

## Research Article

# Electrochemical and Spectroscopic Characterization of Aluminium(III)-*para*-methyl-meso-tetraphenylporphyrin Complexes Containing Substituted Salicylates as Axial Ligands

Gauri D. Bajju, Deepmala, Sunil Kumar Anand, Sujata Kundan, and Narinder Singh

*P.G. Department of Chemistry, University of Jammu, Jammu 180006, India*

Correspondence should be addressed to Gauri D. Bajju; [gauribajju@gmail.com](mailto:gauribajju@gmail.com)

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A series of aluminium(III)-*p*-methyl-meso-tetraphenylporphyrin ( $p\text{-CH}_3\text{TPP-Al(III)}$ ) containing axially coordinated salicylate anion [ $p\text{-CH}_3\text{TPP-Al-X}$ ], where X = salicylate (SA), 4-chlorosalicylate (4-CSA), 5-chlorosalicylate (5-CSA), 5-fluorosali-cylate (5-FSA), 4-aminosalicylate (4-ASA), 5-aminosalicylate (5-ASA), 5-nitrosali-cylate (5-NSA), and 5-sulfosalicylate (5-SSA), have been synthesized and characterized by various spectroscopic techniques including ultraviolet-visible (UV-vis), infrared (IR) spectroscopy, proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectroscopy,  $^{13}\text{C}$  NMR, and elemental analysis. A detailed study of electrochemistry of all the synthesized compounds has been done to compare their oxidation and reduction mechanisms and to explain the effect of axial coordination on their redox properties.

## 1. Introduction

The field of the macrocyclic chemistry of transition metals is developing very rapidly because of its applications [1] and importance in the area of coordination chemistry [2]. Among the various macrocyclic systems studied, metalloporphyrins constitute an important class. Metalloporphyrins and their complexes with various ligands, which play an important role in biological processes and exhibit catalytic properties, are continuing to remain the subject of systematic experimental and theoretical studies [3, 4]. The axial ligation on the metal center is a synthetic way to synthesize large multiporphyrinic systems [5–10]. Actually much attention has been paid to porphyrin containing zinc(II), magnesium(II), tin(IV), and rhodium(III) as metal centers [11, 12]. Although aluminium(III) porphyrins are well known for their catalytic properties and their rich photo- and electrochemistry [13–15], their use as molecular building blocks for the design of porphyrin arrays remains limited. The synthesis of porphyrin arrays including aluminium(III) porphyrins is mostly limited to the use of phenolates [16] and carboxylates [17] as the axial ligand. Surprisingly, there is no example of aluminium(III) porphyrins axially bonded to salicylate anion.

Here, we report the synthesis and characterization of aluminium(III)-*p*-methyl-meso-tetraphenylporphyrins ( $p\text{-CH}_3\text{TPP-Al-X}$ ) complexes axially bonded to substituted salicylate anions and study their electrochemistry.

## 2. Materials and Methods

Pyrrole (Fluka, Switzerland) was distilled over KOH pellets under reduced pressure before use. Benzaldehyde was procured from Aldrich, USA, and aluminium oxide (basic) was purchased from Fluka, Switzerland. Anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) was procured from Ranbaxy Labs. Ltd. (India). Anhydrous aluminium(III) chloride, benzonitrile, and various salicylic acid were purchased from Alfa Aesar, Japan. Benzonitrile was dried and vacuum distilled before use.  $(\text{TBA})\text{PF}_6$  was obtained from Himedia Laboratories Pvt. Ltd. and recrystallized twice from EtOAc and dried in vacuum prior to use.

The optical absorption spectrum of the compounds was recorded on a T90+ UV/VIS spectrophotometer using a pair of matched quartz cells of 10 mm path length at an ambient temperature. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra

were recorded on a Bruker Avance III (400 MHz) in  $\text{CDCl}_3$  and  $\text{CD}_3\text{OH}$  using tetramethylsilane as an internal standard.

Cyclic voltammetry measurements were carried out with an Autolab Computer-controlled electrochemical measurement system equipped with a potentiostat, a three electrode system comprised a gold electrode, a Pt wire, and an (Ag/AgCl/KCl) wire as working, counter, and reference electrode, respectively. A 0.1 M solution of n-tetrabutylammonium hexafluorophosphate ( $\text{TBA}^+\text{PF}_6^-$ ) in freshly distilled  $\text{CH}_2\text{Cl}_2$  was used as a supporting electrolyte during the electrochemical experiments. The scan rate was 20 mV/s and the range was  $-2$ – $2$  V. The concentration of the porphyrins was  $10^{-6}$  M. The solutions were purged with oxygen-free nitrogen gas prior to measurements and all measurements were made at room temperature (300 K).

*p*-Methyl-meso-tetraphenylporphyrin (*p*- $\text{CH}_3$ -TPP). The metal free-base  $\text{H}_2$ TPP was synthesized by the conventional method of condensation of benzaldehyde with pyrrole by modified Adler method [18]. The purified porphyrin was obtained in  $>20\%$  yields. UV-Vis spectra:  $\lambda_{\text{max}}$  (nm) in  $\text{CHCl}_3$  420, 517, 552.5, 592, 649.

*p*-Methyl-meso-tetraphenylporphyrinatoaluminium(III) Chloride (*p*- $\text{CH}_3$ -TPP-Al-Cl). A 0.1 g of  $\text{H}_2$ TPP was refluxed with 0.1 g of anhydrous  $\text{AlCl}_3$  in 16 mL of dry benzonitrile for 1–3 h. The reaction course was monitored by absorption spectra of the reaction mixture. The refluxing was stopped when the absorption bands of  $\text{H}_2$ TPP disappeared. The reaction mixture was filtered to remove the presence of excess  $\text{AlCl}_3$ . To the filtrate excess hexane was added for complete precipitation of the complex. The precipitates were washed with hexane and dissolved in methanol. A 3 N HCl solution was added to precipitate the complex which was then recrystallized from the solution of acetone and hexane. Reddish purple crystals thus obtained were of *p*- $\text{CH}_3$ -TPP-Al-Cl- $4\text{H}_2\text{O}$ . More reddish crystals of *p*- $\text{CH}_3$ -TPP-Al-Cl- $4\text{H}_2\text{O}$  were obtained by drying *p*- $\text{CH}_3$ -TPP-Al-Cl- $4\text{H}_2\text{O}$  at  $110$ – $120^\circ\text{C}$  for 2 hours. Anal. Calcd. for  $\text{C}_{48}\text{H}_{36}\text{ClN}_4\text{Al}$ : C 78.85, H 4.92, N 7.66; Found: C 78.32, H 4.66, N 7.24; UV-Vis. (in  $\text{CHCl}_3$ )  $\lambda_{\text{max}}$ (nm): 418.0, 466.0, 510.0sh, 549.0, 592.0; IR (KBr) $\nu_{\text{max}}$ :  $528.15\text{ cm}^{-1}$  ( $\nu_{\text{Al-N}}$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.0 (8H, s,  $\beta$ -pyrrole), 8.38(d) and 8.16(d) due to  $\text{H}_{2,6}$ , 7.65(d) and 7.55(d) due to  $\text{H}_{3,5}$ , 2.70 (s, 12H, *p*- $\text{CH}_3$ ).

