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Electropolymerization of cobalto(5,10,15-tris(4-aminophenyl)-20-phenylporphyrin) for electrochemical detection of antioxidant-antipyrine

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ABSTRACT: Porphyrins are a kind of aromatic molecules possessing unique physic-chemical properties. In this manuscript, it was thus utilized to synthesize 5,10,15-tris(4-aminophenyl)-20-phenylporphyrin and cobalto(5,10,15-tris(4-aminophenyl)-20-phenylporphyrin). In addition, conducting cobalto(5,10,15-tris(4-aminophenyl)-20-phenylporphyrin) polymeric films were successfully prepared by electropolymerization approach on glassy carbon electrode in the presence of dimethyl formamide solution and 0.1 M tetra-*n*-butyl ammonium perchlorate at 100 mV/s scan rate. The synthesized polymeric films were evaluated as the active electrode materials to detect an antioxidant (Antipyrine) present in pharmaceuticals and the limit of detection is ~74 μM.

KEYWORDS: porphyrin, metalloporphyrin, electropolymerization, antioxidant, electrochemical detection.

INTRODUCTION

The chemistry of porphyrins has attracted the attention of many researchers in different fields of disciplines ranging from medicine to materials science due to the presence of conjugated and highly delocalized pi-bonds in its structure [1–7]. Further owing to its high stability and redox potential, porphyrin molecules can be easily modified by coordinating to metal which can act as mediators in electrocatalytic processes [8–10]. On the other hand, electrochemical polymerization of metal porphyrins is a well established method for conducting films preparation, which may serve a useful tool as transducers, chemical and biological sensors [11–15]. For example, polymeric films of tetrakis(aminophenyl) porphyrin of Cu(II) and Ni(II) analogs were grown on conducting glass electrodes and characterized as electrocatalysts for the reduction of nitrate in two different aqueous media [16]. Co(II) tetra-3-aminophenyl porphyrin [Co(II)TAPP] polymeric film [17, 18] has been studied as a catalyst for oxidation and reduction of NO_2 and CO_2. Also, Lvova *et al.* [19] developed a novel carbonate-selective potentiometric sensors based on 5,10,15-tris(4-aminophenyl)-20-phenyl porphyrinates of Co(II) and Cu(II). Like-wise, Rishpon *et al.* reported Manganese loaded tetra(*o*-aminophenyl)porphyrin polymeric film can mediate electron transfer for the electrooxidation of glucose oxidase [20]. Furthermore, Wang and Golden [21] also investigated the catalytic activities of metalloporphyrins polymeric film towards biological

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[◊] SPP full member in good standing

*Correspondence to: Sambandam Anandan, email: sanand@nitt.edu, tel: +91 431-2503639, fax: +91 431-2500133; Jerry J. Wu, email: jjwu@fcu.edu.tw, tel: +886 4-24517250 ext. 5206, fax: +886 4-24517686 and pharmaceutical compounds, such as ascorbic acid and penicillamine. The presence of Acetaminophen in paracetamol was determined by Huang *et al.* [22] using the nickel(II) polytetraaminophenylporphyrin electrode.

In this regard, our aim is to detect one of the antioxidant (antipyrine; 1,5-dimethyl-2-phenyl-4-pyrazolin-3-one) present in pharmaceuticals using modified cobalto (5,10,15-tris(4-aminophenyl)-20-phenylporphyrin) polymeric film by electrochemical determination approach. The main reason for choosing such an antioxidant here is its frequent use for the treatment of febrile patients as antondine injection, paracetamol injection, *etc*. even though it is a forbidden pharmaceutical [23]. Furthermore, Meng *et al.* [24] successfully determined antipyrine in pharmaceutical formulations with recovery from 96 to 103.5% using Bi_2S_3 modified glassy carbon electrode by electrochemical approach. Since electrochemical approach is of inherent miniaturization, high sensitivity, low cost, and low power requirements compared to laboratory quantification analysis through high-performance liquid chromatography [25], liquid chromatography-electrospray tandem mass spectrometry [26], capillary electrophoresis [27], *etc*. the primary development of electrochemical detection for pharmaceutical compounds is conducted in this study.

