



# Effect of amine substituted at *ortho* and *para* positions on the electrochemical and electrocatalytic properties of cobalt porphyrins self-assembled on glassy carbon surface



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## ABSTRACT

This work addresses the influence of amine group substituted at *para* and *ortho* positions of the phenyl groups on the electrochemical and electrocatalytic properties of cobalt porphyrins self-assembled on glassy carbon electrode (GCE). We have synthesized *meso*-tetra(*para*-aminophenyl)porphyrinatocobalt(II) (Co(II)MTpAP) and *meso*-tetra(*ortho*-aminophenyl)porphyrinatocobalt(II) (Co(II)MToAP) and were self-assembled on GCE through Michael addition of nucleophilic amine with olefinic GCE surface. Cyclic voltammetry, reflectance spectroscopy and X-ray photoelectron spectroscopy (XPS) techniques were employed to confirm the formation of the self-assembled monolayers (SAMs) of Co(II)MTpAP and Co(II)MToAP on GCEs. Interestingly, the SAM of Co(II)MTpAP in 0.1 M H<sub>2</sub>SO<sub>4</sub> shows two redox waves at 0.37 and 0.60 V whereas the SAM of Co(II)MToAP shows a single redox wave at 0.32 V, indicating the influence of amine group position in the phenyl ring on the redox chemistry of porphyrin. In contrary, the SAMs of the corresponding free base porphyrins prepared under identical conditions show a single redox wave around 0.36 V. Thus, we have assigned the redox wave at 0.37 V to Co(II)Por<sup>1-</sup>/Co(II)Por<sup>2-</sup> and 0.60 V to Co<sup>III/II</sup> redox couples for the SAM of Co(II)MTpAP. In the case of Co(II)MToAP, we have assigned the redox wave at 0.32 V due to both Co(II)Por<sup>1-</sup>/Co(II)Por<sup>2-</sup> and Co<sup>III/II</sup>. The surface coverage estimated from the charge consumed for the oxidation of Co<sup>III/II</sup> was used to study the thermodynamics and kinetics of Co(II)MTpAP and Co(II)MToAP self-assembled on GCE. Further, the electrochemical reduction of dioxygen was studied at the SAMs of Co(II)MTpAP and Co(II)MToAP in 0.1 M H<sub>2</sub>SO<sub>4</sub>. The dioxygen reduction potential was shifted to less positive potential with enhanced current at both the SAMs of Co(II)MTpAP and Co(II)MToAP when compared to bare GCE. Among the two SAMs, Co(II)MTpAP significantly reduced the overpotential of dioxygen reduction (65 mV) when compared to Co(II)MToAP.

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## 1. Introduction

Porphyrins are nature preferred compounds to carry out oxygen transport and electron transfer processes in biological systems [1]. The preparation of thin films of porphyrins on solid substrates has received huge interest for the past three decades because of their potential applications in sensors, light-energy conversion, catalysis, and energy harvesting arrays [2–5]. The thin films of metalloporphyrins can be prepared by different methods which include dip-coating [6], electropolymerization [7–13], Langmuir–Blodgett [14], thermoevaporation [15], spin-coating [16] and self-assembly [4,17]. Among these, self-assembly is one of the best methods to fabricate a thin film on electrode surface because an ordered film with controlled thickness can be prepared

by this method. Generally, the self-assembly of porphyrins on a suitable surface can be achieved by functionalizing them with an appropriate functional group [18–20]. While searching the literature, several reports were available for the preparation of both free base porphyrins and metalloporphyrins on metallic surfaces by self-assembly method [4,17,21–38]. Two strategies were frequently employed to self-assemble them on gold surface. First strategy involves the adsorption of thiol or disulfide functionalized free base porphyrins and metalloporphyrins on gold surface and post-assembly of metal ions on thiol functionalized free base porphyrins adsorbed on gold surface [4,21–32]. Even though this strategy was successfully used to prepare self-assembled monolayers (SAMs) of porphyrins, it involves several problems. The SAMs formed on Au electrode were stable only at limited potential window. Further, the SAM formed from thiol functionalized metalloporphyrins can co-ordinate to metal centre of porphyrin to form a multilayer which leads to mask the catalytic centre [31,32].

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The second strategy involves the axial ligation of metalloporphyrins on gold surface [4,17,33–37]. This was achieved on gold surface by two methods. The first method is the adsorption of nitrogen heterocyclic ligand having thiol or both thiol and amine groups on gold surface and then metalloporphyrin was axially co-ordinated with the terminal nitrogen of the ligand. The second method is the adsorption of alkanethiol with carboxylic acid functional group on gold surface and then nitrogen heterocyclic ligand was attached via acid-amine coupling and subsequently metalloporphyrin was co-ordinated through axial ligation. The axial ligation method of SAM preparation has several drawbacks. For example, the monolayer of ruthenium porphyrin attached on gold surface via axial ligation was decomposed upon repeated cycling. Further, the excess of ligands diminished the cyclic voltammetric response of cobalt porphyrin axially ligated with 1-(10-mercaptodecyl)imidazole on gold electrode [36]. This method of preparation involves multistep and consumes more time. Moreover, high surface coverage cannot be achieved by this method because only parallel orientation is possible [33]. Although metal and ring based redox peaks were resolved for the ruthenium porphyrin self-assembled via axial ligation using 11-mercaptoundecylisonicotinate as ligand the electroactive material was lost from the electrode upon scanning the potential beyond +0.90 V vs. SCE [17]. Moreover, the self-assembly of free base porphyrins and metalloporphyrins by the above methods was achieved only on gold surface. It is well known that the gold-sulfur linkage was unstable under ambient conditions besides its stability at limited potential window [39]. Therefore, preparation of stable porphyrin SAMs on suitable electrode surfaces for electrocatalytic applications is one of the challenging tasks for the researchers.