*p*-Methyl-meso-tetraphenylporphyrinatoaluminium(III) Hydroxide (*p*- $\text{CH}_3$ -TPP-Al-OH). *p*- $\text{CH}_3$ -TPP-Al-Cl- $4\text{H}_2\text{O}$  (mg) was dissolved in a mixture of  $\text{CHCl}_3$  and MeOH in 10:1 ratio. The solution was shaken with 0.1%  $\text{AgNO}_3$  solution and the  $\text{CHCl}_3$  layer was separated. The process was repeated until no further precipitates of AgCl separated out. Finally, the solution was passed through  $\text{Na}_2\text{SO}_4$  and dried to obtain purple crystals of *p*- $\text{CH}_3$ -TPP-Al-OH.

Anal. Calcd. for  $\text{C}_{48}\text{H}_{37}\text{N}_4\text{AlO}$ : C 80.89, H 5.19, N 7.86; Found: C 80.32, H 5.06, N 7.24; UV-Vis. (in  $\text{CHCl}_3$ )  $\lambda_{\text{max}}$ (nm): 404.0, 425.0, 516.0, 556.0, 569.0; IR (KBr) $\nu_{\text{max}}$ :  $528.15\text{ cm}^{-1}$  ( $\nu_{\text{Al-N}}$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.0 (8H, s,  $\beta$ -pyrrole), 8.35(d) and 8.12(d) due to  $\text{H}_{2,6}$ , 7.65(d) and 7.55(d) due to  $\text{H}_{3,5}$ , 2.70 (s, 12H, *p*- $\text{CH}_3$ ).

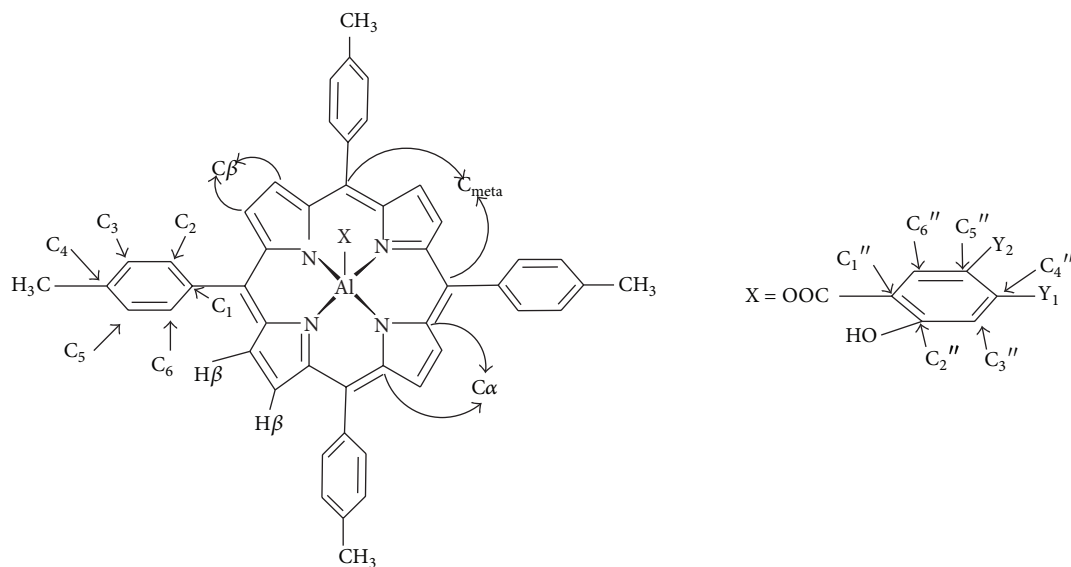
*Axially Coordinated p*-Methyl-meso-tetraphenylporphyrinatoaluminium(III)-salicylate (*p*- $\text{CH}_3$ -TPP-Al-X). To a solution of *p*-methyl5,10,15,20-tetraphenylporphyrin aluminium(III) hydroxide (0.020 g, 0.03 mmol) in 10 mL  $\text{CHCl}_3$  was added, as a solid, 5 equiv. of salicylic acid (SA) (15 nmol). The resulting solution was stirred at room temperature for 12 h, at which time it was filtered to remove excess acid. The solution was evaporated to yield purple colored complex (92%). Similar procedure was followed with all other substituted salicylic acids (Figure 1). The purified axially ligated aluminium porphyrin complexes were obtained in yields of 80–85%.

*p*- $\text{CH}_3$ -TPP-Al-SA. Purple solid; Anal. Calcd. for  $\text{C}_{55}\text{H}_{41}\cdot\text{N}_4\text{O}_3\text{Al}$ : C 79.32, H 4.92, N 6.73; Found: C 79.12, H 4.76, N 6.63; UV-Vis. (in  $\text{CHCl}_3$ )  $\lambda_{\text{max}}$ (nm): 417, 546, 581 nm. ESI-MS ( $\text{CH}_3\text{OH}$ ): *m/z* calcd. for  $\text{C}_{55}\text{H}_{41}\text{N}_4\text{O}_3\text{Al}$ : 832; found 832; IR (KBr) $\nu_{\text{max}}$ :  $528.21\text{ cm}^{-1}$  ( $\nu_{\text{Al-N}}$ ),  $736.19\text{ cm}^{-1}$  ( $\nu_{\text{Al-O}}$ , carboxylic SA);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.0 (8H, s,  $\beta$ -pyrrole), 8.38(d) and 8.16(d) due to  $\text{H}_{2,6}$ , 7.65(d) and 7.55(d) due to  $\text{H}_{3,5}$ , 2.70 (s, 12H, *p*- $\text{CH}_3$ ), 6.78 (t,  $\text{H}_4''$ ), 6.21 (d,  $\text{H}_3''$ ), 6.16 (d,  $\text{H}_6''$ ), 6.08 (d,  $\text{H}_5''$ );  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 169.8(COO), 149.9( $\text{C}_\alpha$ ), 141.6( $\text{C}_1$ ), 134.9( $\text{C}_{2,6}$ ), 132.2( $\text{C}_\beta$ ), 127.6( $\text{C}_4$ ), 126.6( $\text{C}_{3,5}$ ), 122.2( $\text{C}_m$ ), 159.4( $\text{C}_2''$ ), 129.8( $\text{C}_6''$ ), 112.5( $\text{C}_1''$ ), 117.3( $\text{C}_5''$ ), 115.7( $\text{C}_3''$ ), 133.6( $\text{C}_4''$ ), 21.5(*p*- $\text{CH}_3$ ).