EXPERIMENTAL

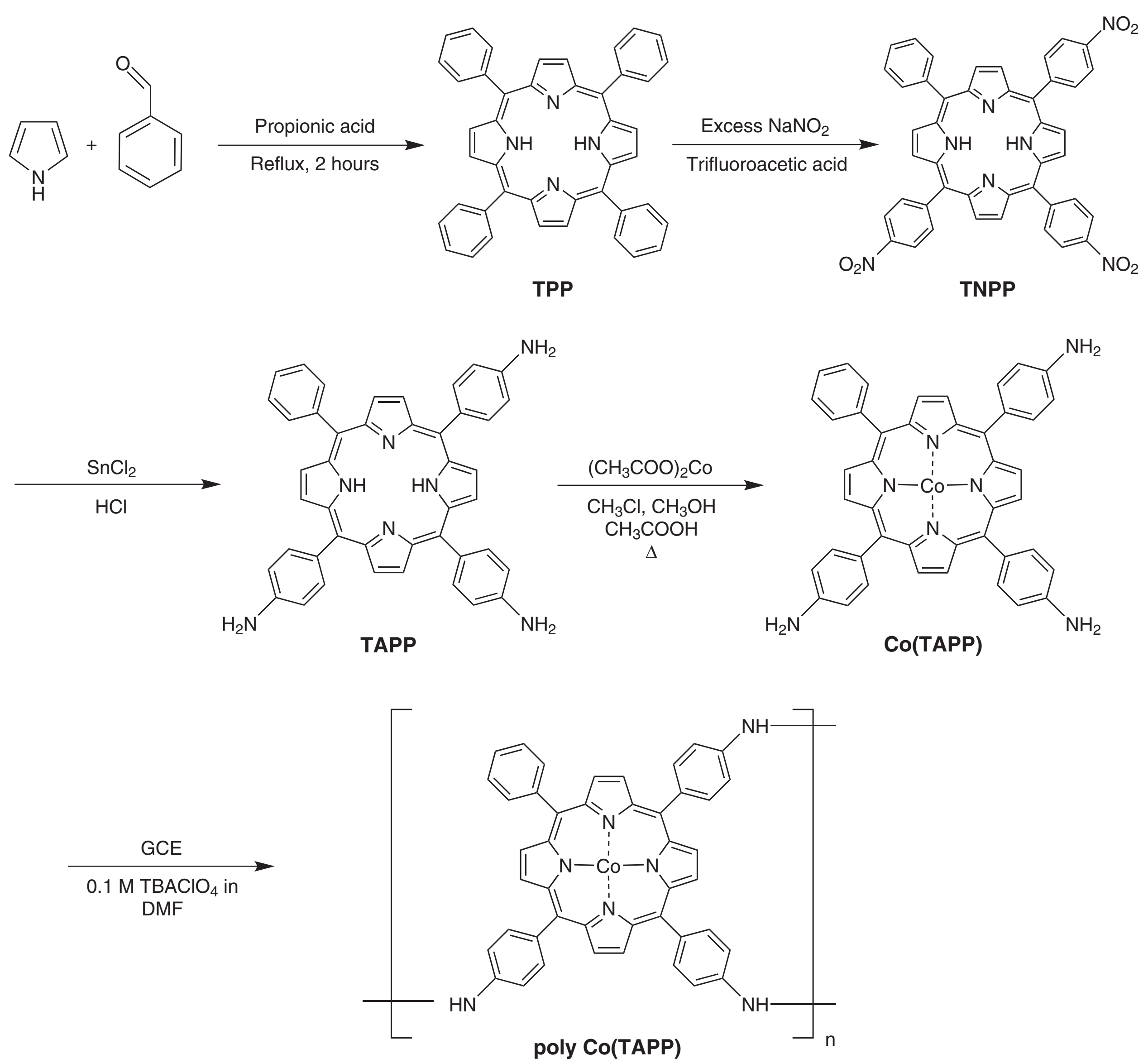
All chemicals were of the highest purity available and were used as received without further purification. Sodium nitrate ($NaNO_2$) and tin chloride ($SnCl_2$) were purchased from Sigma Aldrich. Pyrrole and benzaldehyde were purchased from Sisco Research Laboratories, (SRL) Mumbai. Propionic acid was purchased from Kempesol chemicals. Neutral alumina powder for column chromatography (Brockmann activity 1) and silica powder for TLC were procured from Merck. Tetra-*n*-butyl ammonium perchlorate ($TBAClO_4$) used as the background electrolyte was obtained from Fluka, Switzerland. All the experiments were carried out at room temperature (25 ± 2 °C).

