso*-aryl protons. The ^{1}H NMR spectrum of the other thiaphlorins **2a-3a** also showed similar NMR spectra like **1a** and all protons were identified using the same 1D and 2D NMR techniques.

Absorption and electrochemistry studies

The absorption and electrochemical properties of compounds **1a-3a** were studied and the relevant data are included in Table 1. The comparison of absorption spectra of compound **1a** and its protonated form is shown in Figure 3. The compound **1a** showed one broad featureless Q-type band at 690 nm and one strong Soret type band at 390 nm along with a shoulder band at 411 nm. These absorption features are characteristic of non-aromatic macrocycles. The other two macrocycles **2a** and **3a** also showed similar non-aromatic absorption features (Table 1). Upon addition of TFA to compound **1a** in CH_3CN, the Q-type band experienced bathochromic shifts and appeared as two bands at 856 and 967 nm whereas the Soret type band also resolved into two bands at 412 and 463 due to protonation of inner pyrrole ring of compound **1a**. The electrochemical properties of compounds **1a-3a** were studied with cyclic voltammetry and differential pulse voltammetry using tetrabutylammonium perchlorate as supporting electrolyte in CH_2Cl_2. The representative reduction waves of cyclic voltammogram along with its differential pulse voltammogram of compound **1a** is shown in Figure 3 and the data are included in Table 1. The compounds **1a-3a** showed three to four oxidations and two reductions which are mostly quasi-reversible and irreversible in nature indicating that the macrocycles are not very stable under redox conditions.

As calixphyrins are known to bind various anions,[9-12] the preliminary anion biding studies were performed with 1a and showed that the compound **1a** did not bind to any anion. We then carried out anion binding studies with compound 1a in its protonated state. Our studies indicated that macrocycle **1a** showed potential ability to bind various anions without specificity for any particular anion. Thus, the thiacalixphyrins although binds anions in its protonated state but doesn't show selectivity.

Conclusion

In conclusion, we obtained an unusual dithiaphlorins containing pyrrole and aryl group at the sp^3 *meso* carbon from the condensation of 2,5-bis(hydroxymethylaryl)thiophene with pyrrole under mild acid catalyzed conditions. These kinds of unusual dithiapholorin cannot be prepared by any available rational methods. Our preliminary studies showed that the protonated dithiaphlorins have potential ability to bind various anions. The electrochemical properties of compounds **1a-3a** showed three to four oxidations and two reductions which are mostly quasi-reversible and irreversible in nature indicating that the macrocycles are not very stable under redox conditions.

Materials and methods

Chemicals: The chemicals such as $BF_3 \cdot Et_2O$, 2,3,5,6-tetrachloro-1,4-benzoquinone (DDQ) were used as obtained from Aldrich. All other chemicals used for the synthesis were reagent grade and solvents were dried by routine procedures immediately before use. Column chromatography was performed on basic alumina and silica gel (60-120 mesh).

Instrumentation: All the NMR spectra were recorded with Bruker 400 MHz and 500 MHz instrument using tetramethylsilane ($Si(CH_3)_4$) as internal standard. Absorption spectra were obtained with Perkin-Elmer Lambda-35 instrument. Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) studies were carried out with BAS electrochemical system utilizing the three electrode configuration consisting of a Glassy carbon (working electrode), platinum wire (auxillary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry acetontrile using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The HR-MS were recorded with a Q-Tof Micromass spectrometer using the electron spray ionization technique.