*p*- $\text{CH}_3$ -TPP-Al-4-CSA. Purple solid; Anal. Calcd. for  $\text{C}_{55}\text{H}_{40}\cdot\text{N}_4\text{O}_3\text{ClAl}$ : C 76.16, H 4.61, N 6.46; Found: C 76.12, H 4.46, N 6.23; UV-Vis. (in  $\text{CHCl}_3$ )  $\lambda_{\text{max}}$ (nm): 417, 547, 587 nm. ESI-MS ( $\text{CH}_3\text{OH}$ ): *m/z* calcd. for  $\text{C}_{55}\text{H}_{40}\text{N}_4\text{O}_3\text{ClAl}$ : 866.5; found 866.2; IR (KBr) $\nu_{\text{max}}$ :  $525.21\text{ cm}^{-1}$  ( $\nu_{\text{Al-N}}$ ),  $735.19\text{ cm}^{-1}$  ( $\nu_{\text{Al-O}}$ , carboxylic SA);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.00 (8H, s,  $\beta$ -pyrrole), 8.08(d) and 8.06(d) due to  $\text{H}_{2,6}$ , 7.73(d) and 7.65(d) due to  $\text{H}_{3,5}$ , 2.70 (s, 12H, *p*- $\text{CH}_3$ ), 6.74 (s,  $\text{H}_3''$ ), 6.26 (d,  $\text{H}_5''$ ), 6.44 (d,  $\text{H}_6''$ );  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 169.8(COO), 149.9( $\text{C}_\alpha$ ), 141.6( $\text{C}_1$ ), 134.9( $\text{C}_{2,6}$ ), 132.2( $\text{C}_\beta$ ), 127.6( $\text{C}_4$ ), 126.6( $\text{C}_{3,5}$ ), 122.2( $\text{C}_m$ ), 159.4( $\text{C}_2''$ ), 129.8( $\text{C}_6''$ ), 112.5( $\text{C}_1''$ ), 117.3( $\text{C}_5''$ ), 115.7( $\text{C}_3''$ ), 133.6( $\text{C}_4''$ ), 21.5(*p*- $\text{CH}_3$ ).

*p*- $\text{CH}_3$ -TPP-Al-5-CSA. Purple solid; Anal. Calcd. for  $\text{C}_{55}\text{H}_{40}\cdot\text{N}_4\text{O}_3\text{ClAl}$ : C 76.16, H 4.61, N 6.46; Found: C 76.10, H 4.56, N 6.23; UV-Vis. (in  $\text{CHCl}_3$ )  $\lambda_{\text{max}}$ (nm): 418, 548, 587, ESI-MS ( $\text{CH}_3\text{OH}$ ): *m/z* calcd. for  $\text{C}_{55}\text{H}_{40}\text{N}_4\text{O}_3\text{ClAl}$ : 866.5; found 866.50; IR (KBr) $\nu_{\text{max}}$ :  $523.21\text{ cm}^{-1}$  ( $\nu_{\text{Al-N}}$ ),  $740.19\text{ cm}^{-1}$  ( $\nu_{\text{Al-O}}$ , carboxylic SA);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.00 (8H, s,  $\beta$ -pyrrole), 8.08(d) and 8.06(d) due to  $\text{H}_{2,6}$ , 7.73(d) and 7.65(d) due to  $\text{H}_{3,5}$ , 2.70 (s, 12H, *p*- $\text{CH}_3$ ), 6.74 (d,  $\text{H}_3''$ ), 6.26 (d,  $\text{H}_4''$ ), 6.44 (s,  $\text{H}_6''$ );  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 169.8(COO), 149.9( $\text{C}_\alpha$ ), 141.6( $\text{C}_1$ ), 134.9( $\text{C}_{2,6}$ ), 132.2( $\text{C}_\beta$ ), 127.6( $\text{C}_4$ ), 126.6( $\text{C}_{3,5}$ ), 122.2( $\text{C}_m$ ), 159.4( $\text{C}_2''$ ), 129.8( $\text{C}_6''$ ), 112.5( $\text{C}_1''$ ), 117.3( $\text{C}_5''$ ), 115.7( $\text{C}_3''$ ), 133.6( $\text{C}_4''$ ), 21.5(*p*- $\text{CH}_3$ ).

*p*- $\text{CH}_3$ -TPP-Al-4-ASA. Purple solid; Anal. Calcd. for  $\text{C}_{55}\text{H}_{42}\cdot\text{N}_5\text{O}_3\text{Al}$ : C 77.92, H 4.95, N 8.26; Found: C 77.92, H 4.76, N 8.23; UV-Vis. (in  $\text{CHCl}_3$ )  $\lambda_{\text{max}}$ (nm): 417, 548, 587. ESI-MS ( $\text{CH}_3\text{OH}$ ): *m/z* calcd. for  $\text{C}_{55}\text{H}_{42}\text{N}_5\text{O}_3\text{Al}$ : 847; found



Where X =

Salicylic acid (SA)

4-Chlorosalicylic acid (4-CSA)

5-Chlorosalicylic acid (5-CSA)

4-Aminosalicylic acid (4-ASA)

5-Aminosalicylic acid (5-ASA)

5-Nitrosalicylic acid (5-NSA)

5-Fluoroosalicylic acid (5-FSA)

5-Sulfosalicylic acid (5-SSA)

Y<sub>1</sub> = H, Y<sub>2</sub> = HY<sub>1</sub> = Cl, Y<sub>2</sub> = HY<sub>1</sub> = H, Y<sub>2</sub> = ClY<sub>1</sub> = NH<sub>2</sub>, Y<sub>2</sub> = HY<sub>1</sub> = H, Y<sub>2</sub> = NH<sub>2</sub>Y<sub>1</sub> = H, Y<sub>2</sub> = NO<sub>2</sub>Y<sub>1</sub> = H, Y<sub>2</sub> = FY<sub>1</sub> = H, Y<sub>2</sub> = SO<sub>3</sub>H

FIGURE 1

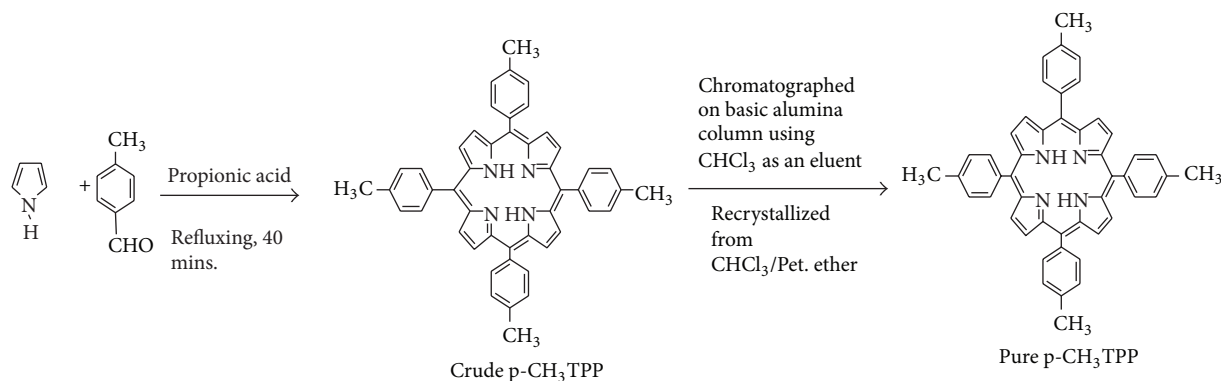
847; IR (KBr)  $\nu_{\max}$ : 528.01  $\text{cm}^{-1}$  ( $\nu_{\text{Al-N}}$ ), 736.13  $\text{cm}^{-1}$  ( $\nu_{\text{Al-O}}$ , carboxylic SA);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.00 (8H, s,  $\beta$ -pyrrole), 8.08(d) and 8.06(d) due to  $\text{H}_{2,6}$ , 7.73(d) and 7.65(d) due to  $\text{H}_{3,5}$ , 2.70 (s, 12H, p- $\text{CH}_3$ ), 6.80 (s,  $\text{H}_3''$ ), 6.29 (d,  $\text{C}_5''$ ), 6.47 (d,  $\text{H}_6''$ ), 4.0 (2H, s, 5- $\text{NH}_2$ );  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 169.8(COO), 149.9( $\text{C}_\alpha$ ), 141.6( $\text{C}_1$ ), 134.9( $\text{C}_{2,6}$ ), 132.2( $\text{C}_\beta$ ), 127.6( $\text{C}_4$ ), 126.6( $\text{C}_{3,5}$ ), 122.2( $\text{C}_m$ ), 159.4 ( $\text{C}_2''$ ), 129.8( $\text{C}_6''$ ), 112.5( $\text{C}_1''$ ), 117.3( $\text{C}_5''$ ), 115.7( $\text{C}_3''$ ), 133.6( $\text{C}_4''$ ), 21.5(p- $\text{CH}_3$ ).

