

Trans-A₂B₂ type *meso*-5-Nitrothien-2-yl Porphyrins: Scalable Synthesis, Spectroscopic and Physicochemical Investigations

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Abstract

Trans-A₂B₂ type porphyrins featuring 5-nitrothien-2-yl group at the *meso*-5,15 positions of tetrapyrrolic macrocycles have been synthesized in a two-step process *via* a modified dipyrromethane approach. In the initial stage of the synthesis, the requisite dipyrromethane building blocks were efficiently synthesized through the acid-catalyzed condensation of the corresponding aldehyde with pyrrole using trifluoroacetic acid (TFA) as a catalyst. The second stage comprises the acidic condensation of substituted dipyrromethane with 5-nitrothiophene-2-carboxaldehyde/4-nitrobenzaldehyde in chloroform using TFA as a catalyst under the N₂ atmosphere, followed by DDQ oxidation. To elucidate the influence of the *meso*-substituent (thienyl *versus* phenyl) on the electronic properties, the structural, photophysical, and redox characteristics were evaluated using ¹H NMR, UV-Vis spectroscopy, and electrochemical analysis. The extent of electron delocalization, driven by the near-coplanarity of the thien-2-yl moieties with the central porphyrin π -core, was probed using electronic spectroscopy and cyclic voltammetry. The anodic shift of the redox potentials and the bathochromic shift in the electronic absorption spectra of the *trans*-A₂B₂ type porphyrins bearing 5-nitrothien-2-yl groups at the *meso*-5,15-positions indicate strong electronic communication between the central porphyrin π -system and the peripheral substituents.

Introduction

Porphyrinoids are ubiquitous natural pigments that bring about diverse functions in the biological system, such as Heme, Chlorophyll, Cytochrome P450, Siroheme synthase, Cofactor F430 and Vitamin B₁₂.¹⁻⁴ Synthetic porphyrins and their metallated derivatives with highly conjugated 18-electron systems have been developed to mimic the properties of natural pigments for use in a variety of applications such as photodynamic therapy (PDT), water-splitting reactions, dye-sensitized solar cells, supramolecular self-assembly, and the oxidation of organic molecules under ambient conditions (as catalysts).⁵⁻⁹ Functionalized porphyrins represent a highly advantageous molecular scaffold, characterized by intrinsic photostability, structural rigidity, and large molar absorption coefficients within the visible spectrum.¹⁰ Furthermore, the amenability of the *meso*- and β -positions to functionalization enables the fine-tuning of their optical, physical, and electrochemical properties.¹¹ While several synthetic strategies have been developed, it is well established that the specific site and nature of peripheral substitutions ultimately dictate the physicochemical properties of the porphyrin scaffold.^{12,13} Consequently, the majority of recent advancements in porphyrin-based chemical transformations and functional group interconversions have leveraged synthetically accessible 5,10,15,20-tetraarylporphyrins, most notably the symmetrical A₄-type tetraphenylporphyrin (TPP). The electronic influence of functional groups on *meso*-phenyl rings is significantly attenuated due to the nearly orthogonal orientation of these rings relative to the porphyrin core. This perpendicular conformation, enforced by a sterically induced rotational barrier, effectively restricts resonance between the two discrete π -systems.^{11,14,15} In this context, functional groups (photo and redox-active moieties) are directly introduced at *meso*-position or *via* linear ethynyl units have been synthesized to tune the physicochemical characteristics. However, the

practical utility of these porphyrins in future applications remains constrained by protracted multi-step synthetic routes and laborious isolation process, which leads to low yields.¹⁶ Thus, *meso*-thienyl porphyrins have emerged as promising alternatives to their *meso*-phenyl counterparts; the reduced steric bulk of the thienyl ring facilitates greater coplanarity with the central macrocycle compared to the out-of-plane oriented phenyl groups.^{15,17,18} Along with the advantages of the smaller *meso*-thienyl ring, the presence of the sulfur heteroatom imparts distinct properties to these macrocycles, particularly regarding their self-assembling behaviour. Major on-going research in this area focuses on various *meso*-tetrathien-2-yl porphyrins (A_4 type) derivatives, which are comparably stable and easy to synthesize. The *meso*-thien-2-yl and thien-3-yl porphyrin derivatives have drawn considerable attention for their energy and electron-transfer properties, for the formation of ultra-thin films, in electrocatalysis, for the detection of explosives, as biosensors, and for the investigation of the structural factors influencing the morphology of various nanostructures.^{11,19} Investigations into the functionalization of thienylporphyrins for synthesizing unsymmetrical derivatives are notably limited. Developing these unsymmetrical architectures is critical to integration of the distinct electro-optical properties inherent to both porphyrin and thiophene moieties.^{18,20} Due to this unique synergy, such derivatives are in high demand for cutting-edge applications spanning catalysis, optoelectronics, biomaterials, and chemical biology.¹⁹ In this context, thienyl porphyrins with mixed *meso*-substituent (electron donor/acceptor, enhancing π -conjugation and photo active groups) patterns are highly promising for tuning the macrocycle.^{11,20,21} Despite their potential, systematic studies on these platforms are limited, leaving a critical gap in the literature regarding their fundamental optical and electrochemical characteristics. In particular, *trans*- A_2B_2 type porphyrins that incorporate two different functionalities within the same porphyrin macrocycles are attractive and emerging materials for their application in numerous areas such as dye sensitized solar cells (DSSCs), photodynamic therapy and nonlinear optics.^{22,23} Therefore, there is a demand to develop a convenient method for the efficient synthesis of thienyl porphyrins with various functional groups at the porphyrin periphery. In light of this, we have designed and synthesized *trans*- A_2B_2 porphyrins that consist of 5-nitrothien-2-yl groups as the 'A' substituent (i.e. at 5,15-positions) and substituted theinyl or phenyl groups as 'B' substituent (i.e. at 10, 20-positions) by two-step process *via* a modified dipyrromethane approach. In the first step the versatile dipyrromethane building blocks were synthesized by condensation of the respective aldehyde and pyrrole using TFA as a catalyst (Scheme-1). The second stage comprises the acidic condensation of substituted dipyrromethane with 5-nitrothiophene-2-carboxaldehyde in chloroform using TFA as a catalyst under the N_2 atmosphere, followed by DDQ oxidation (Scheme-2 and 3). The spectroscopic and electrochemical studies revealed that incorporating two distinct functional groups within the same porphyrin unit brings about significant shifts in the physicochemical properties in contrast to its respective A_4 porphyrin. Also, the effects of substituents at *meso*-thien-2-yl and phenyl ring on the electronic properties of the porphyrin π -system were studied.

Experimental

Materials

Pyrrole, benzaldehyde, 4-bromobenzaldehyde, 4-nitrobenzaldehyde, 2-thiophenecarboxaldehyde, 3-methylthiophene-2-carboxaldehyde, 5-methylthiophene-2-carboxaldehyde, 5-nitrothiophene-2-carboxaldehyde, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), boron trifluoride etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$), trifluoroacetic acid (TFA), and tetrabutylammonium hexafluorophosphate (TBAPF_6) were purchased from Sigma–Aldrich (Merck), India, and used as received. The precursors 5-phenyldipyrromethane and 5-(4-bromophenyl)dipyrromethane were synthesized according to previously reported procedures. Chloroform (CHCl_3) was distilled and purified prior to its use in the condensation reactions. Dichloromethane (CH_2Cl_2) used for electrochemical experiments was refluxed and distilled over calcium hydride CaH_2 , then stored over freshly activated 4 Å molecular sieves. Solvents utilized for photophysical investigations were of spectroscopic grade. The free-base tetra-thienyl and tetra-phenyl (A_4) porphyrins used for comparative studies were synthesized according to our previously reported procedure.^{11,15,24} All reagents and solvents were procured from commercial suppliers and purified according to standard laboratory protocols prior to use.

Measurements

Optical absorption measurements were performed in CH_2Cl_2 on a JASCO V-770 UV-Vis/NIR spectrophotometer utilizing quartz cells with a 1.0 cm optical path length. ^1H NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer in deuterated chloroform (CDCl_3). Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra (HRMS) were recorded on a Bruker microTOF-Q II mass spectrometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed on a BASi Epsilon electrochemical workstation. A conventional three-electrode cell assembly was utilized, comprising a platinum working electrode, an Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. All electrochemical experiments were conducted at a porphyrin concentration of 1 mM in nitrogen-purged CH_2Cl_2 solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) as the supporting electrolyte.

Synthesis

General procedure for the preparation of 5-(2-thienyl) dipyrromethane derivatives.

