Chapter VI

Synthesis, Characterization and Applications of SAMs of Thiophenyl and Thiol Functionalized MPcs on Au Surface
6.1. Introduction

In the previous chapters, self-assembled monolayer and electropolymerization film of amine functionalized metallophthalocyanine and their electrocatalytic application towards biologically important compounds were discussed. In this chapter, synthesis of thiol and thiophenyl functionalized MPcs at peripheral position will be described. The synthetic procedure and experimental results were already described in Chapter 3 (Section 3.3). Generally, thiol derivatized Pc complexes have been less explored than Pc derivatives containing NH$_2$ [1-11], because the preparation of thiol derivatized Pc is tedious. Only, very few reports have been published in the literature for the synthesis of thiol functionalized Pcs [12-15]. Cook and co-workers synthesized a series of three Pc derivatives containing thiol moiety with alkyl chain length of (CH$_2$)$_{11}$, (CH$_2$)$_8$ and (CH$_2$)$_3$. They formed SAMs of these Pc derivatives on gold coated optical waveguides. The SAMs were characterized using reflection absorption infrared spectroscopy (IRRAS). The IRRAS data have shown that the length of the alkyl chain has significant effect on the orientation and packing density of the Pc macrocycle on the gold surface [12,13]. Li and Lieberman synthesized silicon phthalocyanines with thiol anchoring groups in either eight peripheral side chains or with one short thiol in an axial position [14]. These two compounds were used to form SAM on Au surface. They found that the thiol substituted at peripheral side chains of silicon Pc formed poorly organized SAMs whereas thiol substituted
in axial form formed a closely packed SAMs [14]. Recently, synthesis of tetra substituted thiol-derivatized zinc(II) Pc was reported [15]. Although synthesis of thiol functionalized Pc derivatives bearing different alkyl chain lengths has been synthesized, no report is published on the synthesis of thiols substituted directly on Pcs at peripheral position (β-position). Further, the electrochemical and electrocatalytic properties of thiol based SAMs of Pcs have not been studied so far. Thus, in the first part of this Chapter, synthesis and characterization of tetrathiophthalocyananatonicel(II) at β-position (4β-Ni\textsuperscript{II}TTPc) and its self-assembly and electrocatalytic activity towards L-dopa will be described.

Recently, it has been shown that thiophenyl and dodecylmercapto substituted MPcs can also be used to form SAM on Au surface by chemisorption similar to thiol substituted MPcs [16-22]. Thus, in the second part of this chapter, synthesis, characterization of peripheral tetrahydroxythiophenyl substituted cobalt(II) phthalocyanine (4β-Co\textsuperscript{II}THTPhPc) and its self-assembly and electrocatalytic activity towards dioxygen will be discussed. We have also tried to synthesize non-peripheral thiol and thiophenyl functionalized MPcs but we failed to achieve the respective products.


The synthesis of 4β-Ni\textsuperscript{II}TTPc was described in Chapter 3 (Section 3.3.1). The present section deals with the fabrication of 4β-Ni\textsuperscript{II}TTPc SAM on Au
electrode, characterization and its electrocatalytic application. Formation of 4β-Ni\textsuperscript{II}-TTPc SAM on Au surface was confirmed by cyclic voltammetry and Raman spectroscopy. The electrocatalytic activity of the SAM was examined by studying the oxidation of 3,4-dihydroxy-1-phenylalanine (L-dopa).

6.2.1. Electrochemical Characterization of 4β-Ni\textsuperscript{II}-TTPc SAM on Au Electrode

6.2.1.1. Interfacial Capacitance

A defined potential window of a CV, in which no peaks are observed for both bare and modified Au electrodes, will have a charging current \( (i_{ch}) \). This value may be used to calculate the interfacial capacitance \( (C_s) \) from equation (6.1) [23].

\[
C_s = \frac{i_{ch}}{v A}
\]  

(6.1)

![Graph showing CVs](image)

**Figure 6.1.** CVs obtained for (a) bare and (b) 4β-Ni\textsuperscript{II}-TTPc SAM modified Au electrodes in 0.1 M HClO\textsubscript{4}.
where, \( i_{ch} \) is the charging current (\( \mu \text{A} \)), \( v \) is the scan rate (\( V \text{ s}^{-1} \)) and \( A \) is the surface area of the electrode (\( \text{cm}^2 \)). Figure 6.1 shows the CVs obtained for a bare and 4\( \beta \)-Ni\( ^{II} \)TTPc SAM modified Au electrodes in the potential window of \(-0.1 \text{ V} \) to \(+0.2 \text{ V} \). The \( C_s \) value of the SAM modified electrode was lower (\( C_s = 320 \mu \text{F cm}^{-2} \)) than that obtained at the bare Au electrode (\( C_s = 1200 \mu \text{F cm}^{-2} \)). The decrease in \( C_s \) is due to the formation of 4\( \beta \)-Ni\( ^{II} \)TTPc SAM on Au electrode in addition to the presence of hydrophobic end groups (-SH) on the surface of SAM [23-25].