*p*- $\text{CH}_3$  TPP-Al-5-ASA. Purple solid; Anal. Calcd. for  $\text{C}_{55}\text{H}_{42}\text{N}_5\text{O}_3\text{Al}$ : C 77.92, H 4.95, N 8.26; Found: C 77.90, H 4.86, N 8.13; UV-Vis. (in  $\text{CHCl}_3$ )  $\lambda_{\max}$ (nm): 419, 551, 591. ESI-MS ( $\text{CH}_3\text{OH}$ ):  $m/z$  calcd. for  $\text{C}_{55}\text{H}_{42}\text{N}_5\text{O}_3\text{Al}$ : 847; found 847; IR (KBr)  $\nu_{\max}$ : 528.91  $\text{cm}^{-1}$  ( $\nu_{\text{Al-N}}$ ), 736.69  $\text{cm}^{-1}$  ( $\nu_{\text{Al-O}}$ , carboxylic SA);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.00 (8H, s,  $\beta$ -pyrrole), 8.08(d) and 8.06(d) due to  $\text{H}_{2,6}$ , 7.73(d) and 7.65(d) due to  $\text{H}_{3,5}$ , 2.70 (s, 12H, p- $\text{CH}_3$ ), 6.74 (d,  $\text{H}_3''$ ), 6.26 (d,  $\text{H}_4''$ ), 6.44 (s,  $\text{H}_6''$ ), 4.0 (2H, s, 5- $\text{NH}_2$ );  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 169.8(COO), 149.9( $\text{C}_\alpha$ ), 141.6 ( $\text{C}_1$ ), 134.9( $\text{C}_{2,6}$ ), 132.2( $\text{C}_\beta$ ), 127.6( $\text{C}_4$ ), 126.6( $\text{C}_{3,5}$ ), 122.2( $\text{C}_m$ ), 159.4( $\text{C}_2''$ ), 129.8( $\text{C}_6''$ ), 112.5( $\text{C}_1''$ ), 117.3( $\text{C}_5''$ ), 115.7( $\text{C}_3''$ ), 133.6( $\text{C}_4''$ ), 21.5(p- $\text{CH}_3$ ).

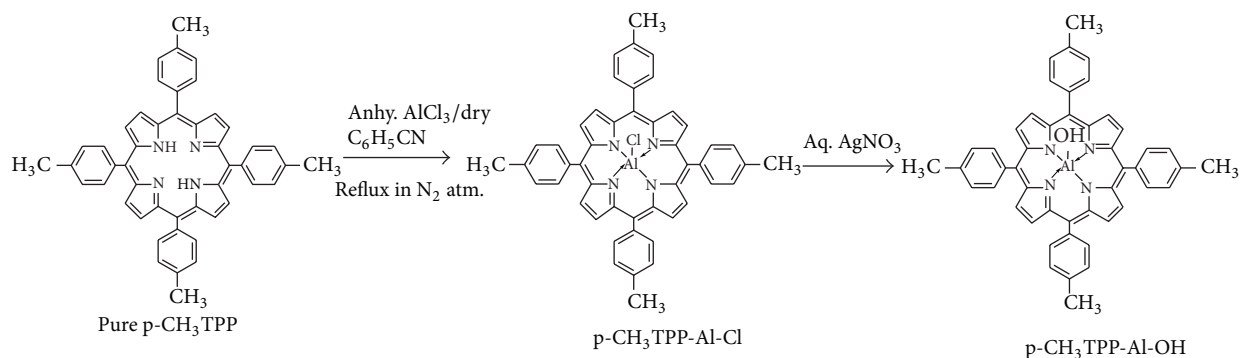
*p*- $\text{CH}_3$  TPP-Al-5-FSA. Purple solid; Anal. Calcd. for  $\text{C}_{55}\text{H}_{40}\text{N}_5\text{O}_3\text{Al}$ : C 77.64, H 4.70, N 6.59; Found: C 77.52, H

4.70, N 6.53; UV-Vis. (in  $\text{CHCl}_3$ )  $\lambda_{\max}$ (nm): 418, 548, 587. ESI-MS ( $\text{CH}_3\text{OH}$ ):  $m/z$  calcd. for  $\text{C}_{55}\text{H}_{40}\text{N}_5\text{O}_3\text{Al}$ : 849.998; found 849.0; IR (KBr)  $\nu_{\max}$ : 528.71  $\text{cm}^{-1}$  ( $\nu_{\text{Al-N}}$ ), 736.56  $\text{cm}^{-1}$  ( $\nu_{\text{Al-O}}$ , carboxylic SA);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.01 (8H, s,  $\beta$ -pyrrole), 8.51(d) and 8.14(d) due to  $\text{H}_{2,6}$ , 7.97(d) and 7.76(d) due to  $\text{H}_{3,5}$ , 2.70 (s, 12H, p- $\text{CH}_3$ ), 6.62 (d,  $\text{H}_3''$ ), 6.79 (d,  $\text{H}_4''$ ), 6.48 (s,  $\text{H}_6''$ );  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 169.8(COO), 149.9( $\text{C}_\alpha$ ), 141.6( $\text{C}_1$ ), 134.9( $\text{C}_{2,6}$ ), 132.2( $\text{C}_\beta$ ), 127.6( $\text{C}_4$ ), 126.6( $\text{C}_{3,5}$ ), 122.2( $\text{C}_m$ ), 159.4( $\text{C}_2''$ ), 129.8( $\text{C}_6''$ ), 112.5( $\text{C}_1''$ ), 117.3( $\text{C}_5''$ ), 115.7( $\text{C}_3''$ ), 133.6( $\text{C}_4''$ ), 21.5(p- $\text{CH}_3$ )).