In a 100 mL dry round-bottomed flask, corresponding aldehyde (1 equiv) and pyrrole (10 equiv) were mixed in a 1:10 ratio and degassed with a stream of N_2 . TFA (0.10 equiv) was then added, and the mixture was stirred for 20 minutes at room temperature under N_2 atmosphere. At the end of the period, triethylamine (Et_3N) (0.10 equiv) was added and stirring was continued for another 5 minutes to quench the reaction. Ethyl acetate was then added to the reaction mixture. The organic phase was treated with

water (10 mL, 3 times) and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure to obtain viscous red compound. The product was purified by column chromatography using 1:1 ratio of hexane and dichloromethane mixture as eluent and subsequent solvent evaporation to obtain dirty white crystalline solid.

Synthesis of 5-(2-thienyl)dipyrromethane.

2-Thiophenecarboxaldehyde (0.95 mL, 10 mmol) and pyrrole (6.93 mL, 100 mmol) were reacted by the general procedure and purified as described above. Dirty white solid; Yield: 39%. ^1H NMR (CDCl_3): δ 8.25–7.80 (bm, 2H, NH), 7.21–7.18 (m, 1H, thienyl-H), 6.95–6.89 (m, 1H, thienyl-H), 6.81 (d, 1H, thienyl-H), 6.69 (d, 2H, $\text{H}^{4,4'}$), 6.25–6.13 (m, 2H, $\text{H}^{3,3'}$), 6.04–5.89 (m, 2H, $\text{H}^{2,2'}$), 5.74–5.55 (bs, 1H, H^1); ^{13}C NMR (100 MHz): 145.80, 131.98, 126.75, 125.48, 124.65, 117.70, 117.42, 108.50, 108.20, 107.25, 107.04, 106.95, 39.22, ESI-MS[M + 1]: 229.101. Anal. found for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{S}$: C 67.94, H 5.26 and N 12.02.

Synthesis of 5-(5-methyl-2-thienyl)dipyrromethane.

5-Methylthiophene-2-carboxaldehyde (1.08 mL, 10 mmol) and pyrrole (6.93 mL, 100 mmol) were reacted by the general procedure and purified as described above. Dirty white solid; Yield: 42%. ^1H NMR (CDCl_3): δ 8.22–7.79 (bm, 2H, NH), 6.81 (d, 1H, thienyl-H), 6.66 (d, 1H, thienyl-H), 6.62–6.60 (m, 2H, $\text{H}^{3,3'}$), 6.27 (d, 2H, $\text{H}^{4,4'}$), 6.06–5.89 (m, 2H, $\text{H}^{2,2'}$), 5.64–5.54 (br, 1H, H^1), 2.43 (s, 3H, $-\text{CH}_3$), ^{13}C NMR (100 MHz): 143.28, 131.94, 126.75, 125.25, 124.72, 117.75, 117.36, 108.45, 108.22, 107.14, 106.95, 106.82, 39.28, 15.40. ESI-MS[M + 1]: 243.101. Anal. found for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$: C 69.29, H 5.75 and N 11.50.

Synthesis of 5-(3-methyl-2-thienyl)dipyrromethane.

3-Methylthiophene-2-carboxaldehyde (1.08 mL, 10 mmol) and pyrrole (6.93 mL, 100 mmol) were reacted by the general procedure and purified as described above. Dirty white solid; Yield: 38%. ^1H NMR (CDCl_3): δ 8.24–7.77 (bm, 2H, NH), 7.10–7.05 (m, 1H, thienyl-H), 6.84–6.80 (m, 2H, $\text{H}^{4,4'}$), 6.68 (bs, 1H, thienyl-H), 6.26–6.13 (m, 2H, $\text{H}^{3,3'}$), 5.84–6.01 (m, 2H, $\text{H}^{2,2'}$), 5.71–5.53 (m, 1H, H^1), 2.15 (m, 3H, $-\text{CH}_3$). ^{13}C NMR (100 MHz): 139.01, 133.95, 131.74, 131.62, 130.32, 122.64, 117.72, 117.34, 108.40, 108.20, 107.12, 37.54, 13.78, ESI-MS[M + 1]: 243.100. Anal. found for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$: C 69.31, H 5.65 and N 11.50.

Synthesis of 5-(5-bromo-2-thienyl)dipyrromethane.

5-Bromothiophene-2-carboxaldehyde (1.91 g, 10 mmol) and pyrrole (6.93 mL, 100 mmol) were reacted by the general procedure and purified as described above. Dirty white solid; Yield: 40%. ^1H NMR (CDCl_3): δ 8.24–7.79 (bm, 2H, NH), 6.88–6.86 (m, 1H, H^4), 6.81 (d, 1H, thienyl-H), 6.69 (d, 1H, thienyl-H), 6.62–6.58 (m, 1H, H^4), 6.25–6.05 (m, 2H, $\text{H}^{3,3'}$), 5.99–5.86 (m, 2H, $\text{H}^{2,2'}$), 5.63–5.44 (br, 1H, H^1). ^{13}C NMR (100 MHz): 147.50, 131.14, 129.48, 121.82, 117.72, 111.18, 108.64, 108.20, 107.30, 39.48. ESI-MS[M + 1]: 307.010. Anal. Found for $\text{C}_{13}\text{H}_{11}\text{BrN}_2\text{S}$: C 50.78, H 3.54 and N 8.89.

General procedure for the preparation of trans-A₂B₂-type meso-thienyl porphyrins.

A mixture of 5-substituted dipyrromethane (1.0 mmol) and corresponding aldehydes (1.0 mmol) was dissolved in freshly distilled 250 ml of chloroform and purged with N₂ gas for 15 minutes. The reaction was wrapped with aluminium foil and cooled to 0–5°C by keeping it in ice bath. Then, TFA (0.15 mL, 2.0mmol) was added to the solution slowly via syringe under stirring condition. The reaction mixture temperature was gradually increased to room temperature and stirred for 1 hr under N₂ atmosphere. Then, DDQ (0.57 g, 2.5 mmol) was added to the reaction mixture and the solution was stirred for a further period of 1 hr in open atmosphere. At the end of this period, 0.28 mL (2.0mmol) of Et₃N was added to neutralize the reaction and the organic phase was treated with water (3 times) and dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation under reduced pressure and the product was purified by column chromatography using 1:1 ratio of chloroform and hexane mixture as eluent.

*Synthesis of 5,15-bis(5-nitrothien-2-yl)-10,20-di(thien-2-yl)porphyrin, **t-H₂5NThP**:*

5-(2-thienyl)dipyrromethene (0.23 g, 1.0mmol) and 5-nitrothiophene-2-carboxaldehyde (0.16 g, 1.0mmol) were reacted by the general procedure and purified as described above. Yield: 16%. ¹H NMR (CDCl₃):δ 9.14–9.12 (d, 4H, pyrrole β-H^{1,1'}), 9.04–9.02 (m, 4H, pyrrole β-H^{2,2'}), 8.34–8.35 (d, 2H, thienyl-H^{3,3'}), 7.95–7.93 (d, 2H, thienyl-H^{5,5'}), 7.91–7.89 (d, 2H, thienylH^{7,7'}), 7.88–7.87 (d, 2H, thienyl-H^{4,4'}), 7.54–7.52 (dd, 2H, thienyl-H^{6,6'}), -2.70 (s, 2H, NH). Anal. Found for C₃₆H₂₀N₆O₄S₄: C, 59.25; H, 2.75; N, 11.50; S, 17.62. ESI-MS: m/z [M]⁺Calcd.: 728.0429. Found: 728.110.

*Synthesis of 5,15-bis(5-methylthien-2-yl)-10,20-bis(5-nitrothien-2-yl)porphyrin, **t-H₂5N5MeThP**:*

5-(5-methyl-2-thienyl)dipyrromethene (0.24 g, 1.0 mmol) and 5-nitrothiophene-2-carboxaldehyde (0.16 g, 1.0 mmol) were reacted by the general procedure as described above. Yield: 18%. ¹H NMR (CDCl₃):δ 9.18–9.16 (d, 4H, pyrrole β-H^{1,1'}), 9.04–9.02 (d, 4H, pyrrole β-H^{2,2'}), 8.35–8.34 (d, 2H, thienyl-H^{3,3'}), 7.88–7.87 (d, 2H, thienyl-H^{5,5'}), 7.71–7.70 (d, 2H, thienyl-H^{4,4'}), 7.20–7.18 (d, 2H, thienyl-H^{6,6'}), 2.85 (s, 6H, -CH₃), -2.66 (s, 2H, NH). Anal. Found for C₃₈H₂₄N₆O₄S₄: C, 60.29; H, 3.17; N, 11.15; S, 16.91. ESI-MS: m/z [M]⁺Calcd.: 756.0742. Found: 756.100.