6.2.1.2. Electrochemical Behaviour of 4\( \beta \)-Ni\( ^{II} \)TTPc SAM on Au Electrode Towards $[\text{Fe(CN)}_6]^{3-/4-}$ Redox Couple

The ability of a monolayer to block the electron transfer between the redox probe in solution and the underlying electrode has been shown to be a good nature of its defectiveness [26,27]. The compactness of the modified electrode was usually examined using $[\text{Fe(CN)}_6]^{3-/4-}$ redox probe. Figure 6.2 shows the CVs of bare and 4\( \beta \)-Ni\( ^{II} \)TTPc SAM modified Au electrodes in 0.1 M KCl containing 1 mM K\(_3\)[Fe(CN)\(_6\)] at a scan rate of 0.05 V s\(^{-1}\). Bare Au electrode shows a reversible voltammogram for the $[\text{Fe(CN)}_6]^{3-/4-}$ redox couple with a peak separation of 71. In contrary, the 4\( \beta \)-Ni\( ^{II} \)TTPc SAM modified Au electrode partially blocked (\( \Delta E = 140 \text{ mV} \)) the redox reaction between the underlying Au surface and $[\text{Fe(CN)}_6]^{3-/4-}$ solution. This result indicates that the SAM of 4\( \beta \)-Ni\( ^{II} \)TTPc was not compact and it may contain defects or pinholes.
Figure 6.2. CVs obtained for (a) bare and (b) 4β-Ni^{II}TTPc SAM modified Au electrodes in 0.1 M KCl solution containing 1 mM K₃[Fe(CN)₆] at a scan rate of 50 mV s⁻¹.

6.2.1.3. CVs of 4β-Ni^{II}TTPc SAM Modified Au Electrode in HClO₄

Figure 6.3A shows the CVs obtained for the SAMs of 4β-Ni^{II}TTPc and 4β-H₂TTPc on Au electrodes in 0.1 M HClO₄ at a scan rate of 100 mV s⁻¹. The SAM of 4β-Ni^{II}TTPc on Au electrode shows two oxidation waves at 0.34 V and 0.52 V and a broad reduction wave at 0.45 V. The oxidation wave appeared at 0.34 V was assigned to Ni^{II}/Ni^{III} redox couple and the oxidation wave at 0.52 V was assigned to Ni^{III}Pc⁺⁻/Ni^{III}Pc²⁻ (curve a). To ascertain the first oxidation wave was due to Ni^{II}/Ni^{III}, we have prepared a SAM of metal free tetrathiolphthalocyanine (4β-H₂TTPc) on Au electrode and run the CV under identical conditions. It shows a
**Figure 6.3.** CVs obtained for (a) 4β-Ni$^{II}$TPc and (b) 4β-H$_2$TPc SAM modified Au electrodes in 0.1 M HClO$_4$ at a scan rate of 100 mV s$^{-1}$. CVs obtained for 4β-Ni$^{II}$TPc SAM modified Au electrode in 0.1 M HClO$_4$ at scan rates of 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 V s$^{-1}$.

Single oxidation wave at 0.52 V corresponding to the H$_2$Pc$^{+}$/H$_2$Pc$^{2-}$ (curve b) along with a reduction wave at 0.38 V. This confirms that the oxidation wave obtained at 0.34 V was due to Ni$^{II}$/Ni$^{III}$. Further, the potential of the reduction wave obtained for 4β-H$_2$TPc (curve b) was very similar to 4β-Ni$^{II}$TPc. However, the reduction peak current obtained at 4β-H$_2$TPc is less than that obtained at 4β-Ni$^{II}$TPc. The obtained higher reduction current suggests that the reduction of both ring and metal occur at the same potential. Further, if we run the CV upto +0.8 V, the oxidation peaks due to H$_2$Pc$^{+}$/H$_2$Pc$^{2-}$ and Ni$^{II}$/Ni$^{III}$ were appeared whereas if we restricted the potential at 0.5 V, the ring reduction peak
was absent which is evidenced from curve c. This again shows that the reduction of ring also occurs at the same potential where Ni^{III}/Ni^{II} occurs. The surface coverage of 4β-Ni^{II}TTPc was calculated by integrating the charge under anodic wave corresponding to Ni^{II}/Ni^{III} and was found to be $1.01 \times 10^{-10}$ mol cm$^{-2}$.