Electrochemical measurements were performed on a CHI 650C electrochemical workstation (Austin, TX, USA). A conventional three-electrode system was used for cyclic voltammetric (CV) and Differential Pulse Voltammetric (DPV) studies. A platinum wire was used as counter electrode; a glassy carbon (3 mm) as working electrode while Ag/AgCl electrode purchased from BASi (USA) was used as the reference electrode. Before initiating the experiments, pure argon gas was purged through the solution for 15 min in order to remove dissolved oxygen. Prior to recording each cyclic voltammograms, the GC electrode was polished carefully and it was standardized using $K_4[Fe(CN)_6]$. Dimethyl formamide was used as the solvent for the CV studies. The absorption and emission spectra were recorded on a double beam ultraviolet-visible spectrophotometer (Model: T90+, PG Instruments Ltd, UK) and Shimadzu spectrofluorometer (RF-5301 PC), respectively. The infrared spectra were recorded by Thermo scientific Nicolet iS5 FTIR spectrometer. ^1H NMR spectra were recorded on BRUKER 400 MHz spectrometer using $CDCl_3$ as the solvent with chemical shifts reported relative to the TMS as the internal standard.

RESULTS AND DISCUSSION

Cobalto(5,10,15-tris(4-aminophenyl)-20-phenylporphyrin) monomer and polymer was synthesized as shown in Scheme 1 (see detailed preparation methods and characterization results in Supporting information). That is by following the available procedures from the literatures [28, 29]. First, 5,10,15,20-tetraphenylporphyrin (TPP) was synthesized starting from pyrrole and benzaldehyde. Then it was allowed to react with excess $NaNO_2$ under acidic conditions to yield 5,10,15-tris(4-nitrophenyl)-20-phenylporphyrin (TNPP). The reduction of the TNPP (nitro group to amino group) was carried out by using excess $SnCl_2$/HCl mixture, which yields 5,10,15-tris(4-aminophenyl)-20-phenylporphyrin (TAPP). TAPP on reaction with Cobalt acetate yields cobalto(5,10,15-tris(4-aminophenyl)-20-phenylporphyrin) (Co-TAPP). The electrochemical polymerization of (Co-TAPP) (1×10^{-3} M) was performed in a solution of dimethylformamide and 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$) as the supporting electrolyte at 100 mV/s scan rate. The synthesized porphyrins and metalloporphyrins were characterized by NMR (see Figs S1–S3; Supporting information), FT-IR, and optical and electrochemical techniques.