*Synthesis of 5,15-bis(3-methylthien-2-yl)-10,20-bis(5-nitrothien-2-yl)porphyrin, **t-H₂5N3MeThP**:*

5-(3-methyl-2-thienyl)dipyrromethane (0.24 g, 1.0 mmol) and 5-nitrothiophene-2-carboxaldehyde (0.16 g, 1.0 mmol) were reacted by the general procedure as described above. Yield: 17%. ¹H NMR (CDCl₃):δ 9.14–9.12 (m, 4H, pyrrole β-H^{1,1'}), 9.04–9.02 (m, 4H, pyrrole β-H^{2,2'}), 8.40–8.39 (d, 2H, thienyl-H^{3,3'}), 7.94–7.93 (d, 2H, thienyl-H^{6,6'}), 7.82–7.80 (d, 2H, thienyl-H^{4,4'}), 7.39–7.41 (d, 2H, thienyl-H^{5,5'}), 2.20 (m, 6H, -CH₃), -2.65 (s, 2H, NH). Anal. Found for C₃₈H₂₄N₆O₄S₄: Found: C, 60.27; H, 3.16; N, 11.12; S, 16.90. ESI-MS: m/z [M]⁺Calcd.: 756.0742. Found: 756.110.

Synthesis of 5,15-bis(5-bromothien-2-yl)-10,20-bis(5-nitrothien-2-yl)porphyrin, t-H₂5N5BrThP:

5-(5-Bromo-2-thienyl)dipyrromethane (0.30 g, 1.0 mmol) and 5-nitrothiophene-2-carboxaldehyde (0.16 g, 1.0 mmol) were reacted by the general procedure and purified as described above. yield: 18%. ¹H NMR (CDCl₃): δ 9.20–9.19 (d, 4H, pyrrole β-H^{1,1'}), 9.08–9.07 (d, 4H, pyrrole β-H^{2,2'}), 8.38–8.37 (d, 2H, thienyl-H^{3,3'}), 7.92–7.91 (d, 2H, thienyl-H^{4,4'}), 7.72–7.71 (d, 2H, thienyl-H^{5,5'}), 7.54–7.53 (d, 2H, thienyl-H^{6,6'}), -2.69 (s, 2H, NH). Anal. Found for C₃₆H₁₈Br₂N₆O₄S₄: C, 48.72; H, 2.02; N, 9.50; S, 14.42. ESI-MS: m/z [M]⁺Calcd.: 885.8619. Found: 885.912.

5,15-bis(4-nitrophenyl)-10,20-bis(thien-2-yl)porphyrin, t-H₂Th4NPP:

5-(2-thienyl)dipyrromethane (0.23 g, 1.0 mmol) and 4-nitrobenzaldehyde (0.15 g, 1.0 mmol) were reacted by the general procedure and purified as described above. Yield: 16%. ¹H NMR (CDCl₃): 9.14–9.13 (d, 4H, pyrrole β-H^{1,1'}), 8.77–8.76 (d, 4H, pyrrole β-H^{2,2'}), 8.69–8.67 (d, 4H, phenyl-H^{3,3'}), 8.43–8.41 (d, 4H, phenyl-H^{4,4'}), 7.97–7.96 (dd, 2H, thienyl-H^{5,5'}), 7.91–7.90 (dd, 2H, thienyl-H^{7,7'}), 7.56–7.54 (dd, 2H, thienyl-H^{6,6'}). Anal. Found for C₄₀H₂₄N₆O₄S₂: C, 67.05; H, 3.35; N, 11.70; S, 8.93. ESI-MS: m/z [M]⁺ Calcd.: 716.1300. Found: 716.119.

Synthesis of 5,15-bis(5-nitrothien-2-yl)-10,20-diphenylporphyrin, t-H₂5NThPP:

5-Phenyldipyrromethane (0.22 g, 1.0 mmol) and 5-nitrothiophene-2-carboxaldehyde (0.16 g, 1.0 mmol) were reacted by the general procedure and purified as described above. Yield: 20%. ¹H NMR (CDCl₃): δ 9.08–9.07 (d, 4H, pyrrole β-H^{1,1'}), 8.95–8.94 (d, 4H, pyrrole β-H^{2,2'}), 8.37–8.36 (d, 2H, thienyl-H^{3,3'}), 8.23–8.21 (m, 4H, phenyl-H^{5,5'}), 7.91–7.90 (d, 2H, thienyl-H^{4,4'}), 7.86–7.80 (m, 6H, phenyl-H^{6,6',7,7'}), -2.76 (s, 2H, NH). Anal. Found for C₄₀H₂₄N₆O₄S₂: C, 67.05; H, 3.40; N, 11.70; S, 8.92. ESI-MS: m/z [M]⁺Calcd.: 716.1300. Found: 716.200.

Synthesis of 5,15-bis(4-bromophenyl)-10,20-bis(5-nitrothien-2-yl)porphyrin, t-H₂5NTh4BrPP:

5-(4-Bromophenyl)dipyrromethane (0.30 g, 1.0 mmol) and 5-nitrothiophene-2-carboxaldehyde (0.16 g, 1.0 mmol) were reacted by the general procedure and purified as described above. Yield: 20%. ¹H NMR (CDCl₃): δ 9.10–9.09 (d, 4H, pyrrole β-H^{1,1'}), 8.93–8.92 (d, 4H, pyrrole β-H^{2,2'}), 8.38–8.37 (d, 2H, thienyl-H^{3,3'}), 8.08–8.10 (d, 4H, phenyl-H^{5,5'}), 7.96–7.98 (d, 4H, phenyl-H^{6,6'}), 7.91–7.92 (d, 2H, thienyl-H^{4,4'}), -2.81 (s, 2H, NH). Anal. Found for C₄₀H₂₂Br₂N₆O₄S₂: C, 54.90; H, 2.52; N, 9.64; S, 7.35. ESI-MS: m/z [M]⁺Calcd.: 873.9490. Found: 874.124.

Result and Discussion

Synthesis

The synthesis of thienyl porphyrins featuring mixed peripheral *meso*-substituents has attracted considerable attention. This structural modification enhances electron delocalization and induces a push-pull effect, thereby effectively tuning the macrocycle's photophysical and electrochemical properties.^{11,25,26} Unsymmetrical *meso*-substituted thienylporphyrins represent a critical class of functional materials with pivotal applications in dye-sensitized solar cells (DSSCs), photodynamic therapy (PDT), and nonlinear optics (NLO).²⁷ The synthesis of these target unsymmetrical *meso*-substituted thienylporphyrins is routinely accomplished *via* a modified Lindsey method.¹² This method involves the condensation of pyrrole with a stoichiometrically controlled mixture of distinct aldehydes. However, a major limitation of this mixed-aldehyde condensation approach is the inherently low yield of the targeted asymmetric porphyrin. This low efficiency stems from competitive statistical condensation, which generates a complex mixture of undesired symmetric and structural porphyrin isomers (i.e., A_4 , B_4 , *cis*- A_2B_2 , *trans*- A_2B_2 , A_3B , AB_3).¹⁸ Isolation of the pure unsymmetrical target compound from the resulting multi-component mixture demands exhaustive chromatographic separation, ultimately severely limiting the overall efficiency and scalability of this synthetic approach. To resolve this challenge, we have designed and synthesized *trans*- A_2B_2 porphyrins bearing 5-nitrothien-2-yl/4-nitrophenyl groups at 5,15-positions and various functional groups at the 10,20-positions. This *trans*- A_2B_2 porphyrins are physiochemically advantageous because the *trans* arrangement facilitates a superior π -electron conjugation pathway, leading to a pronounced "push-pull effect" and consequently, enhanced tunability of the porphyrin's electronic properties compared to the *cis*-isomers.²⁸ The *trans*- A_2B_2 porphyrins were synthesized utilizing an efficient two-step methodology. The initial step is the synthesis of dipyrromethene, involved combining the corresponding aldehyde and pyrrole in a 1:10 stoichiometric ratio under an inert nitrogen atmosphere. Trifluoroacetic acid (TFA), at a concentration of 0.10 equivalents, was subsequently introduced, and the resulting mixture was stirred at ambient temperature. The reaction progress was monitored *via* TLC until the complete consumption of the starting material was observed. At the end of the reaction, the reaction mixture was quenched with triethylamine (Scheme-1). Confirmation of dipyrromethane formation was achieved through ^1H NMR spectroscopy, evidenced by the presence of a characteristic signal for the -NH protons within the range of 8.25–7.77 ppm in the spectra of all synthesized derivatives. The methine proton (H^1) situated on the bridging carbon between the two pyrrole rings exhibited a distinctive chemical shift near 5.50 ppm in the ^1H NMR spectrum. The influences of substituents on the thienyl ring are reflected in the position of signals of -NH and H^1 protons of dipyrromethane.

