Chapter 5

Fabrication of Monolayer of Azobenzene Based Molecular Wire Containing Bis-Ferrocenyl Porphyrin on Conducting Substrate
5.2. *Electrochemical fabrication of azobenzene molecular wire on conducting surface*

5.2.1. *Electrochemical attachment of aminophenyl group on glassy carbon electrode*

Recent report has shown that aminophenyl group can be attached on conducting substrates by the electrochemical reduction of aminophenyl diazonium cation generated in situ from the corresponding diamine in acidic medium (Scheme 5.1) [19]. Further, it has been demonstrated that 1 equivalent of NaNO₂ leads to diazotation of the starting amine with higher yield. Thus, we have used 1 mM $p$-phenylenediamine dissolved in 0.5 M HCl and 1 equivalent of

![Diagram of aminophenyl monodiazonium chloride](image)

**Scheme 5.1.** Preparation of aminophenyl monodiazonium chloride.

NaNO₂ to generate mono-aryldiazonium salt in the electrochemical cell (in situ). For this solution, the linear sweep voltammogram (LSV) shows a well-defined reduction peak at -0.2 V due to the formation of aryl radical (Figure 5.1). This aryl radical attacks the surface of the GC electrode to establish a C-C covalent bond as shown in Scheme 5.2. To avoid multilayer formation, the LSV was restricted to a single scan [20]. The electrochemical response obtained for aminophenyl diazonium cation at GC electrode is consistent with that reported earlier [19].
Figure 5.1. LSV obtained for 1 mM \( p \)-phenylenediamine at GC electrode in 0.5 M HCl at a scan rate of 100 mV s\(^{-1} \).

Scheme 5.2. Electrochemical attachment of aminophenyl monolayer on GC surface.

The chemically attached aminophenyl moiety (AP) was characterized by cyclic voltammetry and attenuated total reflectance (ATR) FT-IR spectroscopy.
techniques. The cyclic voltammogram obtained for the AP monolayer on GC electrode in 0.5 M HCl is shown in Figure 5.2. The AP monolayer does not show any electrochemical response between 0 and +0.8 V. Therefore, the formation of polyaniline or oligomers of polyaniline, which are electroactive in this potential range is ruled out [21]. However, the observed oxidation wave around 1 V could be assigned to the irreversible oxidation of aminophenyl (free $-\text{NH}_2$) groups attached at the GC electrode surface. This is in agreement with the reported oxidation potential of aniline to its radical cation form during the polymerization process of aniline in acidic medium [22]. As demonstrated recently, the electrochemical oxidation of the chemically attached AP groups does not form a polyaniline layer because the electrochemically generated radicals cannot

Figure 5.2. CV obtained for aminophenyl modified GC electrode in 0.5 M HCl at a scan rate of 100 mV s$^{-1}$. 
efficiently recombine or react with another aniline unit since they are not properly oriented as a result of attachment on the GC surface.

The electrochemically attached AP monolayer on GC surface was also characterized by ATR FT-IR spectroscopy. Figure 5.3 shows the ATR FT-IR spectrum of aminophenyl modified on screen printed carbon surface. The presence of aminophenyl group on the carbon surface was confirmed from the observed bands at 1600, 1500, and 1250 cm\(^{-1}\). The intense band at 1617 cm\(^{-1}\) is attributed to the angular deformation of N-H in NH\(_2\) and to the C=C bond stretch in the aromatic rings. Further, the ATR FT-IR spectrum of the aminophenyl modified electrode exhibits three weak bands at 3440, 3385, and 3230 cm\(^{-1}\), which correspond to N-H.

![Figure 5.3. ATR FT-IR spectrum of AP attached on screen printed carbon surface.](image)
bond stretching which is in agreement with the ones observed for aniline [23]. Thus, in addition to cyclic voltammetry, ATR FT-IR spectrum also confirmed the electrochemical attachment of AP on GC surface as shown in Scheme 5.2.