Recently, it has been shown that the spontaneous assembly of alkyl and aryl amines can be achieved on carbon surfaces and coinage metals [40]. The SAMs formed by this method on GCE is stable at a wide potential window. Similar strategy is used in the present study to prepare the SAM of metalloporphyrin on GCE. Since the SAM formed on GCE is stable at wide potential window, it is easy to study the redox properties of both metal and ring besides possible electrocatalytic applications. Earlier, the amine functionalized porphyrins have been synthesized and extensively used for electropolymerization [7–13]. However, no report has been published for their self-assembly on GCE. Thus, the objective of the present work is to synthesize amine functionalized porphyrins and self-assemble them on GCE to study their electrochemical and electrocatalytic properties. It has been already shown that the physical and chemical properties of metalloporphyrins in solution

differ in various ways by changing the substituents on  $\beta$ -pyrrole and *meso* position of metalloporphyrins [41–48]. Kadish et al. extensively studied the electrochemistry of porphyrins and metalloporphyrins in non-aqueous media with respect to substituents at different positions [41]. They have concluded that the effect of substituents on metalloporphyrin redox potential depends upon the number of parameters such as position of substituents, planarity of macrocycle and number and type of substituents. Generally, the effect of substituent at *meso* position is more than the same substituent at the  $\beta$ -pyrrole position [42]. Although plenty of electrochemical studies have been carried out for both porphyrins and metalloporphyrins with respect to substituents at different positions in solution to the best of our knowledge no report has been published on the effect of electron releasing amine group at different positions in metalloporphyrins self-assembled on solid surface. In the present study, we have synthesized amine functionalized cobalt porphyrins at both *para* (*meso*-tetra(*para*-aminophenyl)porphyrinatocobalt(II) (Co(II)MTpAP)) and *ortho* (*meso*-tetra(*ortho*-aminophenyl)porphyrinatocobalt(II) (Co(II)MToAP)) (Fig. 1) positions and studied their electrochemical and electrocatalytic properties after self-assembled them on GCE. Further, the effect of amine group position was studied with respect to adsorption kinetics and thermodynamics. The SAMs of Co(II)MTpAP and Co(II)MToAP were characterized by reflectance spectroscopy, cyclic voltammetry and XPS. Interestingly, the SAM of Co(II)MTpAP shows two redox peaks, corresponding to metal and ring based redox reactions whereas Co(II)MToAP shows one redox peak due to both metal and ring based redox reactions. The electrochemical reduction of dioxygen was studied using Co(II)MTpAP and Co(II)MToAP SAMs. Although both the SAMs showed higher electrocatalytic activity towards dioxygen reduction compared to bare GCE the SAM of Co(II)MTpAP significantly decreased the overpotential of dioxygen reduction when compared to Co(II)MToAP.

## 2. Experimental

### 2.1. Chemicals and reagents

The chemicals and reagents were used as received unless otherwise mentioned. Pyrrole, 4-nitrobenzaldehyde, 2-nitrobenzaldehyde and boron trifluoride etherate complex ( $\text{BF}_3\text{-Et}_2\text{O}$ ) were purchased from Aldrich, India.  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  and  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  were purchased from Merck, India. Chloroform, methanol and dichloromethane were purchased from Merck, India

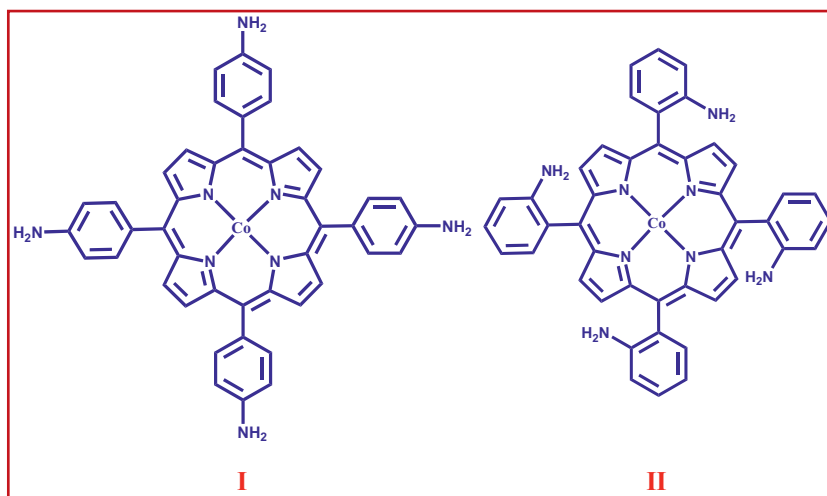


Fig. 1. Chemical structures of (I) Co(II)MTpAP and (II) Co(II)MToAP.

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