[Scheme-1]

The second synthetic step yielded the targeted *trans*- A_2B_2 -type thien-2-yl porphyrins. This was achieved *via* the condensation of the synthesized dipyrromethanes with 5-nitrothiophene-2-carboxaldehyde, utilizing trifluoroacetic acid (TFA) as an acid catalyst. The resulting intermediate was subsequently subjected to oxidation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Scheme-2 and 3).

[Scheme-2]

[Scheme-3]

The ^1H NMR spectra of the synthesized porphyrins provided definitive evidence for the *trans*-isomeric structure. This confirmation was based on the observation of two doublets with equal integration values corresponding to the pyrrolyl β -protons, which appeared in the deshielded region of the spectrum. The proximity of these doublets resulted in a loss of their symmetric nature corresponding to symmetric A_4 type porphyrins where it appeared as a unique singlet peak. A comparative ^1H NMR spectroscopic analysis was performed on *trans*- A_2B_2 type 5,15-nitrothien-2-yl porphyrin ($t\text{-H}_2\text{5NTh4BrPP}$) versus symmetric 4-bromotetraphenyl porphyrin ($\text{H}_2\text{4BrPhP}$) to elucidate the electronic influence (or substituent effect) of the nitro groups appended to the thienyl rings on the porphyrin macrocycle (Figure-1a and 1b). The β -pyrrole proton ($\text{H}^{1,1'}$), which is adjacent to the *meso*-5-nitrothien-2-yl ring, experienced a significant downfield shift to 9.10 ppm. This shift into the deshielded region is attributed to the strong electron-withdrawing effect of the nitro group (NO_2), resulting in its chemical shift being distinct from the other β -pyrrole protons ($\text{H}^{2,2'}$) observed at 8.93 ppm. The chemical shift of the β -protons indicates the electronic influence exerted by the functional groups on the thienyl ring. This influence is effectively transmitted to the central porphyrin π -system through extended conjugation. The protons on the *meso*-5-nitrothien-2-yl ring exhibited two distinct ^1H NMR signals: A doublet at 8.38 ppm corresponding to the thienyl proton $\text{H}^{3,3'}$. This proton is shifted to a more deshielded region (or downfield), a phenomenon attributed to the electron-withdrawing effect of the adjacent nitro group. A doublet at 7.91 ppm corresponding to the $\text{H}^{4,4'}$ proton. The protons of the phenyl ring appeared at 8.08 ppm ($\text{H}^{5,5'}$) and 7.98 ppm ($\text{H}^{6,6'}$), respectively. Due to the symmetric nature of $\text{H}_2\text{4BrPhP}$, the β -pyrrole protons resonated as a distinct singlet at 8.87 ppm. Furthermore, two doublets of equal intensity were observed for the *ortho*- and *meta*-protons of the 4-bromophenyl ring at 8.10 ppm and 7.92 ppm, respectively. The ^1H NMR spectra of $t\text{-H}_2\text{5NTh4BrPP}$ and $\text{H}_2\text{4BrPhP}$ have exhibited a characteristic singlet corresponding to the two inner *imino*-protons of the porphyrin core at a highly shielded region – 2.81 ppm and – 2.85 ppm, respectively.

[Figure-1]

The influence of *meso*-aryl group and the nitro substituent on the electronic and structural properties of the porphyrin macrocycle was systematically examined by comparing two structurally analogous compounds: $t\text{-H}_2\text{Th4NPP}$ (where the NO_2 group is on the phenyl ring) and $t\text{-H}_2\text{5NThP}$ (where the NO_2 group is on the thienyl ring). The ^1H NMR spectra of both $t\text{-H}_2\text{Th4NPP}$ and $t\text{-H}_2\text{5NThP}$ exhibited two distinct doublets of equal integration (4H each), corresponding to the two magnetically non-equivalent sets of β -pyrrolyl protons ($\text{H}^{1,1'}$ and $\text{H}^{2,2'}$). In the spectrum of $t\text{-H}_2\text{5NThP}$, the β -pyrrolyl protons appeared at 9.14–9.12 ppm ($\text{H}^{1,1'}$), 9.04–9.02 ppm ($\text{H}^{2,2'}$), and for $t\text{-H}_2\text{Th4NPP}$ appeared at 9.14–9.13 ppm ($\text{H}^{1,1'}$), 8.77–8.76 ppm ($\text{H}^{2,2'}$) (Figure-2a). The β -pyrrolyl protons $\text{H}^{1,1'}$ of both the porphyrins appeared at same position, whereas a significant difference was observed for the $\text{H}^{2,2'}$ protons. The $\text{H}^{2,2'}$ protons of $t\text{-H}_2\text{5NThP}$ appeared at 9.04–9.02 ppm, whereas for $t\text{-H}_2\text{Th4NPP}$ appeared at 8.77–8.76 ppm.

H₂5NThP are significantly deshielded (shifted downfield by 0.27 ppm) relative to those in H₂Th4NPP. This deshielding in *t*-H₂5NThP provides clear evidence that the electronic properties of the porphyrin macrocycle at the H^{2,2'} positions are synergistically influenced by both the nature of the meso-aryl group (thienyl vs phenyl) and the location of the strong electron-withdrawing nitro substitution (directly on the thienyl ring). Among the series of synthesized *trans*-A₂B₂ porphyrins, the compound H₂5N5BrThP exhibits a notably highly deshielded ¹H NMR signal for its β-pyrrolyl protons 9.20–9.19 ppm (H^{1,1'}) and 9.08–9.07 ppm (H^{2,2'}) indicating a strong electronic perturbation of the macrocycle (Figure-2b). This significant downfield shift suggests that the combined electron-withdrawing effects from the nitro and bromo substituents on the meso-aryl groups effectively reduce the electron density within the porphyrin core, leading to the observed strong deshielding. The β-pyrrolyl protons of H₂5N5MeThP exhibit a greater downfield shift (9.18–9.16 ppm (H^{1,1'}) and 9.04–9.02 ppm (H^{2,2'})) compared to those of H₂5N3MeThP (9.14–9.12 (H^{1,1'}), 9.04–9.02 (H^{2,2'})), as evidenced by ¹H NMR spectroscopy. The downfield shift in H₂5N5MeThP is caused by an enhanced macrocyclic ring current effect when the thienyl ring is more effectively conjugated with the porphyrin core (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), whereas in H₂5N3MeThP the methyl groups are pointing towards the porphyrin core and also hindering the thienyl groups to come in conjugation with the porphyrin π-system.

[Figure-2]

The pattern of signals for all the *trans*-A₂B₂ type porphyrins was similar. However, the signals for the nitro phenyl substituted porphyrins were having less effect on imino- and β-pyrrole protons.

Electronic spectroscopy

The UV-Vis electronic absorption spectra of the newly synthesized *trans*-A₂B₂-type free-base porphyrins were recorded in CH₂Cl₂ at 298 K. All derivatives exhibited characteristic features comprising a single intense Soret band and four well-resolved Q bands. The electronic absorption profiles of these porphyrinoids are strongly dictated by the electronic nature (electron-donating or electron-withdrawing) of their peripheral substituents, the extent of macrocyclic π-conjugation, and the conformation of the central macrocyclic core.

It is known that the introduction of meso-heteroaromatic five-membered substituents induces a bathochromic shift in the absorption spectrum relative to their phenyl analogues.¹¹ However, investigations regarding the specific electronic interactions between the porphyrin core and mixed meso-substituents remain relatively sparse in the literature.^{20,24} This conclusion is further supported by the present study, which reveals that systematic modifications to the substituents and their substitution positions on the thien-2-yl and phenyl rings induce distinct bathochromic and hypsochromic shifts, respectively, in the electronic absorption bands of the porphyrin macrocycle.¹⁵

The UV-visible spectral features of *trans*-A₂B₂-type free base porphyrins were compared with those of A₄-type free base porphyrins in the following discussion. Electronic spectral measurements were carried out in dichloromethane at 298 K and the details are summarized in Table 1. The position of the absorption maxima (λ_{max}) of the synthesized porphyrins depend upon the *meso*-substitutions on the porphyrin periphery. Figure-3 and 4 shows the comparative absorption spectra of the synthesized porphyrins in CH₂Cl₂. In *t*-H₂5NThP, 5,15 and 10,20 *meso*-positions are occupied by 5-nitrothien-2-yl and thien-2-yl groups, respectively.