5.2.2. Formation of 4-aminoazobenzene on GC surface

After the successful attachment of aminophenyl on the GC surface, it is subjected to electrochemical oxidation by immersing in THF containing p-phenylenediamine. Figure 5.4 shows a LSV recorded at a scan rate of 100 mV s\(^{-1}\) for the aminophenyl modified GC electrode immersed in THF containing 1 mM p-phenylenediamine containing 0.1 M tetrabutylammonium hexafluorophosphate (n-)

![Graph](image)

**Figure 5.4.** LSV obtained for AP modified GC electrode immersed in THF containing 0.1 mM of PPD and 0.1 M \(n\)-Bu\(_4\)NPF\(_6\).
Bu₄NPF₆). It shows two oxidation peaks at +0.4 V and +0.86 V, corresponding to the oxidation of p-phenylenediamine. For the experiments conducted in THF and dichloromethane solvents, Ag wire was used as a reference electrode and the potential measured was adjusted to Ag/AgCl (KCl sat). Here, again to avoid the multilayer formation, the scan was restricted to single scan. It is assumed that during electrochemical oxidation in the presence of p-phenylenediamine, the amino group present on the surface of the modified electrode undergoes oxidation to form an azo bond (Scheme 5.3). After the formation of azo bond, the electrode was then removed from the solution, washed with THF and finally sonicated in THF to remove any physically adsorbed molecules.

![Diagram of azo bond formation](image)

**Scheme 5.3.** Formation of 4-aminoazobenzene monolayer on GC surface.

Further, the 4-aminoazobenzene (AAB) monolayer formed on the GC surface was characterized by cyclic voltammetry and ATR FT-IR spectroscopy. LSV obtained for a monolayer of AAB on GC surface is shown in Figure 5.5. Initially, the potential was scanned from 0 to -2.0 V to confirm the presence of azo group in the monolayer. A reduction peak was observed at -1.52 V, corresponding to the reduction of an azo bond [24]. As we hold the potential for a minute at
-1.52 V, the reduction peak was disappeared due to the complete reduction of azo bonds.

![Graph showing linear sweep voltammograms](image)

**Figure 5.5.** Linear sweep voltammograms (scanned from 0 to -2 V) obtained for AAB modified GC electrode (a) before and (b) after holding the potential at -1.52 V for a minute in THF containing 0.1 M n-Bu₄NPF₆ at a scan rate of 100 mV s⁻¹.

Cyclic voltammogram obtained for the AAB monolayer on GC surface is shown in Figure 5.6. It can be seen from the CV curve that the reduced azo bond at -1.52 V was oxidized at +0.38 V [24]. Again the appearance of reduction peak at -1.52 V indicating the reduction of the oxidized azo bond. To confirm the oxidation of reduced azo bond at +0.38 V, CV was recorded in the potential window of 0 to +1.2 V. In this case, the reduction of azo bond was restricted by
limiting the potential to 0 V. While scanning the potential from 0 V to +1.2 V, no oxidation peak was observed at +0.38 V corresponding to the oxidation of azo bond. This clearly suggested that the observed oxidation peak at +0.38 V in Figure 5.6 corresponds to the oxidation of reduced azo bond in the AAB monolayer on GC surface.

![Graph](image)

**Figure 5.6.** CV of AAB modified GC electrode immersed in THF containing 0.1 M n-Bu$_4$NPF$_6$ at a scan rate of 100 mV s$^{-1}$.

Further, the presence of azo bond in the AAB monolayer was also confirmed by ATR FT-IR spectroscopy. The ATR FT-IR spectrum of the AAB monolayer is shown in Figure 5.7. The presence of band at 1456 cm$^{-1}$ in addition to the bands at 1600, 1500, 1250, 3440, 3385, and 3230 cm$^{-1}$ strongly suggests the presence of the $–\text{N}=\text{N}–$ bond in the AAB monolayer. The barrier property of the AAB monolayer was examined by studying the electrochemical behavior of
Figure 5.7. ATR FT-IR spectrum of AAB modified screen printed carbon surface.

dissolved $[\text{Fe(CN)}_6]^{3-/4-}$ redox couple in solution. Figure 5.8 shows the CV obtained for 0.5 mM $\text{K}_3[\text{Fe(CN)}_6]$ in 0.1 M KCl at GC and AAB modified GC electrodes. The GC electrode shows an electrochemical response characteristic

Figure 5.8. CV obtained for 0.5 mM of $\text{K}_3[\text{Fe(CN)}_6]$ containing 0.1 M KCl at (a) bare GC and (b) AAB modified GC electrodes at a scan rate of 100 mV s$^{-1}$. 

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for [Fe(CN)_6]^{3-/4-} redox couple. The AAB modified GC electrode also exhibited a typical electrochemical response characteristic for [Fe(CN)_6]^{3-/4-} redox couple however with a slightly increased peak separation indicating that the AAB monolayer facilitates the electron transfer reaction of [Fe(CN)_6]^{3-/4-}.