*p*- $\text{CH}_3$  TPP-Al-5-NSA. Purple solid; Anal. Calcd. for  $\text{C}_{55}\text{H}_{40}\text{N}_5\text{O}_5\text{Al}$ : C 75.25, H 4.56, N 7.98; Found: C 75.02, H 4.36, N 7.63; UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\max}$ : 419, 547, 584, ESI-MS ( $\text{CH}_3\text{OH}$ ):  $m/z$  calcd. for  $\text{C}_{55}\text{H}_{40}\text{N}_5\text{O}_5\text{Al}$ : 877; found 877; IR (KBr)  $\nu_{\max}$ : 528.01  $\text{cm}^{-1}$  ( $\nu_{\text{Al-N}}$ ), 735.19  $\text{cm}^{-1}$  ( $\nu_{\text{Al-O}}$ , carboxylic SA);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.01 (8H, s,  $\beta$ -pyrrole), 8.51(d) and 8.14(d) due to  $\text{H}_{2,6}$ , 7.97(d) and 7.76(d) due to  $\text{H}_{3,5}$ , 2.70 (s, 12H, p- $\text{CH}_3$ ), 6.60 (d,  $\text{H}_3''$ ), 6.75 (d,  $\text{H}_4''$ ), 6.40 (s,  $\text{H}_6''$ );  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 169.8(COO), 149.9( $\text{C}_\alpha$ ), 141.6( $\text{C}_1$ ), 134.9( $\text{C}_{2,6}$ ), 132.2( $\text{C}_\beta$ ), 127.6( $\text{C}_4$ ), 126.6( $\text{C}_{3,5}$ ), 122.2( $\text{C}_m$ ), 159.4( $\text{C}_2''$ ), 129.8( $\text{C}_6''$ ), 112.5( $\text{C}_1''$ ), 117.3( $\text{C}_5''$ ), 115.7( $\text{C}_3''$ ), 133.6( $\text{C}_4''$ ), 21.5(p- $\text{CH}_3$ ).



SCHEME 1: General synthetic route for the synthesis of p-methyl-meso-tetraphenylporphyrin (p-CH<sub>3</sub>TPP).



SCHEME 2: General synthetic route for the synthesis of p-methyl-meso-tetraphenylporphinatoaluminium(III) chloride (p-CH<sub>3</sub>TPP-Al-Cl) and p-methyl-meso-tetraphenylporphinatoaluminium(III) hydroxide (p-CH<sub>3</sub>TPP-Al-OH).

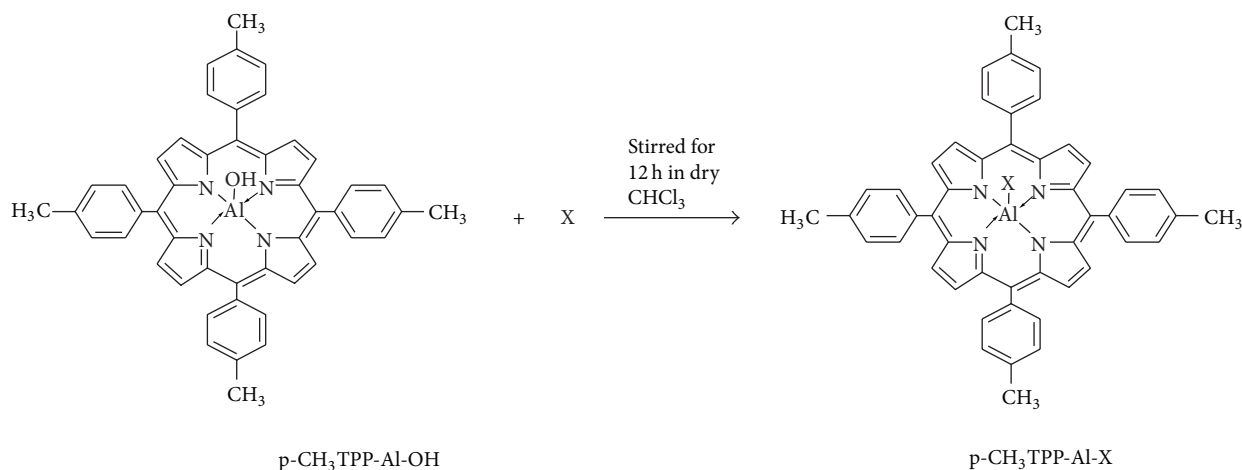
*p*-CH<sub>3</sub>TPP-Al-5-SSA. Purple solid; Anal. Calcd. for C<sub>55</sub>H<sub>41</sub>N<sub>4</sub>O<sub>6</sub>SAI: C 72.36, H 4.49, N 6.14; Found: C 72.12, H 4.76, N 6.13; UV-vis (CHCl<sub>3</sub>)<sub>max</sub>: 417, 547, 587. ESI-MS (CH<sub>3</sub>OH): *m/z* calcd. for C<sub>55</sub>H<sub>41</sub>N<sub>4</sub>O<sub>6</sub>SAI: 912; found 912; IR (KBr)  $\nu_{max}$ : 520.21 cm<sup>-1</sup> ( $\nu_{Al-N}$ ), 733.19 cm<sup>-1</sup> ( $\nu_{Al-O}$ , carboxylic SA); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OH):  $\delta$  (ppm) 9.00 (8H, s,  $\beta$ -pyrrole), 8.51(d) and 8.14(d) due to H<sub>2,6</sub>, 7.97(d) and 7.76(d) due to H<sub>3,5</sub>, 2.70 (s, 12H, p-CH<sub>3</sub>), 6.70 (d, H<sub>3''</sub>), 6.86 (d, H<sub>4''</sub>), 6.55 (s, H<sub>6''</sub>); <sup>13</sup>C NMR (400 MHz, CD<sub>3</sub>OH):  $\delta$  (ppm): 169.8(COO), 149.9(C <sub>$\alpha$</sub> ), 141.6(C<sub>1</sub>), 134.9(C<sub>2,6</sub>), 132.2(C <sub>$\beta$</sub> ), 127.6(C<sub>4</sub>), 126.6(C<sub>3,5</sub>), 122.2(C<sub>*m*</sub>), 159.4(C<sub>2''</sub>), 129.8(C<sub>6''</sub>), 112.5(C<sub>1''</sub>), 117.3(C<sub>5''</sub>), 115.7(C<sub>3''</sub>), 133.6(C<sub>4''</sub>), 21.5(p-CH<sub>3</sub>)).

### 3. Results and Discussion

The general synthetic routes to tetraphenylporphyrin (TPP), their corresponding metallated, and axially ligated aluminium(III) porphyrins are shown in Schemes 1, 2, and 3, respectively. All of these new aluminium(III) porphyrins were purified by column chromatography with aluminium oxide as adsorbent and were characterized by spectral data (UV-visible spectroscopy, IR spectroscopy, <sup>1</sup>H NMR spectroscopy, mass spectral data, and elemental analysis). The characterization data of the new compounds are consistent with the assigned formula.

The structures of free base porphyrin (p-CH<sub>3</sub>TPP), [ClAl(III)p-CH<sub>3</sub>TPP], [OHAl(III)p-CH<sub>3</sub>TPP], and (XAl(III)p-CH<sub>3</sub>TPP) are characterized by UV-Vis spectroscopy. On comparing the UV-vis data of various complexes with the free base porphyrin, it was noticed that the axially ligated metalloporphyrins undergo changes in both the wavelength and the relative intensities of the absorption bands as compared to free base porphyrins. Noticeably free base porphyrins exhibit four Q-banded spectrum, whereas metalloporphyrins having axially coordinated salicylate anions exhibit two Q-bands because, upon metal insertion, the symmetry of the porphyrin increases from D<sub>4h</sub> to D<sub>2h</sub> symmetry present in free-base porphyrins, resulting in the appearance of two banded spectra. Moreover, the absorption bands of Al(III) complexes having electron donating substituents attached to the salicylate ring are red shifted, whereas those having electron withdrawing substituents are blue shifted which can be explained on the basis of four orbital approach of Gouterman [19].