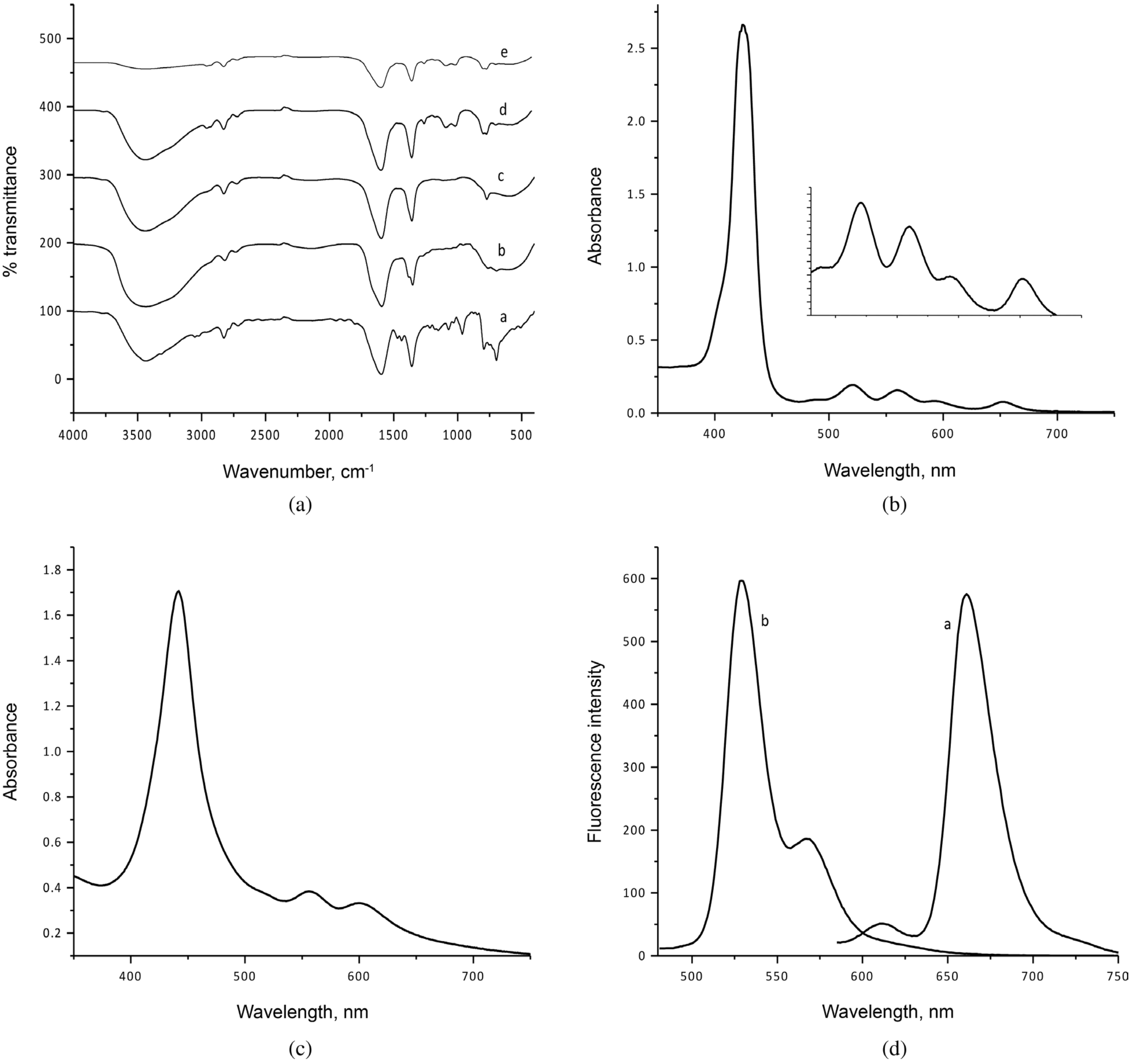
FT-IR spectra of TPP, TNPP, TAPP, and cobalt-triamino phenyl porphyrin (Co-TAPP) monomer and polymer is shown Fig. 1a. TPP (Fig. 1a(a)) results in strong broad peak around 3435 m^{-1}, which indicates the –N-H stretching of the pyrrole ring. The >C-H stretching of the phenyl ring was observed around 3022 cm^{-1}. The –C=C– stretching of the pyrrole ring was noticed around 1596 cm^{-1} as broad peak. The peak appeared around 1469 cm^{-1} is due to –C=N present in TPP. The >C–N appeared around 1358 cm^{-1}. The >C–H stretching of the pyrrole appeared around 1151 and 1050 cm^{-1}. Out of plane bending of the –N-H of the pyrrole was obtained 975 cm^{-1}. Similar pattern was also noticed in the case of TNPP (Fig. 1a(b)) and TAPP (Fig. 1a(c)). In TNPP, there was an extra peak at 1351 cm^{-1}, in addition to the >C-N bond peak. However, both get merged together and the later peak appeared like a small shoulder. In the case of TAPP, the –N-H stretching of the pyrrole ring was seen around 3438 cm^{-1} with a hump for the primary amine group. Generally there will be two sharp peaks around 3400 cm^{-1} for $–NH_2$ group and –N-H stretching of the pyrrole ring, but in our case it was merged with the pyrrole stretching



Scheme 1. Figure illustrates the synthesis pathway of cobalto(5,10,15-tris(4-aminophenyl)-20-phenylporphyrin) monomer and polymer

frequency and appeared as small hump. Similar behavior was noted in the case of Co-TAPP monomer (Fig. 1a(d)). It is expected that the –N-H stretching would cause some effect in the Co-TAPP, but there is no dramatic change in the spectrum. This can be attributed to the peak of amine group in the phenyl ring which might overlaid and appear in the region. However compared to monomer, poly Co-TAPP (Fig. 1a(e)) shows less intense peaks and in addition lack of free –NH_2 bands which illustrate the polymer formation [30].

The absorbance spectrum of TAPP and Cobalt-triamino phenyl porphyrin (Co-TAPP) in $CHCl_3$ solution is shown in Figs 1b and 1c. Before the metalation reaction, the Soret band (transition $a_{1u} \rightarrow e_g$) for the immobilized free porphyrin (TAPP) was observed at 425 nm and the four Q-bands (transition $a_{2u} \rightarrow e_g$) were observed at 520, 560, 593, and 652 nm (Fig. 1b). Such observed bands are almost the same for those of TPP and TNPP in $CHCl_3$ solution (see Figs S4 and S5; Supporting information) [31]. Upon metalation, the Soret band was shifted to 442 nm and the number of the Q-bands decreased from four to two (one at 556 nm and the other a weak shoulder at 590–610 nm), which could be observed in Fig. 1c. This decrease in the number of the Q-bands is due to the symmetry change of the porphyrin molecule from D_{2h} to D_{4h}. Furthermore, it is the evidence that the immobilized porphyrin was metalated by Co(II) [30, 31]. In continuation, under fluorescence spectra TAPP appears two strong fluorescence peaks around 654 and 715 nm (Fig. 1d (a)) when it was excited at soret band position whereas only one fluorescence peak was noticed for Co(TAPP) at 530 nm (Fig. 1d (b)). The incorporation of