5.2.3. Attachment of bis-ferrocenylporphyrin with AAB molecular wire

After the successful formation of the AAB monolayer on GC electrode, a redox probe, 5-(4-aminophenyl)-10,20-bis(ferrocenyl)-15-(anth-9-yl)porphyrin (AAFcP)

![Scheme 5.4. Electrochemical attachment of AAFcP with GC/AAB electrode.](image)

was attached to the AAB molecular wire by electrochemical oxidation of AAFcP. The attachment of AAFcP to AAB on GC electrode by electrochemical oxidation in the presence of 0.1 mM AAFcP containing 0.1 M n-Bu_4NPF_6 in dichloromethane
Figure 5.9. UV-visible diffuse reflectance spectra obtained for AAB-AAnFcP molecular wire formed on screen printed carbon surface.

was achieved through the oxidation of amino groups in AAB and AAnFcP as shown in Scheme 5.4. The successful attachment of AAnFcP to the AAB modified GC (GC/AAB/AAnFcP) electrode was confirmed by CV and UV-visible diffuse reflectance spectroscopy. Figure 5.9 shows the UV-visible reflectance spectrum obtained for the GC/AAB/AAnFcP. It shows the characteristic absorption due to Soret band of porphyrin around 450 nm. Under the present experimental conditions, we could not observe other bands due to less molar extinction coefficient. CV obtained for GC/AAB/AAnFcP in dichloromethane containing 0.1 M n-Bu₄NPF₆ is shown in Figure 5.10. It shows a predominant oxidation wave around +0.65 V along with a shoulder wave around +0.45 V due to the oxidation of ferrocene moiety [24]. We have restricted the potential window within the

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Figure 5.10. CV obtained for GC/AAB/AAnFcP electrode in dichloromethane containing 0.1 M $n$-Bu$_4$NPF$_6$.

oxidation potential range of ferrocene to avoid any complication. The obtained spectral and electrochemical results confirmed the successful formation of a molecular wire using AAnFcP molecule and AAB monolayer. Recently, it has been reported that the formation of a surface confined charge-transfer complex by the reaction of a strong electron acceptor, tetracyanoethylene with a self-assembled monolayer of an electron donor, tetramethylxyleneedithiol on the conducting surface improved the conductance of a single molecule to 50 fold [25]. In the present study, a preliminary attempt is made to form a charge transfer complex on the prepared molecular wire on GC surface as a donor and
tetracyanoethylene as an acceptor. To understand the concept of charge transfer complex, we have first studied the formation of charge transfer complex in solution and then extended this concept to GC surface.

5.3. Charge-transfer interaction of AAB with π-acceptor

In this section, to understand the basics of the CT interaction between donors and acceptor, the interaction between $p$-aminothiophenol (ATP) and 2,3-dichloro-5,6- dicyano-p-benzoquinone (DDQ) in addition to other compounds

\[ \text{Scheme 5.5. Structures of (I) donors: TP, BDT, ATP, HTP and TTP and (II) acceptor: DDQ.} \]

Such as thiophenol (TP), benzene-1,4-dithiol (BDT), $p$-hydroxythiophenol (HTP) and $p$-toluenethiol (TTP) (Scheme 5.5). In the present study, we have chosen DDQ
as an acceptor because the formation of charge-transfer complex using DDQ has been well established in the literature [26].

5.3.1. UV-visible spectral studies and QM calculations of CT complexes

Mixing dichloromethane solutions of 1-5 with DDQ, colored solutions were formed immediately. Figure 5.11 shows the UV-vis spectra of DDQ and 1-5 with DDQ in dichloromethane. DDQ shows a band at 372 nm (line a) while no absorption band was appeared for DDQ and 1-5 in the region of 440 to 800 nm. However, the absorption spectra obtained for 1-5 with DDQ in dichloromethane

![Graph of absorption spectra](attachment:absorption_spectra.png)

**Figure 5.11.** Absorption spectra of (a) DDQ and CT complexes of DDQ with (b) TP, (c) BDT, (d) ATP, (e) HTP, (f) TTP and (g) electrochemically generated DDQ\(^-\) in solution.
solution show a broad absorption band from 440 to 800 nm and a band of DDQ between 300 to 400 nm was enhanced demonstrating the formation of CT complexes between 1-5 and DDQ. The CT absorption band represented in the spectra was appeared at 552 nm for DDQ-TP (line b), 547 nm for DDQ-BDT (line c), 461 nm for ATP-DDQ (line d), 529 nm for HTP-DDQ (line e) and 561 nm for DDQ-TTP (line f).