Infrared spectral data of above porphyrin compounds revealed that the (N-H) stretching and bending frequencies of free base porphyrin are located at ~3400–3320 cm<sup>-1</sup> and ~960 cm<sup>-1</sup>, respectively [20]. When the aluminium ion is inserted into the porphyrin ring, the N-H vibration frequency of free base porphyrin disappeared and the characteristic (Al-N) vibration frequency found at ~800 cm<sup>-1</sup> appeared, which



Where X=

- Salicylic acid (SA)
- 4-Chlorosalicylic acid (4-CSA)
- 5-Chlorosalicylic acid (5-CSA)
- 4-Aminosalicylic acid (4-ASA)
- 5-Aminosalicylic acid (5-ASA)
- 5-Nitrosalicylic acid (5-NSA)
- 5-Fluoroosalicylic acid (5-FSA)
- 5-Sulfosalicylic acid (5-SSA)

SCHEME 3: General synthetic route for the synthesis of axially coordinated p-methyl-meso-tetraphenylporphyrinatoaluminium(III)-salicylate (p-CH<sub>3</sub>TPP-Al-X).

indicated the formation of aluminium(III) porphyrin compounds [21]. The incorporation of salicylates in p-CH<sub>3</sub>TPP-Al system is further confirmed by the appearance of Al-O vibrational frequencies at 528 cm<sup>-1</sup> corresponding to the ligation of aluminium to oxygen of carboxylic groups of salicylate moiety. Thus, the aluminium atom in the centre of porphyrin ring coordinate with the salicylate group axially to form five-coordinate complex of Al(III) porphyrin.

In <sup>1</sup>H NMR data of all the metallated porphyrins in CDCl<sub>3</sub> at 298 K there was absence of signal related to N-H protons and shift in other signals indicating the insertion of aluminium into the porphyrin macrocycle [22]. Generally, the presence of Al(III) metal in the porphyrin ring shifts the resonances of the porphyrin's protons to down-field accompanied by marginal changes in the pattern. In axially coordinated Al(III) porphyrin complexes, the signals of axial salicylate fragment protons are shifted to higher field in comparison to the signals of porphyrin protons and also in comparison to proton signals of free salicylic acid derivatives [23]. These positions of protons show that axial ligand is under the influence of π-conjugated system of porphyrin macrocycle [24]. This is most probably due to deshielding effect resulting from the σ-donation of electron density upon

bond formation as compared to the shielding effect of the porphyrin.

#### 4. Electrochemistry

An electrochemical study was carried out to determine the formation potential of porphyrins dianion radical. The porphyrins ring system can be reduced or oxidized during the electrolysis process. Electrochemical studies by cyclic voltammetry (CV) show that porphyrins can be reduced or oxidized in two one-electron-transfer steps to form π-anion or cation radicals [25–28]. p-CH<sub>3</sub>TPP shows two reduction and two oxidation processes. The reduction process in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) occurs at -1.03 V, -1.35 V and the oxidation process takes place at 1.13 V, 1.37 V. These processes should be the porphyrins ring redox processes because p-CH<sub>3</sub>TPP does not contain other constituents that can be reduced or oxidized. As reported in the literature [29–32], factors affecting stability of the ionic forms of the macrocyclic compounds, (both cationic and anionic), yielded by proton transfer are electronic factors (or polarization), structural (or steric), and solvation factors.

These factors are particularly significant for weak acids and bases with rigid reaction centers, as porphyrins. The

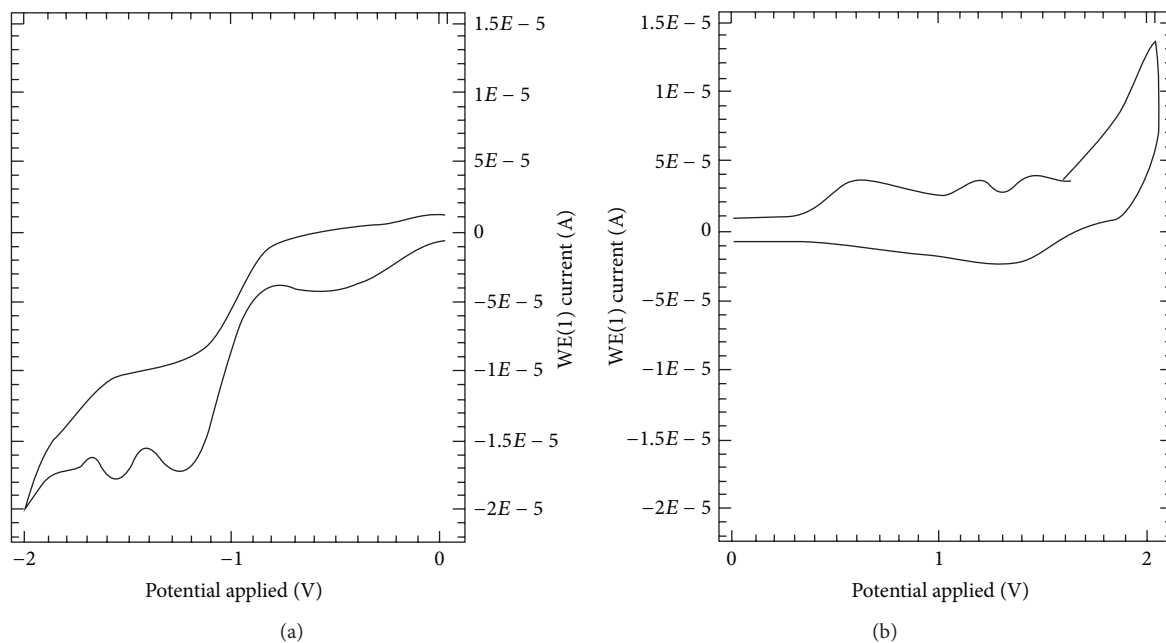


FIGURE 2: Cyclic voltammogram of p-CH<sub>3</sub>TPP-Al-Cl.

contribution of these factors on the overall stabilization of the ionic species depends on the group to which the porphyrins macrocycle and the solvent belong.

Porphyrins are usually subdivided into classical (with moderate distortion of the planarity of the macrocycle and well-known properties), and nonclassical (with nontraditional structures and properties) [29]. The lightly nonplanarity of p-methyl meso-tetraphenylporphyrins makes the NH centers more accessible to an attack of a base or a deprotonation.

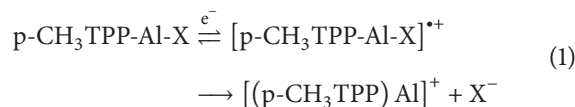
The values obtained for p-CH<sub>3</sub>TPP-Al-X where X = substituted salicylate anion are close to those of the corresponding monomeric free base and Al(III) porphyrins.

p-CH<sub>3</sub>TPP-Al-Cl undergoes two reversible reductions at  $E_{1/2} = -1.15$  and  $-1.50$  V in CH<sub>2</sub>Cl<sub>2</sub> and 0.1 M (TBA)PF<sub>6</sub>. The absolute potential difference between these two processes is 0.35 V, which suggests that both electron additions occur at the porphyrin  $\pi$ -ring system to generate an anion radical and dianion [33, 34]. A dissociation of the Cl-counter ion may occur after electroreduction of p-CH<sub>3</sub>TPP-Al-Cl.