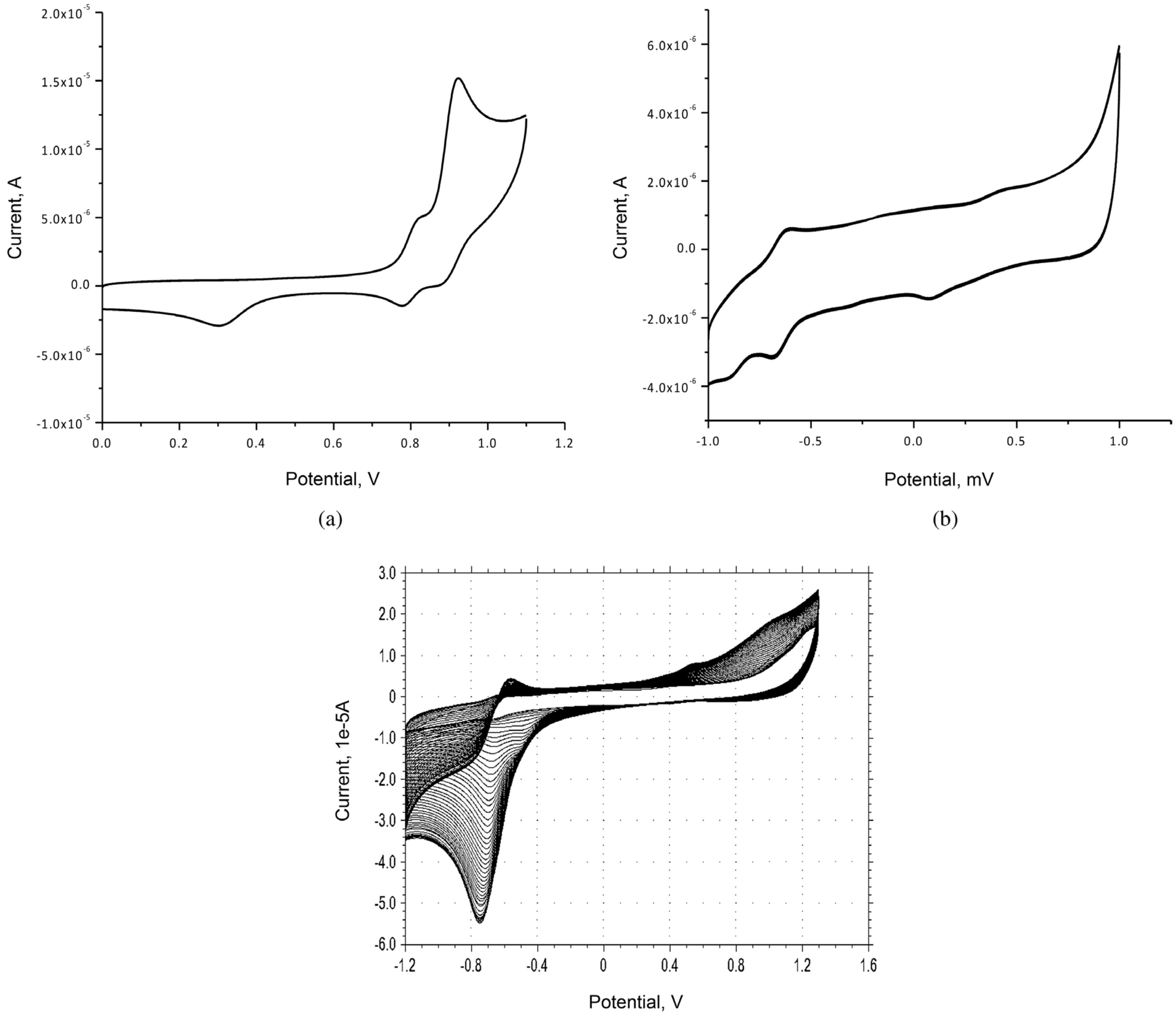


(a) (b) (c) (d)

Fig. 1. (a) FT-IR spectra of TPP (a), TNPP (b), TAPP (c), Co(TAPP) monomer (d) and Co(TAPP) polymer (e). (b) The UV-visible absorbance spectrum of the TAPP (4.33×10^{-5} M^{-1}) in $CHCl_3$ (inset shows the expanded view of the Q-bands) (c) The UV-visible absorbance spectrum of the Co(TAPP) monomer (4.33×10^{-5} M^{-1}) in $CHCl_3$ (inset shows the expanded view of the Q-bands). (d) Fluorescence spectra of TAPP (a) and Co(TAPP) monomer (b) excited at Soret band

the cobalt ion enhances the symmetry of the porphyrin and hence the LUMO (e_g) energy gets increased, which results in blue shift in the emission band [32].