As the number of nitro groups increases in *t*-H₂5NThP (428 nm) compared to the basic H₂TThP (426 nm), it is observed that the absorption maximum of solet band red-shifted to 2 nm. In the H₂5MeThP series, the solet band of *t*-H₂5N5MeThP is red-shifted by 2 nm as similar to the H₂TThP series. In contrast, the solet band of *t*-H₂5N3MeThP red-shifted by 4 nm in the H₂3MeThP series. This can be rationalized by a comparison between the methyl isomers H₂5MeThP and H₂3MeThP. The solet band of H₂3MeThP is 6 nm blue-shifted compared to H₂5MeThP, due to the near perpendicular orientation of 3-methylthien-2-yl ring caused by the methyl group at the third position of the ring which prevents the on-plane orientation and restricts the electron delocalization between the two aromatic systems. Two of the substitutions at the 5,15 *meso*-positions in H₂3MeThP were replaced with the 5-nitrothien-2-yl group (*t*-H₂5N3MeThP), there is a significant red-shift (4 nm) due to the enhanced conjugation arose by the combination of on-plane oriented thienyl ring and an increase in the number of electron-withdrawing (mesomeric, -M effect) nitro groups. As anticipated, a bathochromic shift of 2 nm is observed in *t*-H₂5N5BrThP relative to H₂5BrThP, consistent with the expected electronic effects of the substituent. In order to gain further insight into the influence of group orientation at the porphyrin *meso*-position on electronic properties, the electronic absorption spectrum of *t*-H₂5NTh4BrPP, *t*-H₂5NThPP, and *t*-H₂Th4NPP were analysed.

The solet band of *t*-H₂5NThPP (422 nm) is red-shifted by 5 nm compared to parent porphyrin H₂TTP (417 nm), similarly the solet band position of *t*-H₂5NTh4BrPP (423 nm) red-shifted by 4 nm compared to H₂4BrPhP (419 nm). The significant red-shift in *t*-H₂5NThPP and *t*-H₂5NTh4BrPP caused by replacing phenyl and 4-bromo phenyl with 5-nitrothien-2-yl groups is owing to the combined effect of extended conjugation and inductive interaction of electron-withdrawing nitro substituent with porphyrin-system *via* near planar thienyl ring. When the solet band positions of *t*-H₂Th4NPP and H₂TThP are compared, there is a blue-shift of 2 nm on substituting the thien-2-yl group with 4-nitrophenyl group at 5,15-position of H₂TThP. The solet band is red-shifted by 2 nm while the thien-2-yl group is replaced with the 5-nitrothien-2-yl group at the 5,15-position of H₂TThP. On comparing *t*-H₂5NThP and *t*-H₂Th4NPP the difference in the solet band is 4 nm, revealing the conjugation of π -electrons between the porphyrin core and substituent on the phenyl ring decreases, and the substituents on the thien-2-yl ring can easily come into conjugation with the core. This similar trend was observed in the cases of bromo derivatives (*t*-H₂5N5BrThP (431 nm) and *t*-H₂5NTh4BrPP (423 nm)) and the difference in the shift is 8 nm. This high magnitude in the solet band shift is attributed by the combined -I (inductive) and + M (mesomeric) effect of the bromo

groups on the thien-2-yl ring(s). But these effects on the phenyl ring have a minimal impact on the electronic properties. It is also worth noting that the substituents on the thien-2-yl ring increase the full width at half maximum (fwhm) over the phenyl ring, indicating that the interaction between the porphyrin core and the substituent is quite strong.

[Table-1]

[Figure-3]

The synthesized *trans*-A₂B₂-type porphyrins shows an interesting trend in red-shift and aligns in the following order: *t*-H₂5NThPP (422 nm) < *t*-H₂5NTh4BrPP (423 nm) < *t*-H₂Th4NPP (424 nm) < *t*-H₂5NThP (428 nm) < *t*-H₂5N3MeThP (429 nm) < *t*-H₂5N5BrThP (431 nm) < *t*-H₂5N5MeThP (433 nm). These findings strongly suggest that the substituent and conformation of thien-2-yl rings provide tuneable optical absorption spectrum features with considerable electronic interactions amongst the porphyrin π -systems.

[Figure-4]

Electrochemical analysis

To elucidate the effects of *meso*-thienyl and phenyl substitution on the electronic properties of *trans*-A₂B₂-type porphyrins, cyclic voltammetry (CV) was performed in CH₂Cl₂ containing 0.1 M TBAPF₆ at 298 K. The resulting electrochemical data are summarized in Table 2. The ligand-centred redox processes comprised two one-electron oxidations and two one-electron reductions were reversible, quasi-reversible or irreversible in nature. The conformation and electronic properties of substituents at the *meso*-positions significantly modulate the redox potentials of the porphyrin π -electron system.^{11,15} The comparative cyclic voltammogram of H₂4BrPhP (black) and *t*-H₂5NTh4BrPP (red) are shown in Fig. 5.

[Table-2]

[Figure-5]

The redox properties of the synthesised *trans*-A₂B₂ type porphyrins have been significantly altered by the substituents, and the effects predominantly depend on whether the substitution is on the thienyl or phenyl ring.¹¹ The first oxidation and reduction potentials of the porphyrins were utilised to analyze the results. An analysis of the redox data reveals that the oxidation potentials were shifted to more positive potential in *t*-H₂5NThP (1215 mV) when nitro groups were appended on the meso thien-2-yl rings, suggesting that *t*-H₂5NThP are harder to oxidize than H₂TThP (892 mV). Similarly, the reduction potentials shifted to the anodic region (-1092 mV $\rightarrow$ -904 mV).

The first ring redox potentials of H₂5BrThP and *t*-H₂5N5BrThP were analyzed by comparing its non-bromo analog H₂TThP and *t*-H₂5NThP, respectively. The oxidation and reduction potentials of H₂5BrThP

(965 mV) and *t*-H₂5N5BrThP (1255 mV) were anodically shifted relative to H₂TThP and *t*-H₂5NThP, respectively. The notable shift in the redox potentials of bromo groups on the thien-2-yl ring can be attributed to the combined effect of -I (inductive) and +M (mesomeric). The larger anodic shift (443 mV) was found for *t*-H₂5N5MeThP (1280 mV) relative to H₂5MeThP (837 mV), showing that the influence of the electron-withdrawing nitro group on the thienyl ring to the core porphyrin π -system is stronger than the methyl group. On analyzing the redox potentials of *t*-H₂5N5MeThP and *t*-H₂5N3MeThP, it is found that the first oxidation and reduction potentials significantly shifted to the anodic region compared to parent *t*-H₂5MeThP and *t*-H₂3MeThP, respectively. However, there is only a 262 mV difference in the first oxidation potential between *t*-H₂5N3MeThP and *t*-H₂3MeThP, indicating the position of methyl group drastic influence in dictating the electronic properties of porphyrin core. The position of methyl group in *t*-H₂5N3MeThP and *t*-H₂3MeThP makes the corresponding thien-2-yl group of the molecule nearly perpendicular to the π -system at the centre. To gain further insight into the impact of conformation on the redox characteristics, phenyl derivatives of *trans*-A₂B₂ type porphyrins were studied. The following trend of the first oxidation potential of H₂TThP (892 mV) < H₂TPP (1000 mV) < *t*-H₂Th4NPP (1125 mV) < *t*-H₂5NThP (1215 mV) < *t*-H₂5NThPP (1255mV) < H₂TaNThP(1442 mV) indicates (an ease of oxidation potential in *t*-H₂Th4NPP relative to *t*-H₂5NThP) that the high influence on the redox potentials (Table-2) in the case of porphyrins in which nitro group is on the thien-2-yl ring is owing to nearly in plane orientation of thienyl ring with the mean plane of the porphyrin core. Cases where the nitro substitutions on phenyl ring have only less effect on the redox potentials (H₂TPP (1000 mV) → H₂Th4NPP (1125 mV)) due to perpendicular disposition of the phenyl groups precludes the electronic communication between the substituent and porphyrin π -system.

This is supported further by comparing the redox potentials of H₂5BrThP and *t*-H₂5N5BrThP to those of their phenyl analogs H₂4BrPhP and *t*-H₂5NTh4BrPP, respectively. The first oxidation potential of *t*-H₂5N5BrThP (1255 mV) was found to be 290 mV anodically shifted relative to H₂5BrThP (965 mV). In contrast, the first oxidation potential of *t*-H₂5NTh4BrPP (1310 mV) was only 162 mV anodically shifted related to H₂4BrPhP (1148 mV). The reduction potentials were also showed the same trends. The observed variations in redox potentials strongly indicate that substituents and functionalization on the thien-2-yl rings enable enhanced tunability of electronic interactions within the porphyrin π -system.