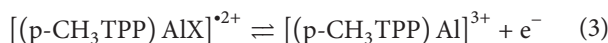
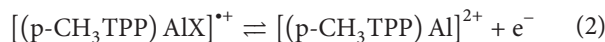
The electrooxidation of p-CH<sub>3</sub>TPP-Al-Cl is complicated in CH<sub>2</sub>Cl<sub>2</sub> and 0.1 M (TBA)PF<sub>6</sub>; there are three reversible oxidations located at  $E_{1/2} = 0.89, 1.21,$  and  $1.46$  V. The first involves a two-electron transfer step, while the second and third involve a single electron transfer. The apparent two-electron reduction peak may be due to equilibrium between the original complex and the anion of the supporting electrolyte, to oxidation of Cl<sup>-</sup> and/or to oxidation of one or more porphyrin decomposition products. This was not investigated in detail, but it should be noted that a  $\mu$ -oxo dimer of the type [(p-CH<sub>3</sub>TPP)Al]O is known [35] and such species might conceivably be formed as a side product upon electrooxidation of p-CH<sub>3</sub>TPP-Al-Cl.

The electrochemistry of p-CH<sub>3</sub>TPP-Al-X, where X = SA, 4-CSA, 5-CSA, 4-ASA, 5-ASA, 5-SSA and 5-NSA, was

investigated in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBA(PF<sub>6</sub>) as supporting electrolyte. Cyclic voltammograms for the oxidation and reduction of all the complexes under these solution conditions are shown in Figures 2, 3, 4, 5, and 6. The p-CH<sub>3</sub>TPP-Al-CSA complexes are reduced via two one-electron-transfer steps. The absolute half-wave potential difference between the first and the second reductions of a given p-CH<sub>3</sub>TPP-Al-X complex ranges between 0.35 and 0.39 V in CH<sub>2</sub>Cl<sub>2</sub>. All these values are in good agreement with the  $0.42 \pm 0.05$  V separation generally observed for  $\pi$ -ring centered reductions [33, 36–38]. The oxidation potentials and overall electrochemical behavior of a given p-CH<sub>3</sub>TPP-Al-X system depend upon the specific solvent/supporting electrolyte system. Under CH<sub>2</sub>Cl<sub>2</sub> solution conditions, p-CH<sub>3</sub>TPP-Al-4-CSA complex undergoes two oxidations at  $-0.60$  and  $0.57$  corresponding to Al<sup>+</sup>/Al<sup>2+</sup> and Al<sup>2+</sup>/Al<sup>3+</sup>. The occurrence of a chemical reaction following the first one-electron oxidation of all p-CH<sub>3</sub>TPP-Al-X complexes has been suggested on the basis of data available from the literature [34]. This reaction involves a cleavage of the -X group and leads to the formation of [(p-CH<sub>3</sub>TPP-Al)]<sup>+</sup>, as shown in the following:



The second oxidation of p-CH<sub>3</sub>TPP-Al-X varies only slightly with the changes in the axial ligand and is assigned as involving electrogenerated [(p-CH<sub>3</sub>TPP-Al)]<sup>2+</sup>, as shown in the following:



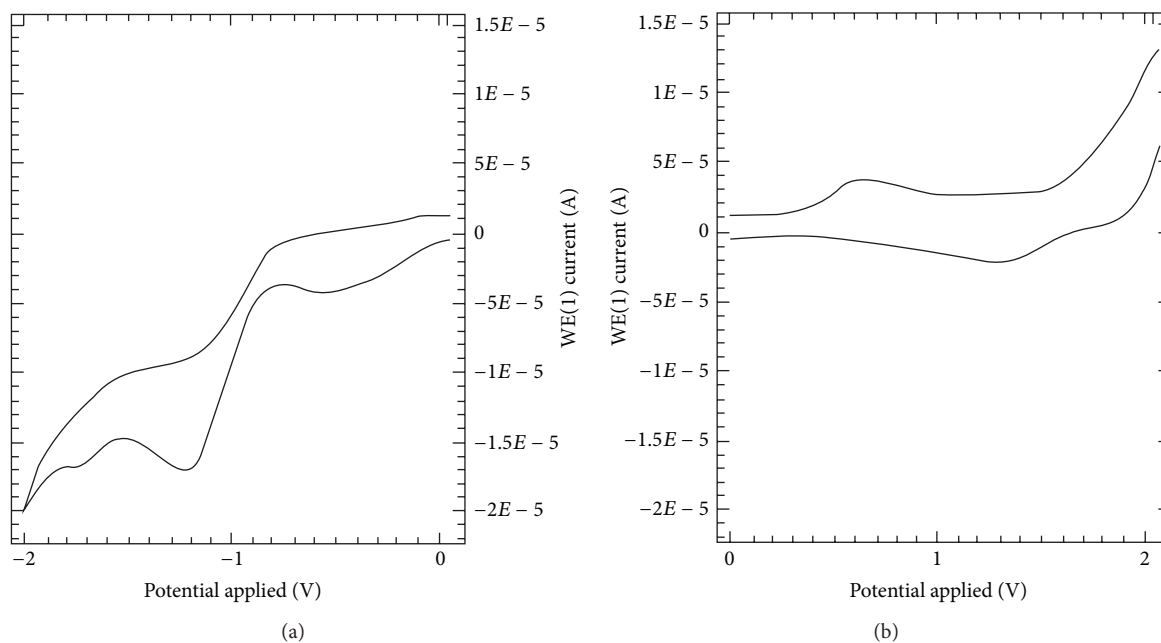


FIGURE 3: Cyclic voltammogram of p-CH3TPP-Al-SA.

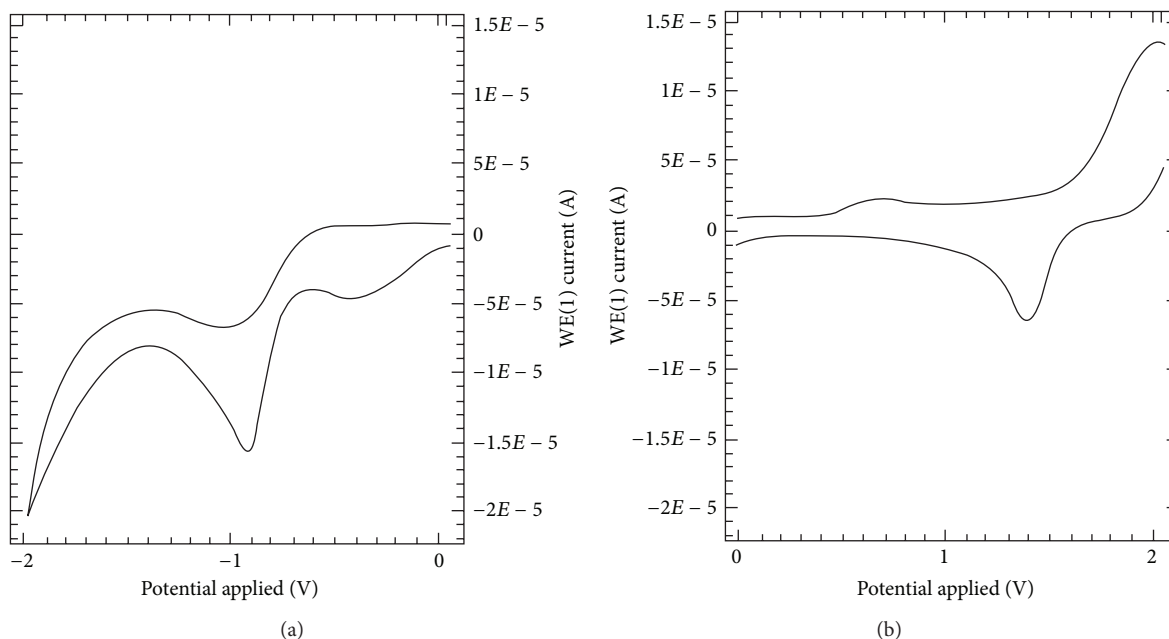


FIGURE 4: Cyclic voltammogram of p-CH3TPP-Al-4-CSA.