*Ab-initio* and semiempirical calculations were performed for the isolated donors and acceptor. The energies of HOMO of donors and LUMO of the acceptor were calculated without considering the solvent effects. The calculated molecular

![LUMO π* (a2) of DDQ](image)

![π (b1)](image)

![π (a2)](image)

**Figure 5.12.** Molecular orbitals of DDQ, benzene (BEN) and aromatic thiols.
orbitals (MOs) for the aromatic thiols are shown in Figure 5.12. Among the number of filled MOs, we consider only first two HOMOs which are having orbital symmetry with the LUMO of DDQ. Since benzene molecule has two degenerate $\pi(e_{1g})$ orbitals [27,28], only one CT band was expected. However MO’s ($\pi(e_{1g})$) degeneracy will be removed when substituents like thiol, amino, hydroxyl and methyl are present in the benzene nucleus and these MOs split into

![Energy-Level Diagram](image)

**Figure 5.13.** MO energy-level diagrams and transitions of the CT complexes of aromatic thiols (1-5) and DDO.

$\pi(b_1)$ and $\pi(a_2)$ with the appreciable energy separation depending upon the nature, number and position of the substituent [28]. The possible CT transitions are shown in Figure 5.13. It shows that the lowest energy transition is $\pi^*(a_2) \leftrightarrow \pi(b_1)$. We
have calculated vertical ionization potential of donors ($I^D$) for the bands observed in the spectra and are given in Table 5.1. The values are in good agreement with the theoretical values. Now it is possible to assign the transitions for the CT band including two bands enhanced in the absorbance obtained for 1-5 with DDQ

**TABLE 5.1. MO energies and ionization potentials of aromatic thiols (1-5) and DDQ.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>MO Energy*</th>
<th>Ionization Potential#</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\pi(b_1)$</td>
<td>$\pi(a_2)$</td>
</tr>
<tr>
<td>BDT</td>
<td>-8.9907</td>
<td>-9.8724</td>
</tr>
<tr>
<td>HTP</td>
<td>-8.6778</td>
<td>-9.7717</td>
</tr>
<tr>
<td>TTP</td>
<td>-8.5363</td>
<td>-9.4696</td>
</tr>
<tr>
<td>DDQ</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

* values obtained from *ab-initio* calculation  
# Values obtained from the electronic spectra

(Figure 5.11). The CT band falls in the 440 to 800 nm corresponds to $\pi^*(a_2)\leftarrow \pi(b_1)$ (lowest energy band) and the band observed between 300 to 400 nm corresponds to $\pi^*(a_2)\leftarrow \pi(a_2)$ transition. In the present study, we are interested in the broad lowest energy band observed in the 440-800 nm region (Figure 5.14) corresponding to $\pi^*(a_2)\leftarrow \pi(b_1)$ transition for detailed investigation. The broadness of the CT band in Figure 5.14 is due to the weak $\pi-\pi^*$ interaction [29] between 1-5 and DDQ. The non-involvement of DDQ anion radical in the CT complex formation was confirmed by recording the UV-vis spectrum of 0.1mM DDQ
**Figure 5.14.** Absorption spectra of (a) DDQ and CT complexes of DDQ with (b) TP, (c) BDT, (d) ATP, (e) HTP and (f) TTP in the visible region.

in dichloromethane after 3 min continuous electrolysis at -0.39 V [27] and the corresponding spectrum is shown as curve g in Figure 5.11. It shows absorption band characteristic of DDQ anion radical [30] but not matches with the broad spectra of CT complexes in the region of 440-800 nm, indicating that the DDQ anion radical was not participated in the formation of CT complexes. Further, non-participation of DDQ anion radical in the formation of CT complex is proved by recording ESR spectra for CT complexes of 1-5 with DDQ in dichloromethane. It shows no signal corresponding to DDQ anion [31] (spectrum not shown).
5.3.2. FT-IR spectral studies of CT complexes

FT-IR spectra were recorded for solid CT complexes of 1-5 and DDQ. Figures 5.15 and 5.16 show the spectra of \( \text{>C}=\text{O} \) and \( \text{-C} \equiv \text{N} \) stretching bands of CT complexes. It can be seen from the Figures, significant shifts in the stretching frequencies of both \( \text{-C} \equiv \text{N} \) and \( \text{>C}=\text{O} \) were observed for CT complexes with respect to DDQ, confirming the formation of CT complexes between 1-5 and DDQ. The degree of charge transfer between the aromatic thiols and DDQ can be visualized by the change in the stretching frequencies of \( \text{C} \equiv \text{N} \) and \( \text{>C}=\text{O} \) of DDQ.