X-ray crystal structure analysis:

Single crystals of suitable size for X-ray diffractometry were selected under a microscope and mounted on the tip of a glass fiber, which was positioned on a copper pin. The X-ray data for macrocycles 1 and 3 were collected, and graphitemonochromated Mo Kα radiation at 200 K and a θ-2θ scan mode were used. The space group for macrocycles **1a** was determined on the basis of systematic absences and intensity statistics, and the structures of macrocycles **1a** was solved by direct methods using SIR92 or SIR97 and refined with SHELXL-97.14 An empirical absorption correction by multiscans was applied. All non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were placed in ideal positions and fixed with relative isotropic displacement parameters. Selected crystallographic data for the macrocycle (CCDC No. 1421852) are given in Table S1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Experimental Section

Compound 1a: Samples of 2,5-bis(*p*-tolylhydroxymethyl)thiophene (0.617 mmol) and pyrrole (0.740 mmol) in dichloromethane (150 ml) was degassed with nitrogen for 10 minutes with stirring. The condensation was initiated by adding catalytic amount of $BF_3.OEt_2$ (150 μL of 2.5 M) and stirred under nitrogen atmosphere at room temperature for 2.5 h. The oxidant. *p*-chloranil (0.740 mmol) was added and the reaction mixture was stirred in air for additional 2 h. TLC analysis showed the formation of dithiaphlorin **1a** along with the major known macrocycle, 5,10,15,20-tetraaryl 21,23-dithiaporphyrin **1b**. The crude compound was subjected twice to silica gel column chromatography and collected the known dithiaporphyrin macrocycle as first band followed by the desired compound **1a** as second band using petroleum ether/CH_2Cl_2 (65:35). The solvent was removed on rotary evaporator and afforded 5,10,15,20-Tetratolyl dithiaporphyrin[13] **1b** in 14% and dithiaphlorin **1a** as green solid in 4% yields. ^{1}H NMR (400 MHz, $CDCl_3$, δ in

ppm) 2.3 (s, 3H), 2.441 (s, 3H), 2.448, (s, 3H), 2.47 (s, 3H) 5.75 (s, 1H), 6.01 (d, *J* = 3.8 Hz, 1H), 6.14 (dd, *J* = 4.15, 2.55 Hz, 1H), 6.40 (d, *J* = 3.72 Hz, 1H), 6.75 (dd, *J* = 4.15, 2.55 Hz, 1H), 6.73 (d, *J* = 4.64 Hz, 1H), 6.89 (d, *J* = 4.0 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 7.03-7.05 (m, 3H), 7.12 (d, *J* = 5.6 Hz, 1H), 7.25-7.36 (m, 10H), 7.93 (brs, NH), 8.05 (s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 166.6, 152.9, 152.5, 148.4, 141.9, 141.1, 140.7, 138.5, 137.1, 136.6, 136.2, 135.7, 135.6, 135.1, 134.6, 134.1, 132.7, 131.9, 131.6, 131.3, 131.2, 129.3, 129.7, 129.1, 128.9, 188.5, 128.4, 127.2, 125.9, 123.6, 120.6, 117.6, 113.1, 110.1, 108.0, 54.6, 53.6, 37.2, 32.9, 32.1, 31.8, 30.2, , 27.2, 22.8, 21.5, 21.4, 21.2, 21.5, 19.9, 14.3. HRMS m/z calcd for $C_{52}H_{41}N_3S_2$ $(M+H)^+$ 772.2815, found 772.2821.

Compound 2a: The compound **2a** was synthesized by following the procedure of **1a** using 2,5-bis(*p*-phenylhydroxymethyl)thiophene. 5,10,15,20-Tetraphenyl dithiaporphyrin[13] **2b**: 15% and dithiaphlorin **2a**: 4%. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 5.7 (s, 1H), 6.05 (d, *J* = 3.7 Hz, 1H), 6.15 (d, *J* = 2.8Hz, 1H), 6.42 (d, *J* = 3.72 Hz, 1H), 6.71 (d, *J* = 3.64 Hz, 1H), 6.77 (d, *J* =3.6 Hz, 1H), 6.89, (d, *J* = 3.96 Hz, 1H), 7.02 (d, *J* = 4.6 Hz, 1H), 7.12 (d, *J* = 5.72 Hz, 1H), 7.08-7.11 (m, 3H), 7.23-7.26 (m, 2H), 7.32 (d, *J* = 5.8 Hz, 1H), 7.35 (d, *J* = 3.9 Hz, 1H), 7.42-7.50 (m, 12 H), 7.59-7.61 (m, 4H), 7.93 (brs, NH), 8.05 (s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 152.8, 148.6, 144.7, 141.4, 140.5, 139.7, 139.5, 139.0, 135.7, 135.3, 134.4, 134.2, 132.9, 132.0, 131.5, 131.4, 129.9, 129.0, 128.6, 128.5, 128.3, 128.1, 127.9, 127.8, 127.5, 127.4, 127.4, 120.8, 117.8, 113.3, 110.2, 108.1, 54.3, 29.8, 29.5, 14.2, 1.18, HRMS m/z calcd for $C_{48}H_{33}N_3S_2$ $(M+H)^+$ 716.2189, found 716.2198.