The red-shift in the electronic spectrum and the anodic shift in the redox potentials of *trans*-A₂B₂ type porphyrins featuring 5-nitrothien-2-yl groups at the meso-5,10 positions strongly suggest the central porphyrin π -system and the substituent at the meso-positions have good electronic communication. In contrast to meso-phenyl porphyrins, where the phenyl rings adopt an orthogonal orientation due to a sterically induced higher rotational barrier, the thienyl group is free to coplanar with the porphyrin π -system, enhancing resonance interaction. The observed electrochemical shifts in the redox potentials support the electronic properties of the newly synthesized porphyrins.

Conclusion

In summary, *trans*-A₂B₂-type porphyrins incorporating 5-nitrothien-2-yl substituents at the *meso*-5,15 positions of the tetrapyrrolic macrocycle were successfully designed and synthesized *via* a two-step modified dipyrromethane strategy. The initial step involved the efficient preparation of dipyrromethane through trifluoroacetic acid (TFA)-catalyzed condensation of the corresponding aldehydes with pyrrole. In the second step, the synthesized dipyrromethene underwent acid-catalyzed condensation with 5-nitrothiophene-2-carboxaldehyde or 4-nitrobenzaldehyde in chloroform under a nitrogen atmosphere, followed by oxidative aromatization using DDQ, affording the desired porphyrin derivatives. The pronounced electronic perturbation at the porphyrinic π -core effectively rationalizes the influence of nitro substituents located on distinct *meso*-aryl rings. Cyclic voltammetry further substantiates the significant contribution of extended conjugation to the electronic characteristics of the porphyrin, with thienyl substituents exhibiting a greater effect than their phenyl counterparts. The photophysical and electrochemical behaviour of the *trans*-A₂B₂-type porphyrins unequivocally highlights the critical role of the thien-2-yl linker in facilitating efficient electron delocalization between the two highly conjugated π -systems.

Declarations

“Disclosure of Interest”:

The authors declare that there are no competing interests.

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Author Contribution

C. Arunamaheswari: Synthesis, purification, characterization of the compounds and writing of the original manuscript. P. Gayathri: Electrochemical studies, interpretation of results, and manuscript review. P. Bhavana: Spectroscopic characterization, data interpretation, and manuscript review. J. Veerarajan: Data Collection and interpretation, and manuscript review. R. Prasath: Supervision, project administration, interpretation of results, critical revision of the manuscript, and final approval of the manuscript. All authors read and approved the final manuscript.

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Tables

Table-1: UV–Vis absorption spectral data (in nm)^a of the synthesized porphyrins in CH₂Cl₂ at 298 K.

Porphyrin	Soret band	Q bands	FWHM
H ₂ TThP	426 (5.59)	523 (4.30), 560 (4.02), 597 (3.88), 661 (3.86)	16.56
H ₂ T5NThP	432 (5.50)	522 (4.45), 560 (4.12), 596 (4.05), 656 (3.46)	30.73
<i>t</i> -H ₂ 5NThP	428 (5.43)	523 (4.30), 563 (4.05), 596 (3.90), 658 (3.55)	30.43
H ₂ 5MeThP	431 (5.50)	526 (4.14), 567 (3.98), 597 (3.77), 662 (3.49)	18.49
<i>t</i> -H ₂ 5N5MeThP	433 (5.58)	524 (4.41), 566 (4.15), 597 (3.97), 661 (3.38)	28.40
H ₂ 3MeThP	425 (5.42)	520 (4.20), 556 (3.80), 596 (3.76), 661 (3.69)	15.87
<i>t</i> -H ₂ 5N3MeThP	429 (5.66)	522 (4.55), 562 (4.22), 596 (4.10), 656 (3.54)	26.43
H ₂ 5BrThP	429 (5.55)	524 (4.23), 562 (3.91), 597 (3.76), 658 (3.22)	17.80
<i>t</i> -H ₂ 5N5BrThP	431 (5.50)	523 (4.37), 563 (4.08), 596 (3.97), 658 (3.46)	25.75
H ₂ TPP	417 (5.58)	515 (4.19), 550 (3.83), 591 (3.68), 647 (3.61)	14.22
<i>t</i> -H ₂ 5NThPP	422 (5.65)	518 (4.50), 558 (4.38), 593 (4.11), 651 (4.10)	25.75
H ₂ 4BrPhP	419 (5.52)	515 (4.19), 551 (3.81), 590 (3.66), 646 (3.44)	12.78
<i>t</i> -H ₂ 5NTh4BrPP	423 (5.42)	518 (4.25), 557 (4.08), 593 (3.84), 651 (3.75)	24.37
H ₂ T4NPP	424 (5.52)	517 (4.18), 552 (3.80), 591 (3.62), 647 (3.42)	21.54
<i>t</i> -H ₂ Th4NPP	424 (5.58)	520 (4.20), 557 (3.88), 594 (3.64), 652 (3.48)	20.43

^aThe values in parenthesis refer to loge values, ϵ in $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$

Table-2: Half-wave redox potentials (mV) vs. Ag/AgCl of the synthesized porphyrins in CH₂Cl₂ using 0.1 M TBAPF₆ at 298 K.

Porphyrin	Oxidation		Reduction	
	II	I	I	II
H ₂ TThP	1132	892	-1092	-1420
H ₂ TaNThP		1442 ⁱ	-657 ⁱ	-843
<i>t</i> -H ₂ 5NThP	1495 ⁱ	1215 ⁱ	-940 ⁱ	-1130
H ₂ 5MeThP		837 ⁱ	1090	1450
<i>t</i> -H ₂ 5N5MeThP	1525 ⁱ	1280 ⁱ	-710	810
H ₂ 3MeThP	1514 ⁱ	998	-1122	-1486
<i>t</i> -H ₂ 5N3MeThP	1564 ⁱ	1260 ⁱ	-828	-1258 ⁱ
H ₂ 5BrThP	1270 ⁱ	965	-893	-1050
<i>t</i> -H ₂ 5N5BrThP	1550 ⁱ	1255 ⁱ	-735	-975
H ₂ TPP	1335	1000	-1230	-1540
<i>t</i> -H ₂ 5NThPP		1255	-710	-935 ⁱ
H ₂ 4BrPhP	1392	1148	-846	-1166
<i>t</i> -H ₂ 5NTh4BrPP	1425	1310	-750	-1098
<i>t</i> -H ₂ Th4NPP	1240 ⁱ	1125 ⁱ	-1015	-1475 ⁱ

ⁱirreversible.

Scheme

Scheme 1 to 3 are available in the Supplementary Files section.