Further, the surface confinement of 4β-Ni^{II}TTPc on Au electrode was confirmed from the CVs recorded at different scan rates in 0.1 M HClO$_4$ (Figure 6.3B). The CVs are consistent in all respects with that anticipated for an electrochemically reversible reaction involving a surface confined species. For example, the $\Delta E$ values were small ($\Delta E = 36$ mV) and the peak current varies linearly with scan rate in the range of 0.05-0.5 V s$^{-1}$ (Figure 6.3B inset) confirming that the observed redox reaction is due to the surface confined species. Further, the peak potentials and the shape of the CV remained identical for several continuous potential cycles, which demonstrated that the SAM was highly stable.

6.2.2. Raman Studies of 4β-Ni^{II}TTPc SAM on Au Surface

Raman spectral study was carried out to confirm the attachment of 4β-Ni^{II}TTPc on Au surface. Figure 6.4 shows the Raman spectrum obtained for 4β-Ni^{II}TTPc modified Au surface. The stretching bands and their assignments based on literature are given in Table 1 [11,28]. The Raman spectrum of 4β-Ni^{II}TTPc SAM shows the stretching and breathing bands of Pc macrocycle, pyrrole ring and isoindole ring. It shows Au-S stretching at 250 cm$^{-1}$, confirming that attachment of
Figure 6.4. Raman spectrum obtained for 4β-Ni$^{II}$TTPc on Au plate.

Table 6.1. Raman spectral bands obtained for 4β-Ni$^{II}$TTPc SAM modified Au plate

<table>
<thead>
<tr>
<th>4β-Ni$^{II}$TTPc on Au</th>
<th>Assignments</th>
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<tbody>
<tr>
<td>2572</td>
<td>-SH stretching</td>
</tr>
<tr>
<td>1437</td>
<td>Isoindole ring stretch</td>
</tr>
<tr>
<td>1347</td>
<td>Pyrrole in-plane stretch</td>
</tr>
<tr>
<td>1259</td>
<td>C-H inplane deformation</td>
</tr>
<tr>
<td>1181</td>
<td>Pyrrole ring breathing</td>
</tr>
<tr>
<td>962</td>
<td>Benzene breathing</td>
</tr>
<tr>
<td>755</td>
<td>Macrocycle stretch</td>
</tr>
<tr>
<td>652</td>
<td>Pyrrole ring out of plane</td>
</tr>
<tr>
<td>250</td>
<td>Au-S stretch</td>
</tr>
</tbody>
</table>

4β-Ni$^{II}$TTPc on Au surface occurs through the formation of chemical bond between Au and sulfur. This is in accordance with the earlier reports [29,30].
Further, the Raman spectrum of 4β-Ni\textsuperscript{II}TTPc on Au surface shows a band at 2572 cm\textsuperscript{-1} due to -SH stretching [29,30]. This indicates that all the -SH groups of 4β-Ni\textsuperscript{II}TTPc were not involved in bonding with the underlying Au surface. In other words, the 4β-Ni\textsuperscript{II}TTPc SAM contains free –SH group on the surface. The possible attachment of 4β-Ni\textsuperscript{II}TTPc SAM on Au electrode is schematically illustrated in Scheme 6.1.