Compound 3a: The compound **3a** was synthesized by following the procedure of **1a** using 2,5-bis(*p*-bromophenylhydroxymethyl)thiophene precursor. 5,10,15,20-Tetrakis(4-bromo-phenyl) dithiaporphyrin[14] 3b: yield 13%, dithiaphlorin 3a Yield: 5%. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 5.69 (s, 1H), 6.01 (d, *J* =3.76 Hz, 1H), 6.14 (d, *J* = 5.8, 2.69 Hz, 1H), 6.43 (d, *J* = 3.7 Hz,

1H), 6.71 (d, *J* = 5.68 Hz, 1H), 6.78 (d, *J* = 4.01 Hz, 1H), 6.87(d, *J* = 4.0 Hz, 1H), 6.95-7.01 (m, 3H), 7.10 (d, *J* = 5.72 Hz, 1H), 7.28-7.41 (m, 6 H), 7.45 (d, *J* = 8.36 Hz, 4H), 7.52-7.65 (m, 6H), 7.93 (broad, NH), 8.05 (s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 137.7, 135.7, 135.4, 134.2, 133.6, 133.4, 133.0, 131.8, 131.6, 131.5, 131.2, 131.1, 130.7, 130.3, 130.0, 127.6, 123.2, 122.0, 121.7, 121.2, 118.3, 113.7, 110.3, 108.3, 54.6, 45.8, 32.1, 29.8, 29.5, 29.1, 22.8, 14.3, 14.2. HRMS m/z calcd for $C_{48}H_{29}Br_4N_3S_2$ $(M+H)^+$ 1027.8609, found 1031.8570.

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Supporting Information Available. All the NMR and HR mass spectra of compounds are given.

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Legends

Scheme 1: Condensation of 2,5-bis(*p*-arylhydroxymethyl)thiophene and pyrrole in different conditions.

Scheme 2: Synthesis of dithiaphlorins **1a-3a**.