Figures

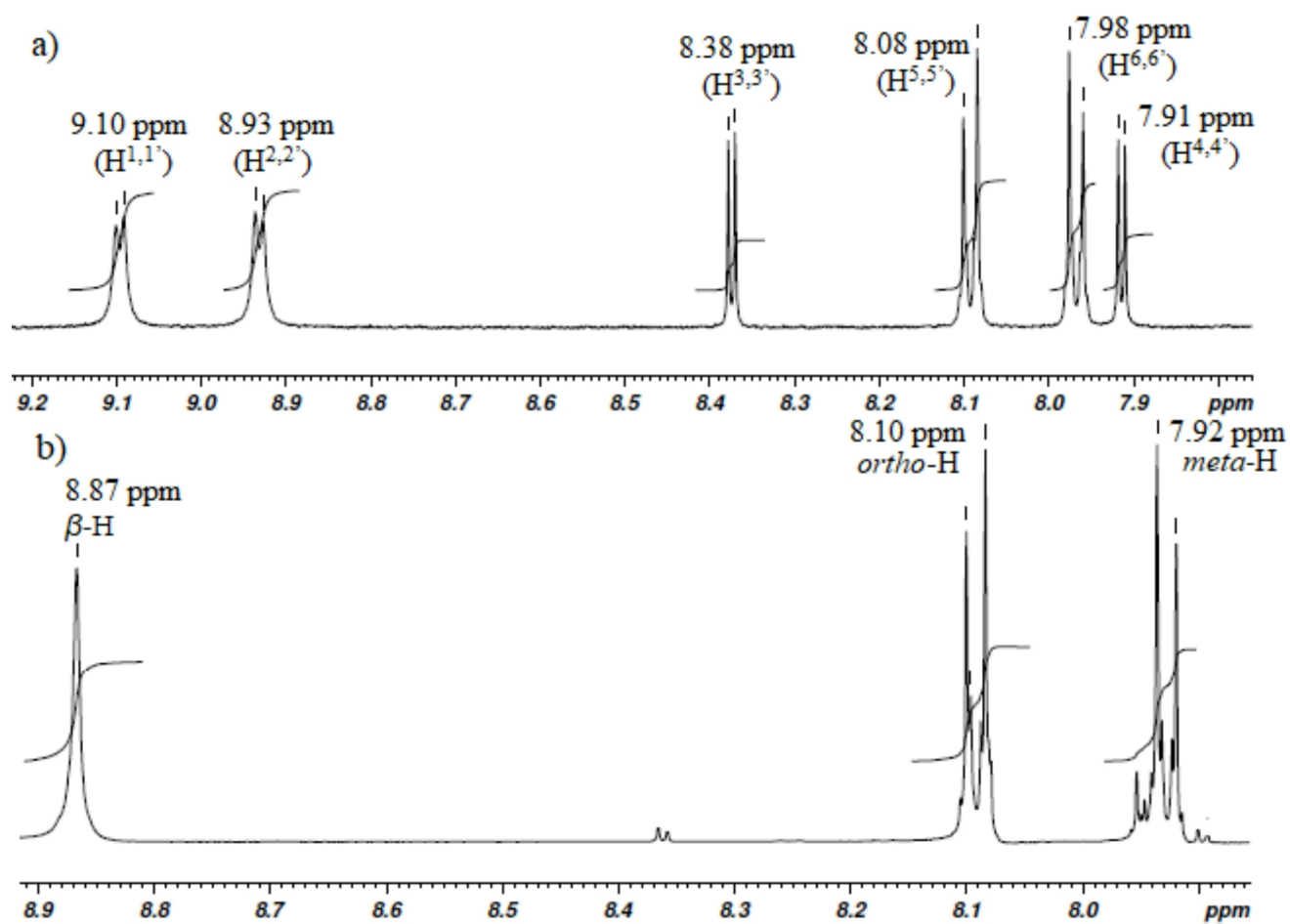


Figure 1

Aromatic region in the ^1H NMR spectrum of (a) $t\text{-H}_2\text{5NTh4BrPP}$ and (b) $\text{H}_2\text{4BrPhP}$.

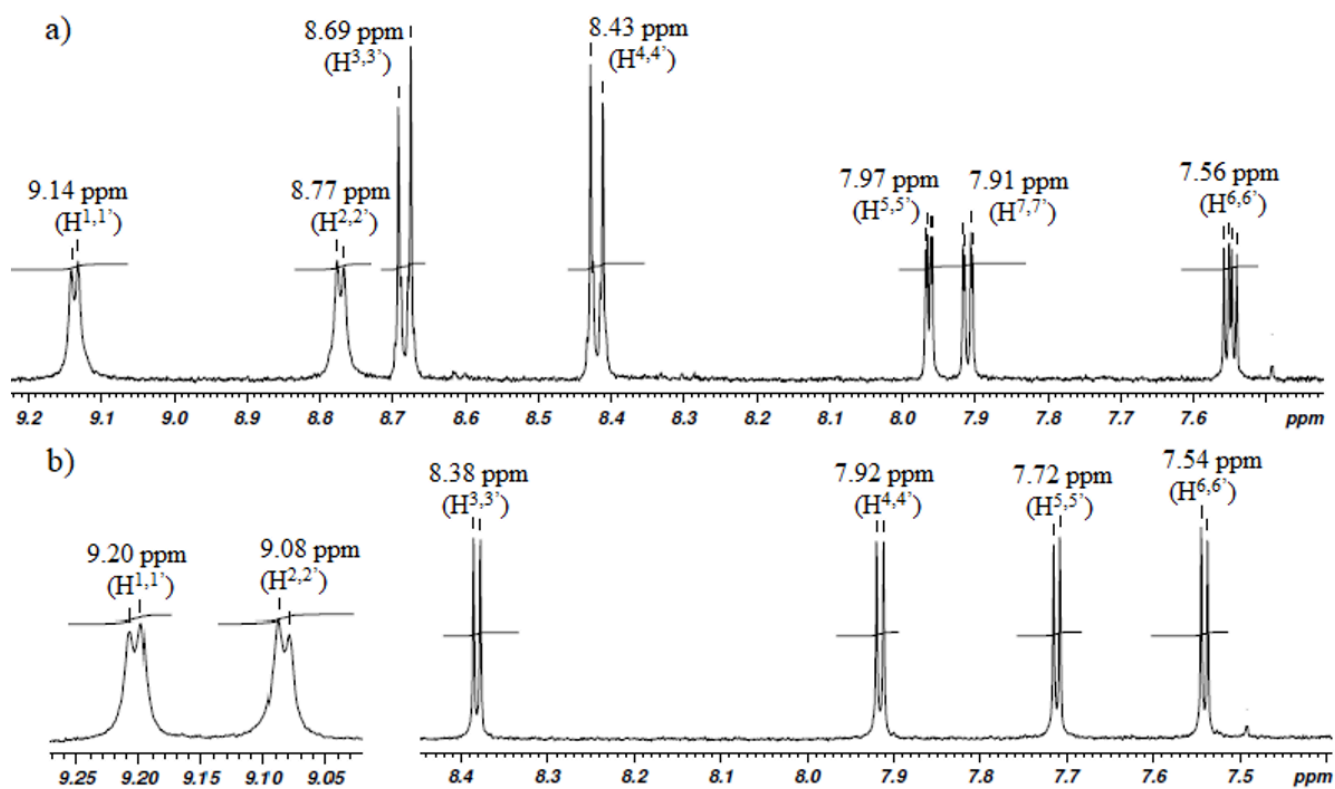


Figure 2

Aromatic region in the ^1H NMR spectrum of (a) $t\text{-H}_2\text{Th4NPP}$ and (b) $\text{H}_25\text{N5BrThP}$.

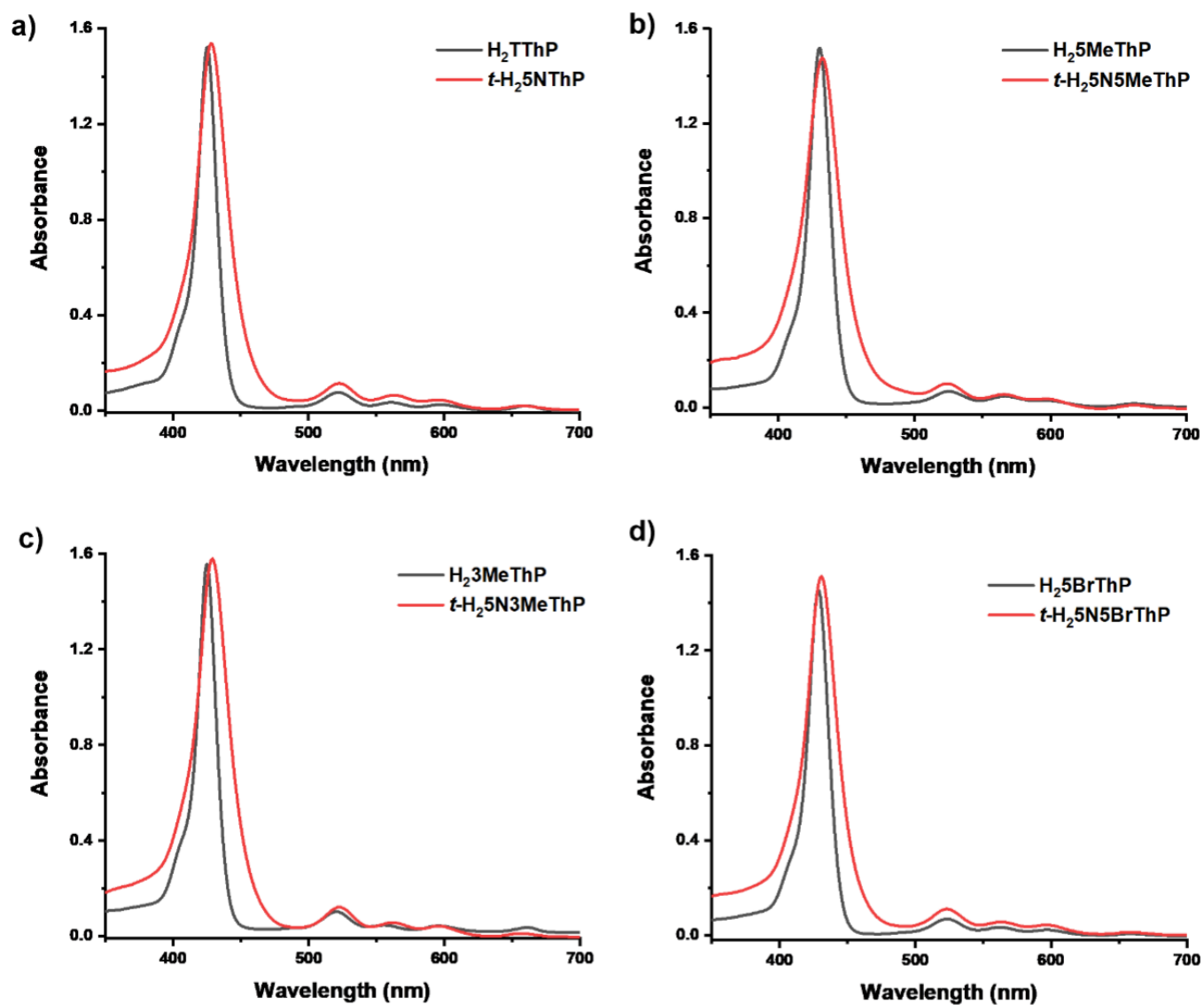


Figure 3

Comparative electronic absorption spectra of the synthesized porphyrins in CH_2Cl_2 at 298 K.