![Scheme 6.1. Schematic illustration of the SAM of 4β-Ni\textsuperscript{II}TTPc on Au electrode.](image)

**Scheme 6.1.** Schematic illustration of the SAM of 4β-Ni\textsuperscript{II}TTPc on Au electrode.

**6.2.3. Reductive Desorption of 4β-Ni\textsuperscript{II}TTPc SAM Modified Au Electrode**

Figure 6.5a shows the typical LSV obtained for the reductive desorption of 4β-Ni\textsuperscript{II}TTPc SAM modified Au electrode in 0.1 M KOH. It shows a reductive desorption at -0.90 V (curve a) and the amount of charge was calculated as 105.48 ± 5 μC cm\textsuperscript{-2} without subtracting the roughness of the electrode (curve a). This shows that the SAM was formed on Au electrode via Au-S bond. The observed
Figure 6.5. LSVs obtained for reductive desorption of (a) 4β-Ni\textsuperscript{II}-TTPc and (b) 4β-Ni\textsuperscript{II}-TTPc/C-AuNPs modified Au electrodes in 0.1 M KOH at a scan rate of 100 m V s\textsuperscript{-1}.

value is consistent with a monolayer coverage. Further, to confirm the availability of free -SH on Au surface, we have immobilized C-AuNPs on 4β-Ni\textsuperscript{II}-TTPc SAM on Au electrode. Then, the attachment of AuNPs was confirmed by reductive desorption measurement. In the case of AuNPs immobilized 4β-Ni\textsuperscript{II}-TTPc SAM modified Au electrode, the reductive desorption peak current increases at -0.90 V (curve b) and the amount of charge was calculated as 173.23 ± 5 μC cm\textsuperscript{-2}. The obtained higher charge suggests that C-AuNPs were covalently attached with the free -SH groups of 4β-Ni\textsuperscript{II}-TTPc SAM modified Au electrode and reductively desorbs at the same potential where the bulk Au-S reduction occurs. The reductive
desorption experiments confirm the SAM formation via chemisorption and also the presence of free -SH groups on the SAM surface.

6.2.4. Electrochemical Oxidation of L-dopa at 4β-Ni^{II}TTPc SAM Modified Au Electrode

L-dopa is one of the catecholamines and a kind of essential precursors for the biosynthesis of dopamine. This drug can be metabolized by an enzymatic reaction to dopamine compensating for the deficiency of dopamine in the brain [31]. L-dopa is associated with the side effects such as gastritis, paranoia and dyskinesia [32,33]. Thus, we have studied the electrocatalytic activity of L-dopa using the 4β-Ni^{II}TTPc SAM modified Au electrode. Figure 6.6 shows the CVs obtained for 0.5 mM L-dopa at bare and 4β-Ni^{II}TTPc SAM modified Au electrodes in PB solution (pH 4) at a scan rate of 50 mV s^{-1}. Bare Au electrode oxidized L-dopa at 0.55 V along with a reduction peak at -0.07 V (curve a). The observed oxidation peak at 0.55 V corresponds to two electron oxidation of L-dopa to dopaquinone and the subsequent reduction of dopaquinone to L-dopa. The oxidized product dopaquinone was cyclized to form cyclodopa in solution which undergoes further oxidation to form dopachrome which was responsible for the oxidation peak at 0.27 V at bare Au electrode [34]. However, L-dopa exhibited a single redox peak at 0.46 V and the reduction peak at -0.07 V corresponding to the reduction of dopachrome to cyclodopa was absent at 4β-Ni^{II}TTPc SAM modified Au electrode (curve b). This may due to the faster electron transfer reaction of L-
dopa at 4β-NiII{TTPc} SAM modified Au electrode when compared to bare Au electrode. Hence, the redox peak corresponding to cyclodopa to dopachrome was

![Graph showing CVs](image)

**Figure 6.6.** CVs obtained for 0.5 mM L-dopa at (a) bare Au (solid: first cycle and dotted: second cycle), (b) 4β-NiII{TTPc} (solid: first cycle and dotted: second cycle) and (c) 4β-H2{TTPc} (solid: first cycle and dotted: second cycle) SAM modified Au electrodes in 0.2 M PB solution (pH 4) at a scan rate of 50 mV s\(^{-1}\). Inset: CV obtained for 4β-NiII{TTPc} SAM modified Au electrode in the absence of L-dopa in 0.2 M PB solution (pH 4) at a scan rate of 100 mV s\(^{-1}\).

absent at the SAM modified electrode [35]. Further, the oxidation of L-dopa was studied using the 4β-H2{TTPc} SAM modified Au electrode. Similar to 4β-NiII{TTPc} SAM modified Au electrode, the reduction peak of dopachrome to cyclodopa was absent at 4β-H2{TTPc} SAM modified Au electrode but it oxidizes L-dopa at 0.52
V. For subsequent cycles, the peak was slightly shifted at 4β-H₂TTPc SAM modified Au electrode whereas it was stable at 4β-Ni⁺TTPc SAM modified Au electrode. This shows that the oxidation of L-dopa was mediated by both metal center and ring. In the absence of L-dopa, the 4β-Ni⁺TTPc SAM modified Au electrode shows characteristic voltammetric responses for metal and ring (Figure 6.6 Inset).