![FT-IR spectra of \( \nu_{\text{CN}} \) for (a) DDQ, (b) DDQ-TP, (c) DDQ-BDT, (d) DDQ-ATP, (e) DDQ-HTP and (f) DDQ-TTP complexes.](image)

**Figure 5.15.** FT-IR spectra of \( \nu_{\text{CN}} \) for (a) DDQ, (b) DDQ-TP, (c) DDQ-BDT, (d) DDQ-ATP, (e) DDQ-HTP and (f) DDQ-TTP complexes.
[32,33]. Since -C≡N and >C=O groups having conjugation with >C=C< group, their IR absorptions are more sensitive to electron transfer to the antibonding orbital of >C=C< of DDQ. Due to the flow of electron density from the π (b₁) orbital of the benzene nucleus of aromatic thiols to π*(a₂) orbital of the DDQ, the stretching frequency of -C≡N group increases as the amount of charge that flow into the π*(a₂) orbital of DDQ increases. This can be seen from Figure 5.15, as the ionization potential of donors increases, the ν_CNstr also increases. Since the dipole

![Graph of FT-IR spectra of ν_CO for different complexes](image)

**Figure 5.16.** FT-IR spectra of ν_CO for (a) DDQ, (b) DDQ-TP, (c) DDQ-BDT, (d) DDQ-ATP, (e) DDQ-HTP and (f) DDQ-TTP complexes.
of the DDQ calculated by *ab-initio* study lies perpendicular to the axis passing through the >C=O groups, the high degree of conjugation is expected for -C≡N than >C=O with >C=C< group. The bond order of >C=C< and -C≡N groups decreases as the charge flow into π*(a2) orbital of >C=C< group increases. In addition to υ_{CNstr}, significant shift in the υ_{COstr} was also observed due to the charge transfer (Figure 5.16). The υ_{COstr} decreases as the ionization potential of aromatic thiols increases. The injection of electron density to the π*(a2) orbital of >C=C< group leads to a decrease in the bond order thereby the >C=O bond could lose conjugation with >C=C< group and the >C=O bond order increases, consequently υ_{COstr} increases. The stretching frequency of >C=O group in DDQ-HTP CT complex was broadened due to the possible hydrogen bonding between the −O-H

![Figure 5.17. Plot of ionization potential of aromatic thiols (1-5) against υ_{CN} of CT complexes.](image)

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or –S-H groups of the aromatic thiol and >C=O group of the DDQ. The reason for the deviation of both TP and HTP from the straight line in Figures 5.17 and 5.18 is likely that the hydrogen atoms of -S-H and -O-H may interact with the >C=O and –C≡N groups of DDQ through hydrogen bonding. As a result, a significant decrease in the stretching frequencies of both -C≡N and >C=O were observed. A large deviation of TP from the straight line in Figure 5.15 (~54 cm⁻¹) when compared to Figure 5.16 (~10 cm⁻¹) suggests that thiol group of TP is more effectively interacting with >C=O than -C≡N. In the case of other CT complexes, the presence of bulky group at para position of aromatic thiols may not favor the hydrogen bonding. It is evidently seen from Figures 5.17 and 5.18 that the change

![Figure 5.18. Plot of ionization potential of aromatic thiols (1-5) against ν_{CO} of CT complexes.](image)

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in $\nu_{\text{CNstr}}$ and $\nu_{\text{COstr}}$ depends only on the ionization potential of the aromatic thiols. For DDQ-ATP complex, the $\text{--NH}_2$ stretching bands in the range of 3500 to 3300 cm$^{-1}$ (doublet) of parent base was replaced by a strong broad band at 3200 cm$^{-1}$ (Figure not shown). It shows that both the symmetric and anti-symmetric stretching modes of $\text{-NH}_2$ group have merged into one in the complex and may be involved in the hydrogen bonding. The large deviation of $\nu_{\text{CNstr}}$ and $\nu_{\text{COstr}}$ of HTP from the straight line in Figures 5.17 and 5.18 suggests the interaction of $\text{--OH}$ group with DDQ.