The redox characteristics of free porphyrin (TAPP) and the Co-TAPP were studied by cyclic voltammetry. All the voltammograms were recorded in glassy carbon (GC) electrode in 0.1 M $TBAClO_4$ in DMF (1 mM). The typical cyclic voltammograms recorded for triamino derivative (TAPP) in 0.1 M $TBAClO_4$/DMF is shown in Fig. 2a. It shows two distinct oxidation peaks around 0.8 V and 0.9 V *vs.* Ag wire as pseudo reference electrode. These peaks are attributed to the formation of porphyrin, dication species, and the oxidation of amino phenyl group in the porphyrin, respectively. It is noted worthy that amino group is electron donating and hence the $TPP^{\bullet+}$ and TPP^{2+} formation occurs at lower aromatic potentials while compared to TPP and TNPP (Figs S6 and S7; see Supporting information). Likewise, the cyclic voltammogram of the Co-TAPP in 0.1 M $TBAClO_4$/DMF is shown in Fig. 2b. The peak starts around 1.0 V corresponding to the oxidation of amino group, which is responsible for the electropolymerization. There is one quasi-reversible couple at -0.74 V attributed to the Co(II)/Co(I) process [33–36]. Figure 2c shows the electropolymerisation of Co-TAPP in GC electrode *vs.* Ag/AgCl electrode. The potential was cycled between -1.2 V to +1.6 V. After successful completion of 50 cycles, the electrode was removed from the cell and



(a)

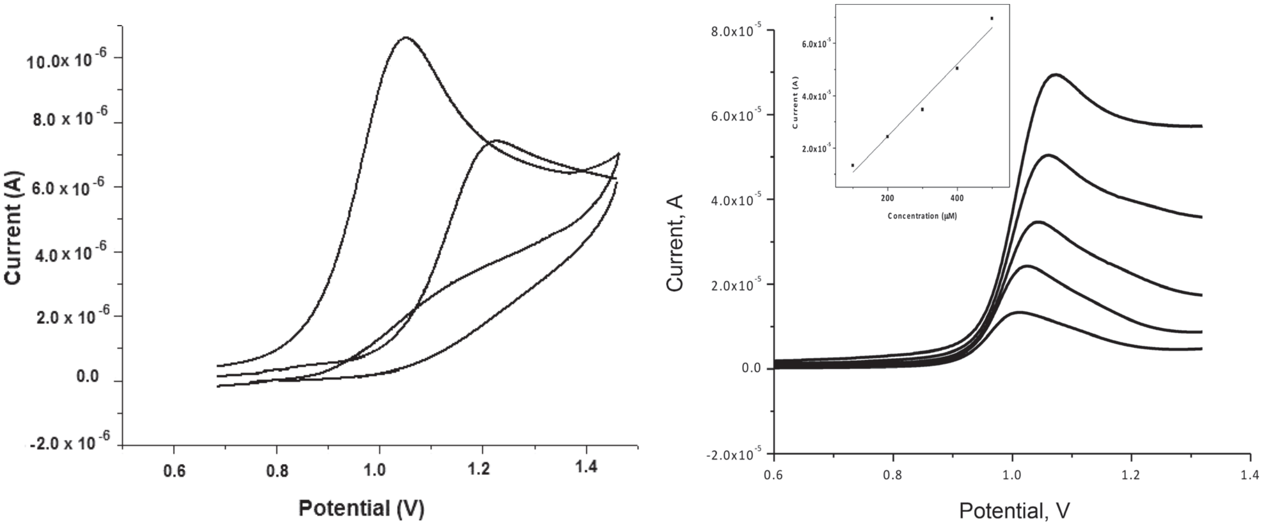
(b)

(c)