6.2.5. Determination of L-dopa at 4β-Ni⁺TTPc SAM Modified Au Electrode by DPV

![Figure 6.7. DPVs obtained for the determination of L-dopa at 4β-Ni⁺TTPc SAM modified Au electrode in 0.2 M PB solution (pH 4). Each addition increases the concentration of L-dopa (a) 5, (b) 10, (c) 50, (d) 75, (e) 100, (f) 125, (g) 150, (h) 175 and (i) 200 μM. Inset: Plot of current vs. concentration of L-dopa.](image)

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Figure 6.7 shows the differential pulse voltammograms (DPVs) obtained for L-dopa in the concentration range of 5-200 μM at 4β-NiIII-TTPc SAM modified Au electrode in 0.2 M PB solution (pH 4). The peak current of L-dopa oxidation increases linearly with an increase in the concentration ranging from 5-200 μM. The plot of peak current versus the concentration of L-dopa is linear with a correlation coefficient of 0.9951. The detection limit for L-dopa was found to be $6.63 \times 10^{-8}$ M (S/N = 3).

6.3. SAM of 4β-CoII-THTPhPc on Au Electrode and its Electrocatalytic Activity Towards Dioxygen Reduction

This section deals with the fabrication of 4β-CoII-THTPhPc SAM, its characterization and electrocatalytic activity towards dioxygen. The cobalt substituted Pc derivatives are one of the well known electrocatalyst for the dioxygen reduction [11,36-38]. Therefore, we have employed 4β-CoII-THTPhPc SAM for the reduction of dioxygen.

6.3.1. Electrochemical Behavior of 4β-CoII-THTPhPc SAM on Au Electrode

The SAMs of 4β-CoII-THTPhPc and 4β-H2THTPhPc were formed on Au electrode by immersing the electrodes for 24 h into their respective solutions. Figure 6.8 shows the CVs obtained for 4β-CoII-THTPhPc and metal free thiophenyl phthalocyanine (4β-H2THTPhPc) SAMs on Au electrodes in 0.1 M HClO4. The 4β-CoII-THTPhPc SAM shows a redox peak at 0.38 V corresponding to CoIII/CoII redox couple (peak I) along with the shoulder redox peak at 0.53 V corresponding
to Co$^{III}$Pc$^{2-}$/Co$^{II}$Pc$^{3-}$ redox couple (peak II) (curve a). To ascertain this, we have prepared a SAM of 4β-H$_2$THTPhPc on Au electrode and run the CV under identical conditions. It shows a single redox wave at 0.51 V corresponding to the H$_2$Pc$^{1-}$/H$_2$Pc$^{2-}$ (curve b). Hence, the obtained redox wave at less positive potential for 4β-Co$^{II}$THTPhPc SAM was due to Co$^{III}$/Co$^{II}$. The surface coverage for the 4β-Co$^{II}$THTPhPc on Au electrode was calculated by integrating the charge under the anodic wave corresponding to Co$^{III}$/Co$^{II}$ in Figure 6.8 (curve a) and it was found to be 1.23 × 10$^{-10}$ mol cm$^{-2}$. Further, the surface confinement of 4β-Co$^{II}$THTPhPc on Au electrode was confirmed from the CVs recorded at different scan rates in 0.1 M HClO$_4$ (Figure 6.9A). The peak separation values were small (ΔE = 65 mV) and the peak current increases linearly with scan rates in the range of 0.05-1.0 V s$^{-1}$.

![Graph](image)

**Figure 6.8.** CVs obtained for (a) 4β-Co$^{II}$THTPhPc and (b) 4β-H$_2$THTPhPc SAM modified Au electrodes in 0.1 M HClO$_4$ at a scan rate of 0.05 V s$^{-1}$.
(Figure 6.9 Inset), confirming that the observed redox reaction was due to surface confined species. Further, the peak potentials and the shape of the CV remained identical for several continuous potential cycles, which demonstrated that the SAM was highly stable. In order to clearly visualize the redox waves of 4β-CoII-THTPhPc SAM on Au electrode, differential pulse voltammetry (DPV) experiment was carried out. Figure 6.9B shows the DPVs obtained for 4β-CoII-THTPhPc SAM modified Au electrode in HClO₄. It can be seen from Figure 6.9B, clear voltammetric peaks were observed for 4β-CoII-THTPhPc SAM modified Au electrode correspond to metal and ring redox couples.