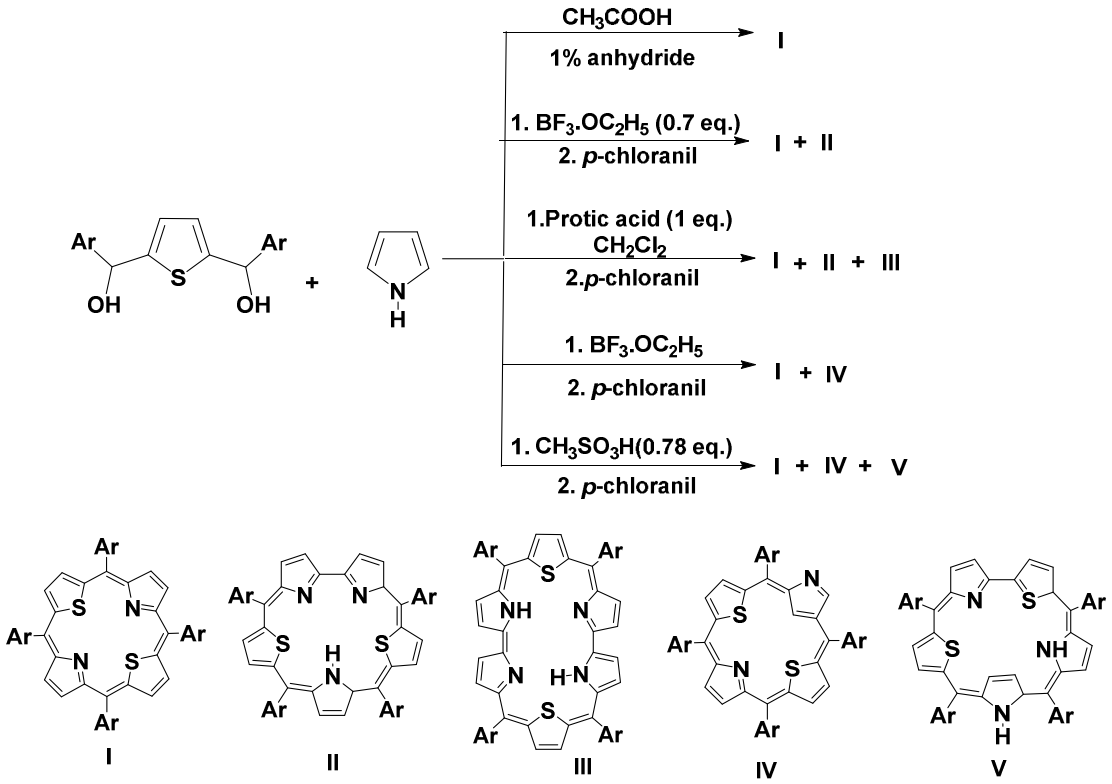
Scheme 3: Plausible mechanism for synthesis of dithiaphlorin.

Figure 1: Single crystal X-ray structure of compound **1a** (a) perspective ORTEP view (b) Front view (*meso*-aryl groups are omitted for clarity) and (c) side view showing the non-planarity distortation in molecular plane due to sp^3 *meso* carbon centre of the macrocycle (All hydrogens are omitted for clarity) Thermal ellipsoids are drawn in 50% probability.

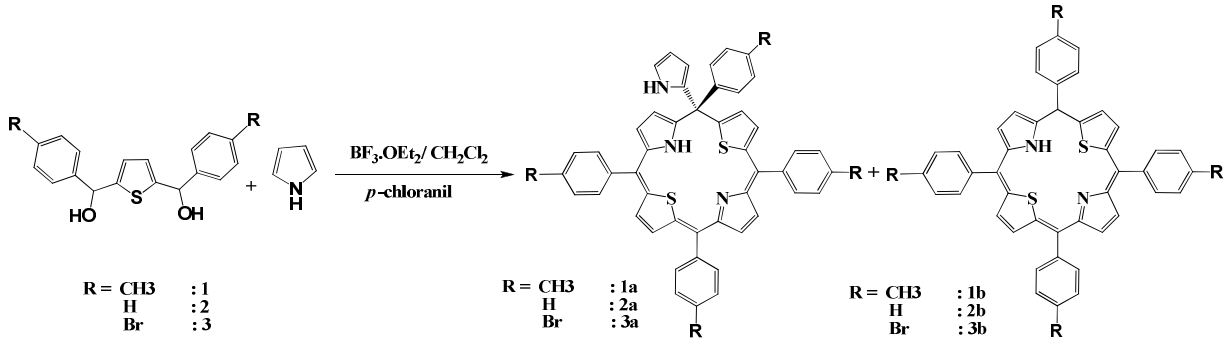
Figure 2: Partial (a) Partial ^1H NMR, (b) Partial ^1H-^1H COSY NMR and (c) Partial ^1H-^1H NOESY NMR spectra of compound **1a** recorded in $CDCl_3$ at room temperature.