Fig. 2. The cyclic voltammogram of TAPP (1 mM) (a) and Co(TAPP) monomer (1 mM) (b) *vs.* Ag/AgCl in a solution of dimethylformamide and 0.1 M tetrabutylammonium perchlorate as supporting electrolyte at 100 mV/s. (c) Voltammetric response of the electropolymerization of Co(TAPP) (50 cycles) on a glassy carbon electrode by cycling the electrode potential between -1.2 and +1.6 V *vs.* Ag/AgCl in a solution of dimethylformamide and 0.1 M tetrabutylammonium perchlorate containing 1 mM of the complex at 100 mV/s

washed with DMF to remove the physically adsorbed monomeric Co-TAPP. Then the modified electrode was subjected for the electrocatalytic detection of antipyrin molecule. Effect of electropolymerisation cycle in the catalytic properties has also been studied by recording 10, 25, 50, and 100 cycles (figure not shown). Among them 50 cycles is given a good catalytic activity.

To evaluate the electrocatalytic activity, poly(Co-TAPP) modified electrode prepared by 50 potential cycles was employed for the electrochemical detection of antipyrine. The typical cyclic voltammograms of the 100 μM antipyrine in 0.1 M phosphate buffer and 0.1 M KCl were recorded and they matches well with the data available in the literatures [23, 24]. Figure 3a shows the oxidation of 100 μM antipyrine in bare GC electrode and poly(Co-TAPP) modified electrode. The oxidation of antipyrine starts at 1.0 V in poly(Co-TAPP) modified electrode, whereas the oxidation process of bare electrode is 200 mV negative shifts. The decrease in over potential may be due to the affinity of antipyrine moiety with the poly(Co-TAPP) modified electrode, which favors the oxidation process at less positive potential. The increase in peak current was also seen in the voltammogram. This is due to the increase in the active surface area of the electrode and the catalytic ability of the poly(Co-TAPP) electrode. Further sensitive detection limit of poly(Co-TAPP) modified electrode towards antipyrine has been investigated by rapid electrochemical differential pulse



(a) (b)

Fig. 3. (a) The cyclic voltammograms of 100 µM antipyrine in bare GC electrode and poly(Co-TAPP) electrode. (b) DPV curves of antipyrine with different concentrations (100, 200, 300, 400 and 500 µM) at poly(Co-TAPP) electrode (Inset show the corresponding linear plot)

voltammetry (DPV) method. That is, DPV experiments were performed using poly(Co-TAPP) modified electrode containing various individual concentration of antipyrine (100 to 500 µM). The results (Fig. 3b) show DPVs of antipyrine oxidation at the surface of poly(Co-TAPP) modified electrode were linearly dependent on the antipyrine concentrations (see inset of Fig. 3b) over the range 100 to 500 µM and the linear regression equation was ($I_p = 1.384C + 0.314$; $R^2 = 0.9819$, where C is the concentration of antipyrine) and the detection limit is estimated to be 74 µM.

In summary, this work provides synthesis and characterization of 5,10,15-tris(4-aminophenyl)-20-phenylporphyrin and cobalto(5,10,15-tris(4-aminophenyl)-20-phenylporphyrin). The remarkable decrease in number of q-bands in the absorption spectra and blue shift in the fluorescence spectra for cobalt complex indicates that it may be a better candidate for electron mediator for electrocatalytic studies. Furthermore, synthesized cobalto(5,10,15-tris(4-aminophenyl)-20-phenylporphyrin) polymeric films by electropolymerization approach exhibits a good electrocatalytic activity towards electrochemical detection of antipyrine (limit of detection at 74 µM). Extension of work is still undergoing in our research group to provide cobalto(5,10,15-tris(4-aminophenyl)-20-phenylporphyrin) polymeric films have any catalytic applications towards other pharmaceuticals.

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Supporting information

A full list of synthesis pathway of cobalto(5,10,15-tris(4-aminophenyl)-20-phenylporphyrin) monomer and polymer and figures (Figs S1–S7) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

REFERENCES

1. *The Porphyrin*, VI(a), VII(b), Dolphin D. (Ed.) Academic Press: New York, 1978.
2. *The Porphyrin Handbook, Applications: Past, Present and Future*, Vol. 6, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: London, 2000.
3. Amstrong NR. *J. Porphyrins Phthalocyanines* 2000; **4**: 414–417.
4. Suslick KS, Rakow NA, Kosal ME and Chou JH. *J. Porphyrins Phthalocyanines* 2000; **4**: 407–413.
5. Kim D and Osuka A. *J. Phys. Chem. A* 2003; **107**: 8791–8816.
6. Zhang ZJ, Hou SF, Zhu ZH and Liu ZF. *Langmuir* 2000; **16***:* 537–540.
7. Li DQ, Swanson BI, Robinson JM and Hoffbauer MA. *J. Am. Chem. Soc.* 1993; **115**: 6975–6980.
8. Balzani V and Scandola F. *Supramolecular Photochemistry*, Ellis Horwood: Chichester, 1991.
9. Shi C and Anson FC. *J. Am. Chem. Soc.* 1991; **113***:* 9564–9570.