![Figure 6.9](image)

**Figure 6.9.** (A) CVs obtained for (A) 4β-CoII-THTPhPc SAM modified Au electrode at scan rates of 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1 V s⁻¹ Inset: Plot of peak current vs. scan rate and (B) DPVs obtained for 4β-CoII-THTPhPc SAM modified Au electrode in 0.1 M HClO₄.
The compactness of the SAMs can be usually understood from their blocking behavior towards \([\text{Fe(CN)}_6]^{3-/4-}\) redox couple. Figure 6.10 shows the CVs obtained for bare and 4β-Co\(^{II}\)THTPhPc SAM modified Au electrodes in 1 mM \(\text{K}_3[\text{Fe(CN)}_6]\) containing 0.1 M KCl at a scan rate of 50 mV s\(^{-1}\). Bare Au electrode exhibits a characteristic voltammetric response for \([\text{Fe(CN)}_6]^{3-/4-}\) with a peak

![Graph showing CVs](image)

**Figure 6.10.** CVs obtained for (a) bare Au and (b) 4β-Co\(^{II}\)THTPhPc SAM modified Au electrode in 0.1 M KCl containing 1 mM \(\text{K}_3[\text{Fe(CN)}_6]\) at a scan rate of 0.05 V s\(^{-1}\).

separation of 68 mV (curve a) whereas 4β-Co\(^{II}\)THTPhPc SAM modified Au electrode was hindered the redox response of \([\text{Fe(CN)}_6]^{3-/4-}\) and a peak separation of 105 mV (curve b) was obtained. The current density also decreased at the SAM modified electrode. Although the 4β-Co\(^{II}\)THTPhPc SAM modified electrode was not completely blocked the electronic communication between \([\text{Fe(CN)}_6]^{3-/4-}\) in
solution and the underlying Au electrode, it hindered the redox reaction of $[\text{Fe(CN)}_6]^{3-/4}$. This indicated the successful formation of SAM on Au electrode. However, the SAM was not compact and contains defects or pinholes.

Figure 6.11 shows the typical linear sweep voltammogram (LSV) obtained for the reductive desorption of 4β-Co$^{II}$THTPhPc SAM on Au electrode in 0.1 M KOH. The 4β-Co$^{II}$THTPhPc SAM shows a reductive desorption peak at -0.92 V. The obtained reduction potential at -0.92 V suggests that 4β-Co$^{II}$THTPhPc was covalently attached on the Au electrode via Au-S linkage and reductively desorbs at -0.92 V. This again indicates the successful attachment of 4β-Co$^{II}$THTPhPc SAM on Au electrode.

![Graph](image)

**Figure 6.11.** LSV obtained for 4β-Co$^{II}$THTPhPc SAM modified Au electrode in 0.1 M KOH at a scan rate of 0.1 V s$^{-1}$.  

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6.3.2. Characterization of 4β-Co^{II}THTPhPc SAM on Au Electrode by Electrical Impedance Spectroscopy

Figure 6.12 shows the Nyquist and Bode plots obtained for bare and 4β-Co^{II}THTPhPc SAM modified Au electrodes in 0.1 M KCl containing 1 mM K₃[Fe(CN)₆] solution at scanning frequencies from 0.01 to 100000 Hz. The impedance data representation is obtained by plotting \( Z'' \) against \( Z' \) and is called the Nyquist plot. Figure 6.12A shows Nyquist plot obtained for bare and 4β-Co^{II}THTPhPc SAM modified Au electrodes. The obtained Nyquist plots were best fit with Randles equivalent circuit model \([R_s (CPE-R_p)]\) (Figure 6.12A inset). The charge transfer resistance \( (R_{CT}) \) can be calculated from the semicircle obtained in the Nyquist plot [39]. The \( R_{CT} \) value of the bare Au electrode (26799 \( \Omega \)) (Figure 6.12A, curve a) was less than at 4β-Co^{II}THTPhPc SAM modified Au electrode (33455 \( \Omega \)) (Figure 6.12A, curve b). This shows that the resistance was increased after the attachment of 4β-Co^{II}THTPhPc on Au electrode. This suggests that the SAM modified electrode hinders the electron transfer between \( K₃[Fe(CN)₆] \) solution and underlying Au electrode. Figure 6.12B shows the Bode-phase angle plot for the bare and 4β-Co^{II}THTPhPc SAM modified Au electrodes. If the phase angle is greater or equal to 90°, the modified electrode behaves like an ideal capacitor indicating the insulating nature of the modified electrode [40]. If the phase angle value is less than 90°, electron transfer reaction is facile due to the pinholes or defects in the SAM [16-18,40]. The bare Au electrode shows phase
angle (θ = 56.5°). However, after the attachment of 4β-Co\textsuperscript{II}THTPhPc on Au electrode the phase angle value (θ = 80.3°) was increased due to the partial blocking nature of 4β-Co\textsuperscript{II}THTPhPc SAM modified Au electrode. This confirms that the modified electrode is permeable to ions from the ferricyanide redox probe.