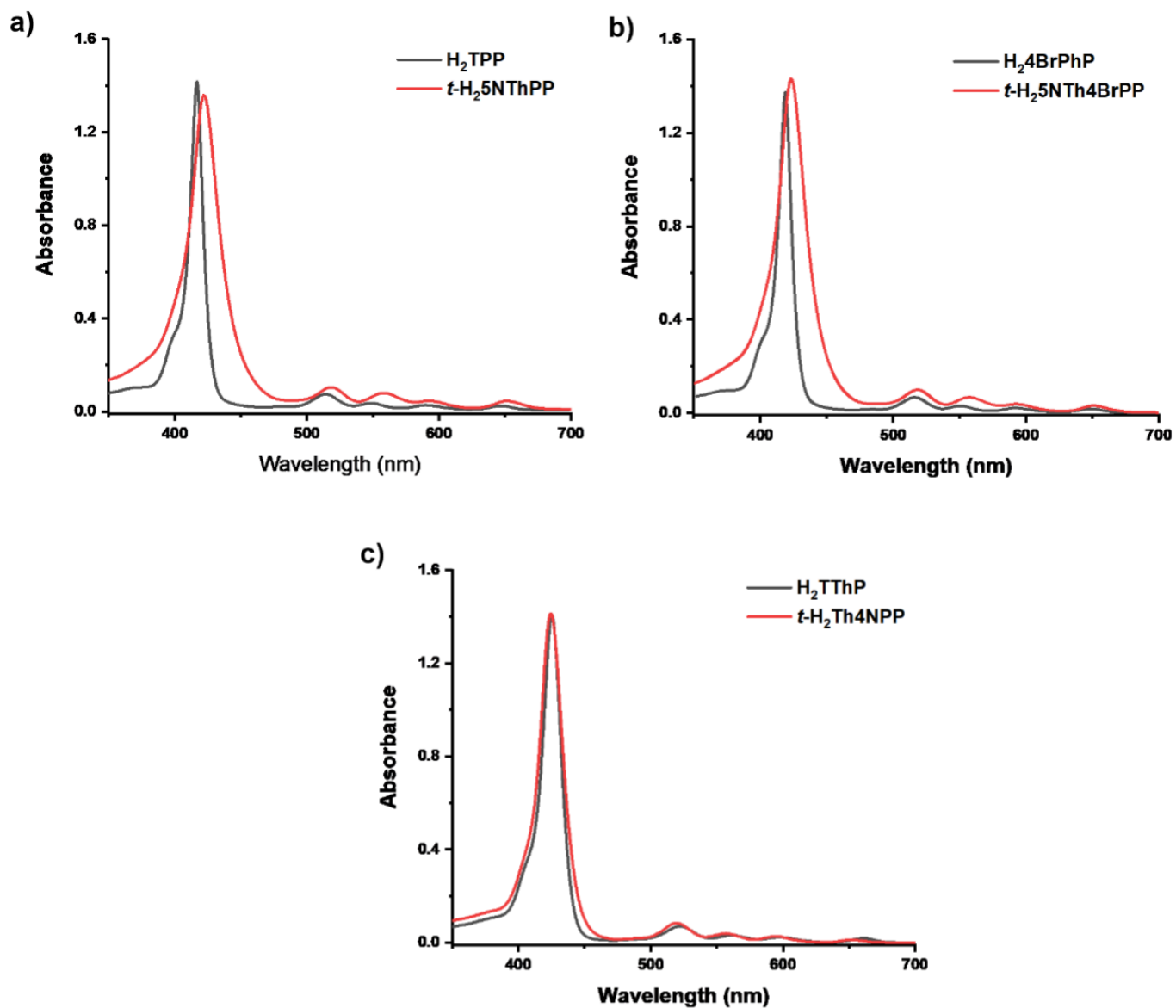


Figure 4

Comparative electronic absorption spectra of the synthesized porphyrins in CH_2Cl_2 at 298 K.

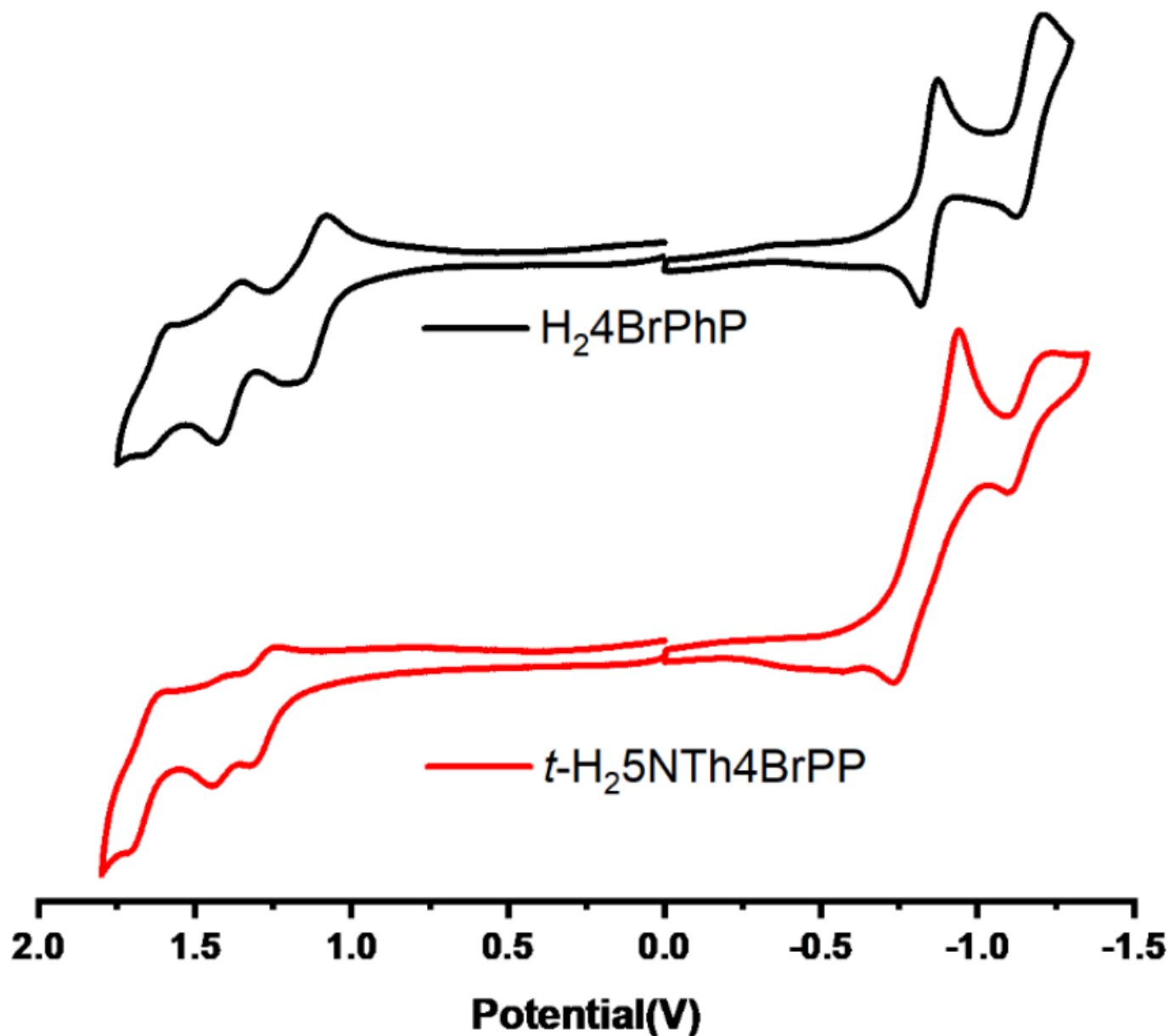


Figure 5

Cyclic voltammogram of $H_{24}BrPhP$ (black) and $t-H_{25}NTh4BrPP$ (red) in CH_2Cl_2 with 0.1M $TBAPF_6$ as the supporting electrolyte at a scan rate of 100 mV s^{-1} .

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme.docx](#)
- [GraphicalAbstract.docx](#)