10. Steiger B, Shi C and Anson FC. *Inorg. Chem.* 1993; **32**: 2107–2113.
11. Czuchajowski L, Bennett JE, Goszczynski S, Wheeler DE, Wisor AK and Malinski T. *J. Am. Chem. Soc.* 1989; **111**: 607–616.
12. Jin J, Miwa T, Mao L, Tu H and Jin L. *Talanta* 1999; **48**: 1005–1011.
13. *N-4 Macrocyclic Metal Complexes*, Zagal JH, Bedioui F and Dodelet JP. (Eds.) Springer: New York, USA, 2006.
14. Zheng L, Ye D, Xiong L, Xu J, Tao K, Zou Z, Huang D, Kang X, Yang S and Xia J. *Analytica Chimica Acta* 2013; **768**: 69–75.
15. Muthukumar P and Arbaham John S. *Electrochimica Acta* 2014; **115**: 197–205.
16. Armijo F, Isaacs M, Ramırez G, Trollund E, Canales J and Aguirre MJ. *J. Electroanal. Chem.* 2004; **566**: 315–322.
17. Dreyse P, Ramırez G, Riquelme A and Isaacs M. *J. Chil. Chem. Soc.* 2006; **51**: 923–926.
18. Kilmartin PA, Zou H and Waterhouse AL. *J. Agric. Food Chem.* 2001; **49**: 1957–1965.
19. Lvova L, Paolesse R, Di Natale C, D'Amico A and Bergamini A. *Int. J. Electrochem.* 2011; 1–8.
20. Rishpon J, Rosen I, Harth R, Ozer D and Bettelheim A. *J. Electroanal. Chem.* 1991; **307**: 293–298.
21. Wang J and Golden T. *Anal. Chim. Acta,* 1989; **217**: 343–351.
22. Huang SS, Tang H and Li BF. *Mikrochim. Acta* 1998; **128**: 37–42.
23. Bashkatova NV, Korotkova EI, Karbainov YA, Yagovkin AY and Bakibaev AA. *J. Pharm. Biomed. Anal.* 2005; **37**: 1143–1147.
24. Meng X, Xu Z, Wang M, Yin H and Ai S. *Anal. Methods* 2012; **4**: 1736–1741.
25. Kitzman J, Martin J, Holley J and Huber W. *J. Chromatogr.* 1988; **437**: 306–310.
26. Annola K, Keski-Rahkonen P, Vähäkangas K and Lehtonen M. *J. Chromatogr., B: Anal. Technol. Biomed. Life Sci.* 2008; **876**: 191–197.
27. Perrett D and Ross G. *J. Chromatogr. A* 1995; **700**: 179–186.
28. Luguya R, Jaquinod L, Fronczek FR, Graca M, Vicenta H and Smith KM. *Tetrahedron* 2004; **60***:* 2757–2763.
29. Doppelt P, Fischer J and Weiss R. *Inorg. Chem.* 1984; **23**: 2958–2962.
30. Uygun A, Myjavcova R, Yavuz AG, Ruppel JV, Fields KB and Frankhauser A. *Electroanalysis* 2011; **23**: 1158–1167.
31. Zhang X, Li Y, Qi D, Jiang J, Yan X and Bian Y. *J. Phys. Chem. B* 2010; **114**: 13143–13151.
32. Sun X, Chen G and Zhang J. *Dyes Pigm.* 2008; **76**: 499–501.
33. *The Porphyrins Handbook, Metalloporphyrins in Nonaqueous Media: Database of Redox Potentials*, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: New York, 2000.
34. Richter-Addo GB, Hodge SJ, Yi GB, Khan MA, Ma T, Caemelbeeke EV, Guo N and Kadish KM. *Inorg. Chem.* 1996; **35**: 6530–6538.
35. D'Souza F, Villard A, Caemelbeeke EV, Franzen M, Boschi T, Tagliatesta P and Kadish KM. *Inorg. Chem.* 1993; **32**: 4042–4048.
36. Behar D, Dhanasekaram T, Neta P, Hosten CM, Ejeh D, Hambright P and Fujita E. *J. Phys. Chem. A*. 1998; **102**: 2870–2877.