![Graph](image)

**Figure 6.12.** (A) Nyquist plots and (B) Bode-phase angle plots for (a) bare and (b) 4β-Co\textsuperscript{II}THTPhPc SAM modified Au electrodes in 0.1 M KCl containing 1 mM K\textsubscript{3}[Fe(CN)\textsubscript{6}] at scanning frequency from 0.01 to 100000 Hz. Inset: Equivalent circuit used to fit the impedance data.

### 6.3.3. Raman Spectral Studies of 4β-Co\textsuperscript{II}THTPhPc SAM on Au Surface

Raman spectrum obtained for the 4β-Co\textsuperscript{II}THTPhPc modified Au surface is shown in Figure 6.13. The stretching bands and their assignments based on the literature are given in Table 6.2 [11,6,39-43]. Raman spectrum of 4β-Co\textsuperscript{II}THTPhPc shows a pyrrole ring out of plane bending at 689 cm\textsuperscript{-1}. It also shows strong isoindole ring and macrocycle inplane stretchings at 1423 and 1556 cm\textsuperscript{-1},
Figure 6.13. Raman spectrum obtained for 4β-Co\textsuperscript{II}THTPhPc on Au plate

Table 6.2. Raman spectral bands (cm\textsuperscript{-1}) obtained for SAM of 4β-Co\textsuperscript{II}THTPhPc on Au plate

<table>
<thead>
<tr>
<th>4β-Co\textsuperscript{II}THTPhPc</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3227</td>
<td>-OH stretching</td>
</tr>
<tr>
<td>1556</td>
<td>Macrocycle in plane stretch</td>
</tr>
<tr>
<td>1423</td>
<td>Isoindole ring stretch</td>
</tr>
<tr>
<td>1323</td>
<td>Pyrrole in plane stretch</td>
</tr>
<tr>
<td>1061</td>
<td>C-H bend</td>
</tr>
<tr>
<td>956</td>
<td>Benzene breathing</td>
</tr>
<tr>
<td>689</td>
<td>Pyrrole ring out of plane band</td>
</tr>
<tr>
<td>250</td>
<td>Au-S stretch</td>
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respectively. In addition, it shows a band at 250 cm\(^{-1}\) corresponding to Au-S. This confirms the self-assembly of 4β-Co\(^{II}\)THTPhPc on Au surface via Au-S bond [41,42]. Further, the Raman spectrum of 4β-Co\(^{II}\)THTPhPc on Au surface showed a band at 3247 cm\(^{-1}\) corresponding to -OH group [43], indicating that the -OH group was present on the modified electrode surface. The SAM of 4β-Co\(^{II}\)THTPhPc on Au electrode was schematically illustrated in Scheme 6.2.

![Scheme 6.1](image)

4β-Co\(^{II}\)THTPhPc

**Scheme 6.1.** Schematic illustration of the SAM of 4β-Co\(^{II}\)THTPhPc on Au electrode.

### 6.3.4. Electrocatalytic Reduction of Dioxygen at 4β-Co\(^{II}\)THTPhPc SAM Modified Au Electrode

The cobalt substituted Pc derivatives are one of the well known electrocatalysts for the dioxygen reduction [11,36-38]. Therefore, we have employed 4β-Co\(^{II}\)THTPhPc SAM for the reduction of dioxygen. Figure 6.14
illustrates the LSVs obtained for bare Au, 4β-Co$^{II}$THTPhPc and 4β-H$_2$THTPhPc SAM modified Au electrodes in the presence and absence of dioxygen in HClO$_4$ at a scan rate of 100 mV s$^{-1}$. Bare Au electrode does not show any characteristic peak for dioxygen reduction in the potential window studied (curve a), whereas the 4β-Co$^{II}$THTPhPc SAM modified Au electrode shows a well-defined reduction peak for dioxygen at -0.06 V with enhanced reduction current (curve b). The obtained enhanced current response with decreased overpotential of dioxygen reduction at 4β-Co$^{II}$THTPhPc SAM modified Au electrode was due to the mediation of

