Chapter 5

Self-Assembled Monolayers of Liquid Crystalline disulphides and Thiols on Gold Surface

Self-assembled monolayers (SAMs) are formed by the spontaneous adsorption of certain molecules on the surface resulting in the formation of a single layer of the molecules. SAMs of organic thiol molecules on the gold surface are of special interest due to their long-term stability and potential applications which have been described in chapter 1. The present chapter describes the formation and electrochemical characterisation of cyanobiphenyl attached disulphides and triphenylene functionalised thiols on gold surface, where the disulphides show nematic phase and the triphenylene thiols show columnar hexagonal phase in the bulk. The electron transfer barrier properties, double layer capacitance and the ionic permeability of these monolayer modified surfaces are discussed in this chapter.
5.1 Introduction

Molecular self-assembly on surfaces refers to the spontaneous adsorption of molecules on a solid surface [1; 2]. In general, adsorption processes involve either chemical or physical forces. An example of physical adsorption of long chain molecules is the formation of Langmuir monolayers, while the chemisorption is involved in the formation of self-assembled monolayers (SAMs) leading to a single layer of the molecules on the surfaces [2]. Due to the high stability of the thiol monolayers on the metal surface, they find a variety of applications in the field of biosensors, molecular electronics, nanolithography, corrosion inhibition etc. A general discussion on the properties and applications of SAMs has already been presented in the chapter 1.

Many interesting aspects of the monolayers can be revealed by the electrochemical characterisation of the monolayer modified electrodes. Due to the insulating hydrocarbon chain or similar organic groups of the monolayers, the electrode surface is not easily accessible by the electrolytes. This results in a blocking of electron transfer process between the electrode and the redox probes in the solution. For an ideally perfect monolayer, the redox reaction will be fully blocked even though due to the presence of pinholes and defects, there may be a small but significant Faradaic current. Due to this, the electrode exhibits a microelectrode array behaviour [1].

Monolayers with specific thiol molecules can be used for the selective permeability of certain molecules. On the other hand, terminally functionalised monolayers are used for the preconcentration of certain analyte molecules on the electrode surface, so that the detection limit of the analyte can be improved. Monolayers with terminal functional groups can be further functionalised with a variety of enzymes that have been widely used for the biosensor applications [3]. The adhesion of the molecules on the electrode can be improved by the modification of the surface with SAMs. For example, it has been shown that the adhesion of polyaniline on 4-aminothiophenol SAM is better compared to the adhesion on bare gold electrode [4].

In the present chapter we describe the following aspects of monolayers, viz the electron transfer barrier properties of the monolayers, the capacitance, permeability and disorganisation of the monolayers.
5.1.1 Double Layer Structure

The double layer structure of the electrode|electrolyte interface is the basis of all the electrochemical properties of the electrode surface. For a typical metal electrode in solution, the double layer consists of the Helmholtz layer and the diffuse layer. Under normal experimental conditions and low concentrations of the electrolyte, the Helmholtz layer dominates the interfacial capacitance values generally about 10 $\mu F/cm^2$ for a clean metal surface. When an insulating layer like SAMs of long chain alkanethiols is formed on the electrode surface, it constitutes the dielectric layer between the electrode surface and the electrolyte. The monolayer formed at the electrode|electrolyte interface is hydrophobic. Therefore, water molecules and ions near the interface do not permeate the dielectric film. The dielectric film formed by SAM increases the thickness of the interface and due to this, the interfacial capacitance decreases drastically. Moreover, it has been observed that the normal metal-electrolyte interfacial capacitance values are dependent on the electrode potential due to the presence of excess ions on the interface, while the capacitance values of monolayer modified electrodes are weakly dependent on the electrode potential [1].

Since the organic layer has a low dielectric constant and finite thickness, the double layer capacitance reduces significantly for the monolayer modified electrode according to the equation

$$C = \frac{\varepsilon_0 \varepsilon_m}{d} A$$

where $\varepsilon_0$ and $\varepsilon_m$ are the dielectric constant for the vacuum and the monolayer molecule respectively, $d$ is the thickness of the monolayer and $A$ is the area of the electrode. The capacitance value varies inversely with the alkyl chain length for a compact impermeable electrode. For short chain alkanethiol monolayers, the capacitance values are always greater than the expected value due to the higher permeability of the solution species through the monolayer. On the contrary, for the monolayers where the terminal groups are highly hydrophobic and are totally impermeable to ions and solvated molecules, there is a significant decrease in the capacitance due to the presence of hydrophobic gap between the monolayer modified surface and the hydrophilic electrolytic medium [5; 6].
5.1.2 Ionic Permeability

For a compact monolayer formed by normal alkanethiol monolayers, the molecules in the electrolytes are not capable of direct contact with the electrode. Under such conditions, as mentioned before, the double layer structure of the electrode|electrolyte interface changes and as a result, the double layer capacitance decreases. On the other hand, for monolayers modified with short chain thiols, where the organisation of the molecules are not perfect, the ions can reach the electrode surface through the pinholes and defects in the monolayer. The smaller the ions, the better they can permeate through the monolayer. As a result of this, the coverage of the monolayers calculated using the electrochemical methods will depend upon the size of the ions used.