Figure 3: (a) Comparison of absorption spectra of compound **1a** (solid line) and **1a.H**$^+$ (dotted line) recorded in CH_3CN. (b) Redox waves of cyclic voltammograms along with differential pulse voltammograms of compound **1a** recorded in CH_2Cl_2 solvent using tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte and the saturated calomel electrode (SCE) as a reference electrode at scan rates of 50 mV s^{-1}.

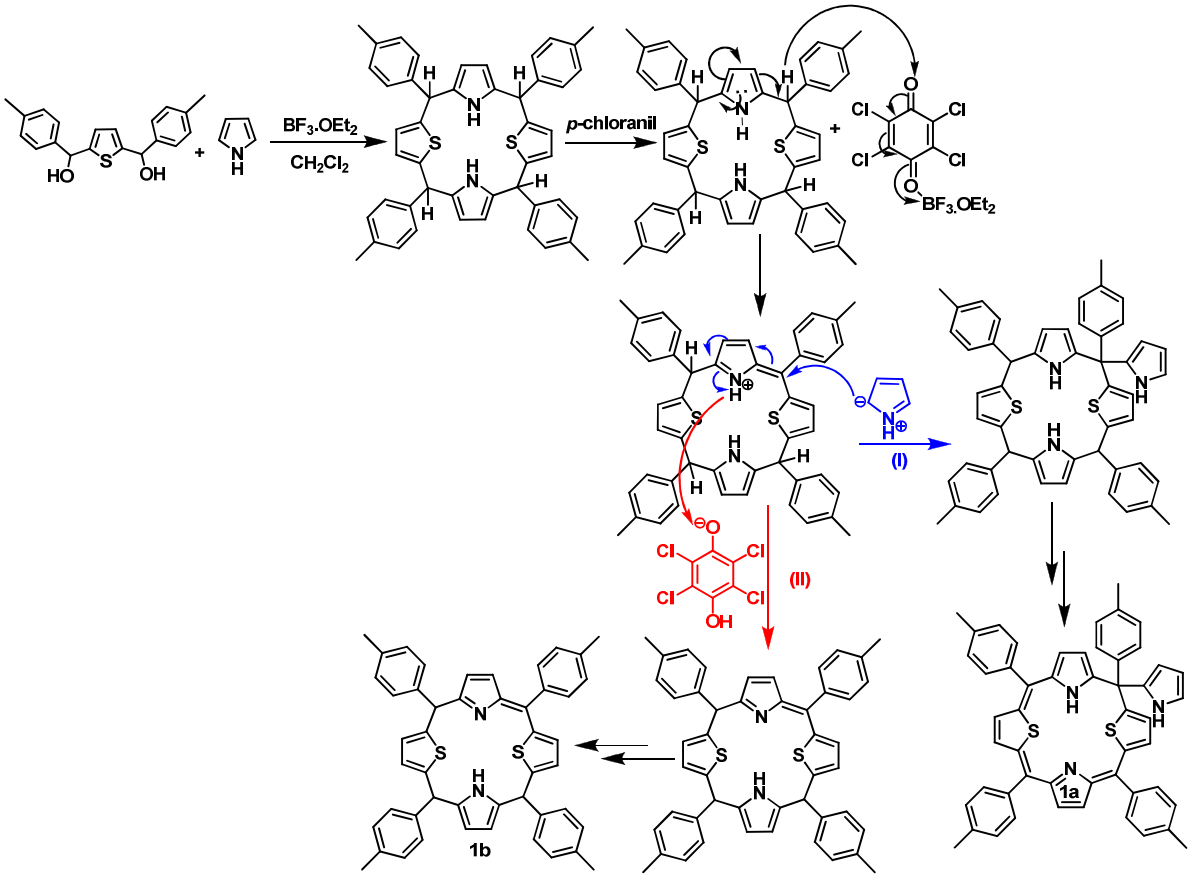
Table 1: Absorption and redox data of compound **1a-3a**.