## 5. Conclusion

In this paper, we have described the synthesis of pure porphyrins and their subsequent reactions with  $\text{Anhy. AlCl}_3$  and salicylic acid derivatives so as to get axially ligated Al(III) porphyrins. The structures of above porphyrin compounds were characterized by UV-vis, IR,  $^1\text{H NMR}$ ,  $^{13}\text{C NMR}$ , and elemental analysis. In axially ligated aluminium(III) porphyrin complexes, bands showed slight red shift corresponding to the structural distortion in the porphyrin macrocycle,

and concomitant electronic coupling of the metalloporphyrin to the salicylate mediated by the aluminium metal ion. The infrared spectra of these compounds showed that salicylate groups axially ligated to aluminium(III) porphyrins to form five-coordinate complexes of Al(III) porphyrins (Figure 1). Additionally, the  $^1\text{H NMR}$  spectral study of these compounds showed that signals of axial ligand protons are shifted to higher field in comparison to the signals of porphyrin protons. The mass spectroscopy provided the information regarding the appearance of the molecular ion

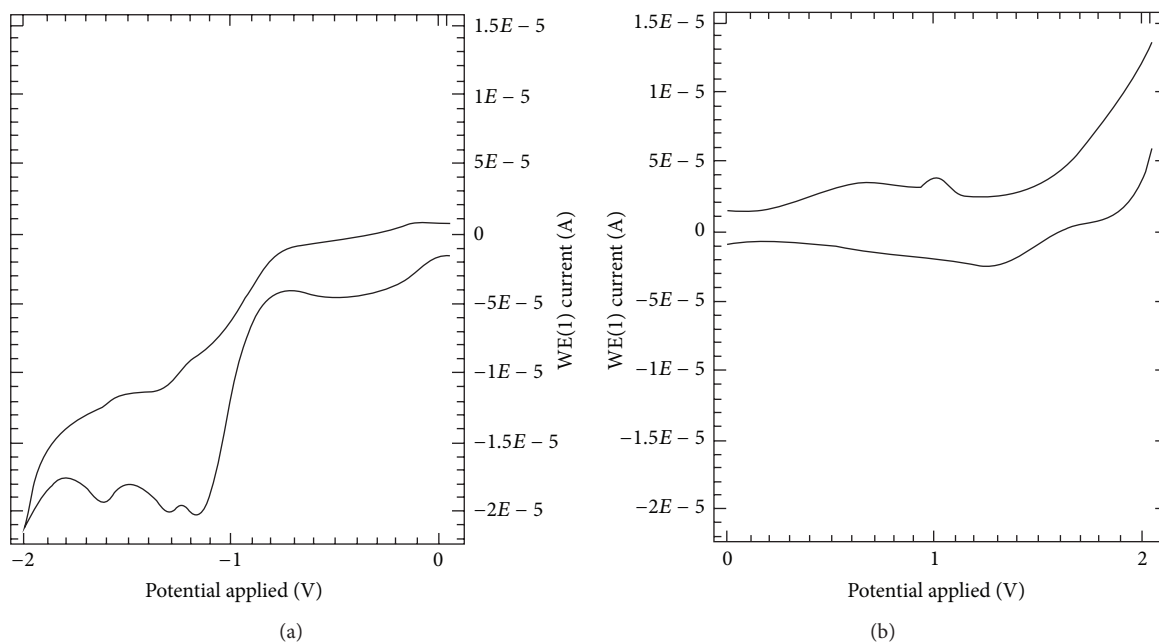


FIGURE 5: Cyclic voltammogram of p-CH3TPP-Al-4-ASA.

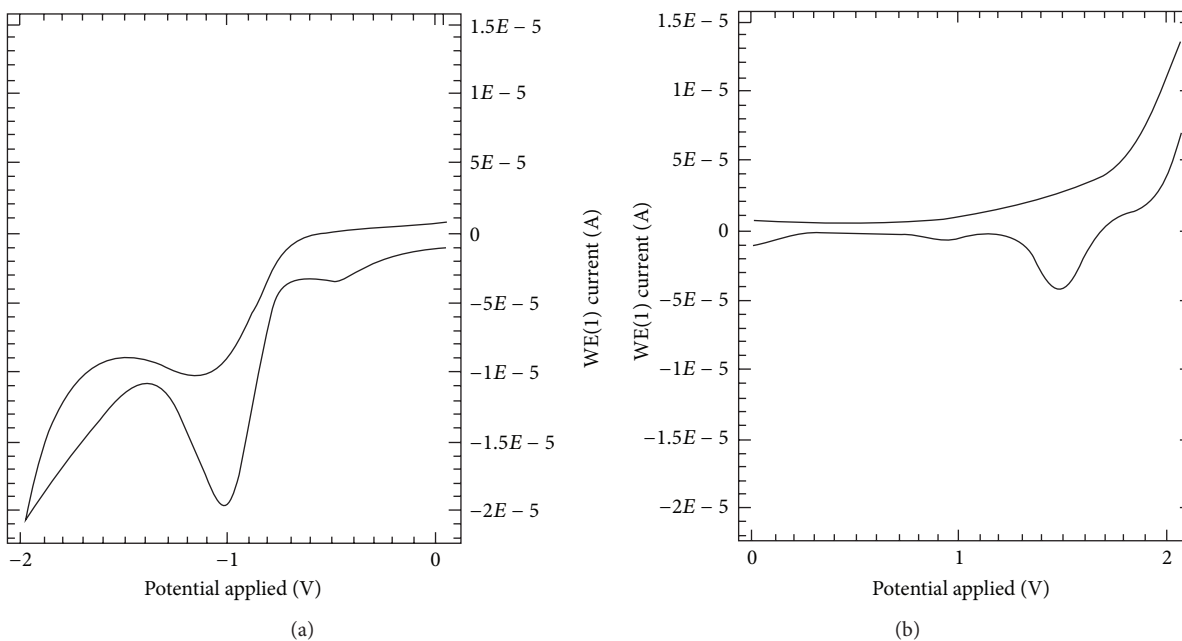


FIGURE 6: Cyclic voltammogram of p-CH3TPP-Al-5-FSA.

peak ( $m/z$ ). Meanwhile, cyclic voltammograms of axially ligated aluminium(III) porphyrins complexes exhibit reversible oxidation and reduction potentials characteristics of the porphyrin.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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