![Graph](image)

**Figure 6.14.** LSVs obtained for (a) bare Au (b) 4β-Co$^{II}$THTPhPc and (c) 4β-H$_2$THTPhPc SAM modified Au electrodes oxygen saturated 0.1 M HClO$_4$ at a scan rate of 0.1 V s$^{-1}$. (d) LSV obtained for 4β-Co$^{II}$THTPhPc SAM modified Au electrode in the absence of oxygen in 0.1 M HClO$_4$ at a scan rate of 0.1 V s$^{-1}$. 

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Co\textsuperscript{III}/Co\textsuperscript{II}. To confirm this, we have examined the reduction of dioxygen at 4β-H\textsubscript{2}THTPhPc modified Au electrode (curve c). Unlike 4β-Co\textsuperscript{II}THTPhPc SAM modified Au electrode, no reduction peak was obtained for dioxygen in the potential window studied. This confirms that the dioxygen reduction was mediated by Co\textsuperscript{III}/Co\textsuperscript{II} redox centre in 4β-Co\textsuperscript{II}THTPhPc SAM modified Au electrode. In the absence of dioxygen, the 4β-Co\textsuperscript{II}THTPhPc SAM modified Au electrode shows characteristic redox response corresponding to the Co\textsuperscript{III}/Co\textsuperscript{II} (curve d). Since the dioxygen reduction was carried out in acidic medium, the possible product is the formation of hydrogen peroxide [44,45].

6.4. Conclusions

In this chapter, we have described the fabrication, characterization and applications of SAMs of thiol and thiophenyl functionalized metal phthalocyanine modified Au electrodes. We have used Ni\textsuperscript{II} as the metal center for thiol functionalized phthalocyanine whereas Co\textsuperscript{II} as the metal center for thiophenyl functionalized phthalocyanine. The attempt to synthesize tetrathiolephthiocyanato-cobalt(II) was not achieved due to experimental difficulties. The SAMs of 4β-Ni\textsuperscript{II}TTPc and 4β-Co\textsuperscript{II}THTPhPc on Au surfaces were prepared by spontaneous adsorption from their respective solution in DMF medium. Further, SAM modified Au electrodes were characterized by Raman spectroscopy, cyclic voltammetry and electrical impedance spectroscopy. The SAM of 4β-Ni\textsuperscript{II}TTPc on Au electrode shows two well-defined oxidation peaks at 0.34 V and 0.52 V corresponding to
Ni^{III}/Ni^{II} and Ni^{III}Pc^-/Ni^{III}Pc^2-, respectively. The surface coverage value was estimated from the charge associated with the oxidation of Ni^{II}/Ni^{III}, yielding 1.01 × 10^{-10} mol cm^{-2}. The Raman spectrum of the 4β-Ni^{III}TTPc SAM shows two characteristic bands at 2572 and 250 cm^{-1}, corresponding to -SH and Au-S stretching vibrations. These two bands clearly suggest that 4β-Ni^{III}TTPc SAM was attached via Au-S band and further all the four -SH groups were not involved in chemisorption. Finally, the electrocatalytic activity of the SAM was examined by taking 3,4-dihydroxy-1-phenylalanine (L-dopa) as an example. The SAM modified electrode oxidizes L-dopa at 0.46 V which is 90 mV less positive potential than bare Au electrode.

The 4β-Co^{II}THTPhPc SAM shows a redox peak at 0.38 V corresponding to Co^{III}/Co^{II} redox couple along with the shoulder redox peak at 0.53 V corresponding to Co^{III}Pc^2-/Co^{III}Pc^- redox couple (curve a), respectively in HClO_4. Raman spectrum shows a characteristic stretching band at 250 cm^{-1} corresponding to Au-S, confirming the formation of SAM via Au-S bond. Further, the electrochemical reduction of dioxygen was carried out using the SAM modified Au electrode in HClO_4. The SAM modified electrode catalyzed the reduction of dioxygen by decreasing its overpotential and also enhancing the reduction current when compared to bare Au electrode.
6.5. References