5.4. Charge-transfer interaction of AAB with tetracyanoethylene

For the formation of charge transfer complex on GC surface, we have used

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.19.png}
\caption{FT-IR spectra of (a) tetracyanoethylene (b) CT complex of tetracyanoethylene and $p$-phenylenediamine and (c) ATR FT-IR spectrum of CT complex of tetracyanoethylene-ANF-P-AAB on screen printed carbon surface.}
\end{figure}
tetracyanoethylene as an acceptor instead of DDQ because it is not a bulky molecule like DDQ. Further, the electron affinity of tetracyanoethylene (2.2 eV) is greater than that of DDQ (1.9 eV) [26]. Therefore, effective charge-transfer complex formation is expected when tetracyanoethylene is used as an acceptor. It is well known that the stretching frequencies of –C≡N group of tetracyanoethylene are highly sensitive when it form a CT complex [34]. Hence, FT-IR spectra was recorded in the in the region of 2000-2300 cm⁻¹. Figure 5.19a shows the FT-IR spectrum obtained for solid tetracyanoethylene. It shows the stretching frequencies

![Nyquist plots](image)

**Figure 5.18.** Nyquist plots of (a) bare GC (b) GC/AAB/AAnFeP and CT complex of tetracyanoethylene-AAnFeP-AAB/GC in 0.5 mM of K₃[Fe(CN)₆] containing 0.1 M KCl.
of \(-\text{C}≡\text{N}\) group centered at 2220 and 2254 cm\(^{-1}\). The stretching frequencies are shifted to lower energy side for the charge-transfer complex of tetracyanoethylene and \(p\)-phenylenediamine. Although the change in \(-\text{C}≡\text{N}\) stretching frequency is relatively weak for the tetracyanoethylene and AAnFcP-AAB complex, the appearance of its bands confirmed the formation of charge-transfer complex. Further, electrochemical impedance measurements were carried out to examine the conductivity of the charge transfer complexes. Figure 5.18 shows the Nyquist plots of bare GC, GC/AAB/AAnFcP and charge transfer complex of tetracyanoethylene and AAnFcP-AAB/GC electrodes. Although the charge transfer resistance, estimated from the diameter of the semicircle of the Nyquist plot, is slightly higher than that of bare GC electrode but less than the charge transfer resistance of GC/AAB/AAnFcP/tetracyanoethylene electrode. This result indicated that the formed charge-transfer complex improved the conductance of the molecular wire AAB/AAnFcP. However, the improved conductance is not significant. It is expected that if the phenyl rings of the molecular wire forms charge transfer complex with the acceptor (\(\pi-\pi\) type), it would increase the conductance as a result of charge depletion in the phenyl rings. In the preset study, the increase in conductance, as a result of charge transfer complex formation is not so significant as expected. This may be due to the fact that in addition to the phenyl rings, N-atoms and/or AAnFcP moieties may also involved in charge transfer complex formation with acceptor as shown in Scheme 5.6. Consequently, such a charge transfer complex formation might have resulted lowering the
conductance as expected. To understand the change in the conductance behavior clearly, as a result of charge transfer complex formation, the mechanism of charge transfer complex formation has to be investigated further in detail and which is out of the scope of the present work. Introduction of another acceptor or tuning the molecular wire by varying the substituents in AAnFcP may improve the conductance significantly.

5.5. Conclusion

In this chapter, an attempt was made to fabricate azobenzene based molecular wire containing bis-ferroceny1 porphyrin on glassy carbon surface. The molecular wire was successfully formed on GC surface by electrochemical method. The formed molecular wire was characterized by cyclic voltammetry, UV-visible diffuse reflectance and FT-IR spectroscopic techniques. Formation of
charge transfer complex on the GC surface covered with the molecular wire was attempted using tetracyanoethylene as an acceptor. To understand the concept of charge-transfer complex on the solid surface, the formation of charge transfer complex in solution using different aromatic thiols as donors and DDQ as an acceptor was also studied. Although the charge transfer complex was successfully formed on AAB-AAnFcP molecular wire, the increase in conductance of this molecular wire was not significant. Further studies are required to improve the conductance of the prepared molecular wire.
5.6. References