Scheme 1



Scheme 2



Scheme 3

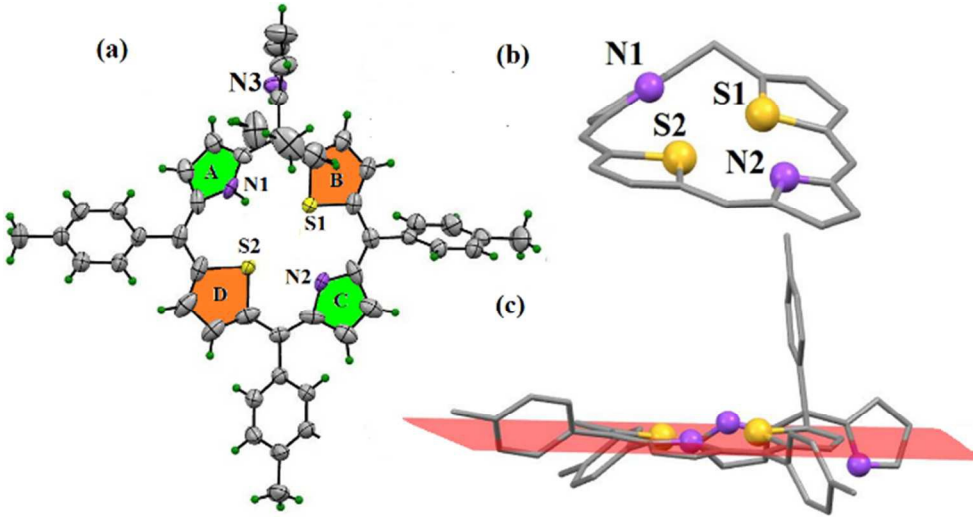


Figure 1

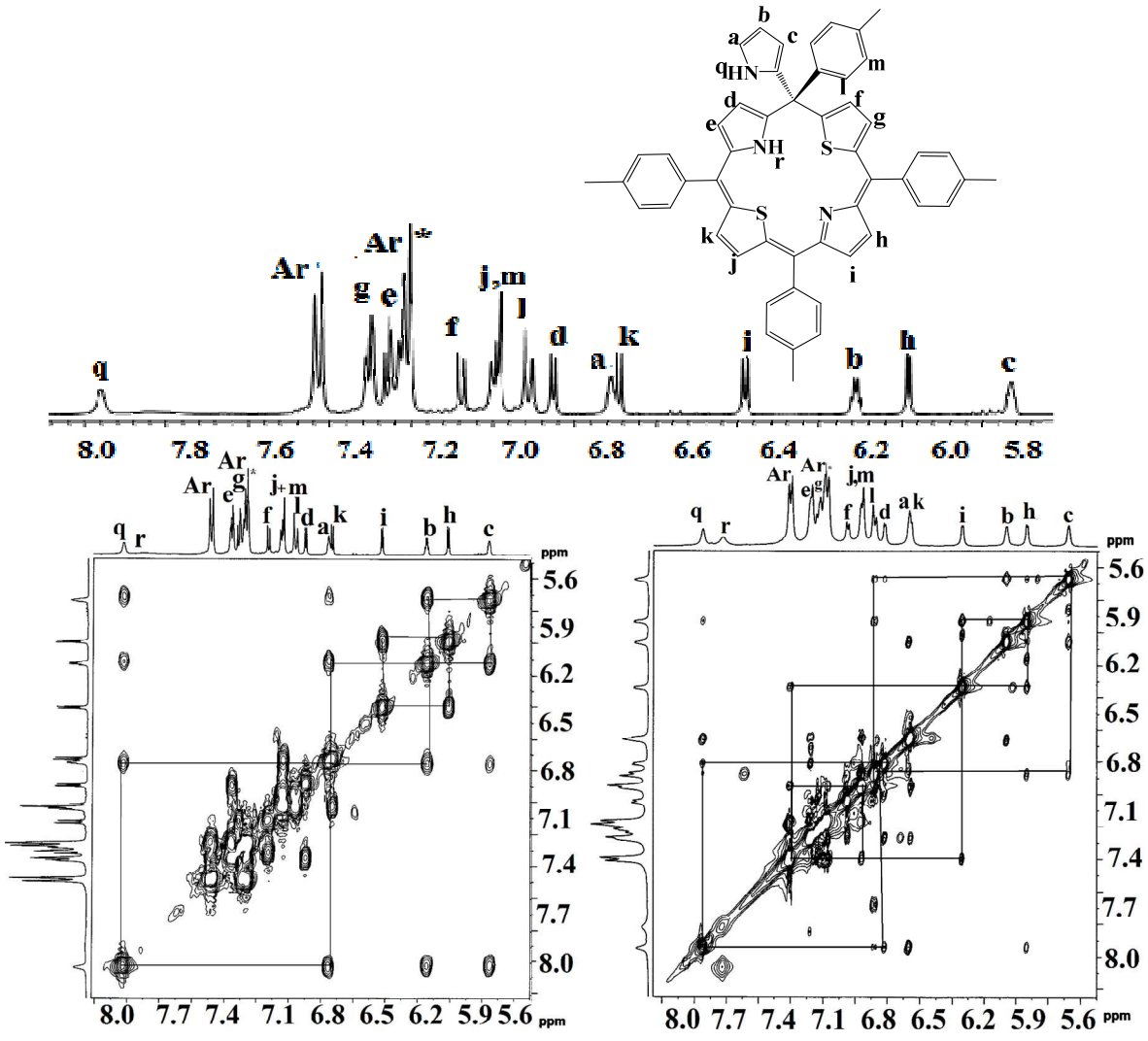


Figure 2

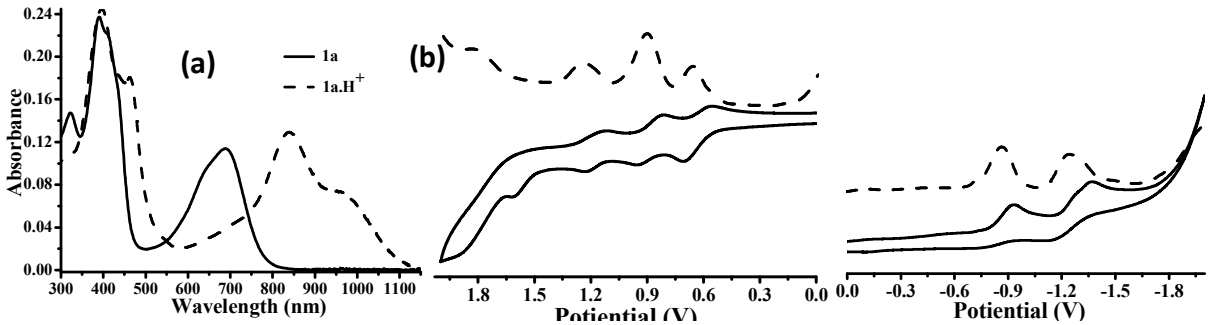


Figure 3

Table 1

	Absorption band [nm] (log ε)	Redox potential	
		Oxidation (V)	Reduction (V)
1a	390 (0.13963), 411 (0.13502), 432 (sh), 636 (sh), 690 (0.06340)	0.63, 0.88, 1.17, 1.62	-0.86, -1.24
2a	389 (0.12726), 409 (0.12396), 433 (sh), 634 (sh), 683 (0.06340)	0.51, 0.77, 1.12, 1.69	-0.77, -1.25
3a	392 (0.12390), 409 (0.12177), 433 (sh), 632 (sh), 686 (0.06140)	0.74, 1.01, 1.31, 1.70	-0.77, -1.25

Graphical Abstract

A new unprecedented dithiaphlorin macrocycle containing pyrrole and aryl groups at the sp^3 meso carbon was obtained from the condensation of 2,5-bis(*p*-arylhydroxymethyl)thiophene and pyrrole under mild acidic conditions.