5.1.3 Gold Oxide Stripping Analysis

The presence of pinholes and defects in the monolayer may be identified by the gold oxide stripping analysis. Here the gold electrode is cycled in perchloric acid solution. As shown in Figure 5.1, a gradual increase in the current during the positive potential scan is followed by a sharp rise at +1.2 V vs. SCE due to the formation of gold oxides on the surface. On the reverse potential sweep, these gold oxides on the metal surface are reduced to gold, which gives rise to the so-called stripping peak. For a pure gold surface, the integrated charge under this peak is measured to be 410 $\mu$C/cm$^2$ [7]. On the other hand, after the monolayer formation, the exposed area of the the electrode towards the electrolyte decreases and hence the corresponding reverse peak. In this case, the gold oxide formation is due to the access of small OH$^-$ ions through the pin holes, voids and defects. From the charge under this peak for the bare gold surface and for the monolayer modified electrode, the coverage of the monolayer on the metal surface can be calculated using the formula [7]:

$$\theta = 1 - \frac{Q_{SAM}}{Q_{Au}}$$

Where $Q_{SAM}$ and $Q_{Au}$ are the integrated area under the reverse peak for the SAM modified electrode and for the bare gold electrode respectively and $\theta$ is the surface coverage. $Q_{SAM}$ corresponds to the charge value due to exposed gold to the electrolyte with the remaining region covered with the monolayer.
Figure 5.1: Cyclic voltammogram of bare gold electrode in 0.1 M HClO₄ showing the formation of gold oxide during the forwards sweep and the stripping of the gold oxide during the reverse sweep

5.1.4 Electron Transfer Barrier Properties

The SAMs introduce a compact insulating film between the metal electrode and the electrolyte. This prohibits the direct approach of the redox probes in the solution to the metal electrode, which means that the electron transfer between the electrode and the solution is totally inhibited in the presence of a perfect monolayer. As mentioned before, cyclic voltammetry and electrochemical impedance spectroscopy can be used to study the electron transfer blocking behaviour of these modified films. On a bare electrode, cyclic voltammogram shows a reversible redox reactions with a peak separation of 59/n mV in an n-electron redox process, as shown in Figure 5.2. On the other hand, on a modified electrode, the CV shows an irreversible behaviour with no peak formation, as shown in Figure 5.3.

Figure 5.4 shows the EIS data for a bare gold electrode and a monolayer modified elec-
Figure 5.2: Cyclic voltammogram of 10 mM ferrocyanide/ferricyanide reaction on a bare gold electrode. It can be seen that the bare gold electrode shows very small semicircle which indicates a facile electron transfer process between the electrode and the redox probe. On the other hand, the monolayer modified electrode as shown in Figure 5.5, shows a very large semicircle indicating that the electron transfer process on the modified electrode is inhibited due to the compact film formed on the surface. On the monolayer modified electrode, the hydrophobic-hydrophobic interactions between the alkyl chains of the thiol molecules lead to a compact impermeable monolayer film. This results in a very high charge-transfer resistance for the normally reversible redox system in the EIS studies. Therefore higher the charge-transfer resistance for the redox reaction, better will be the electron transfer barrier property of the film. This aspect will be discussed later in this chapter.

5.1.5 Disorganisation of Monolayers

The typical long chain alkanethiol monolayers show very high electron transfer barrier properties towards different redox probes under normal conditions. On the other hand, potential
cycling in organic media disrupts the compact structure of these monolayers and results in the disorganisation of the monolayers forming voids. The driving force for the disorganisation is the van der Waals interaction between the alkyl or other hydrophobic chains with the hydrophobic part of the solvent or the redox probes. The disorganised monolayers facilitate the electron transfer between the metal electrode and the redox probe in the solution through the voids. A schematic representation of the disorganisation of the monolayers is shown in Figure 5.6. A disorganised monolayer also facilitates high permeability of ions through the monolayer, that results in the higher capacitance at the interface and lower charge-transfer resistance.

The present chapter deals with our experimental results on the characterisation of different monolayers on the gold surface. We have extensively used the electrochemical techniques like cyclic voltammetry and electrochemical impedance spectroscopy for the characterisation of the monolayer modified surfaces. Using these techniques, we have analysed the electron transfer barrier properties and also measured the double layer capacitance of the monolayer.
5.2 Experimental Section

Gold electrode: A gold sample of 99.99% purity was obtained from Arora Mathey, India. Evaporated gold (about 100 nm thickness) on glass with chromium under layers (~2-5 nm thickness) was used for the monolayer formation and later used for characterisation by electrochemical techniques and grazing angle FTIR spectroscopy. The evaporated gold substrate has been shown to have a very smooth surface with predominantly Au (111) orientation. These gold samples were used as strips of area about 0.25 cm² for the SAM formation. These strips were cleaned with piranha solution for 30 seconds (Caution: Piranha solution is 1:3 v/v mixture of 30% H₂O₂: 96% con. H₂SO₄, which is highly reactive with organic compounds and storing in a closed container and exposure to direct contact should be avoided), washed with distilled water and finally rinsed with millipore water and dried before the formation of SAMs.

Figure 5.6: A schematic representation of a) compact and b) disorganised monolayer modified electrodes. This chapter is divided into 2 sections. The section 5.3 deals with the electrochemical and surface characterisation of SAMs of rod-like disulphides and section 5.4 on the monolayers of discotic triphenylene functionalised thiols that show columnar hexagonal liquid crystalline phase in the bulk.
**SAM preparation:** The thiols were dissolved in dichloromethane to form a 1 mM solution. The gold electrodes after the piranha treatment were immersed in the solution and kept for 12 hours for the SAM formation. The electrodes were then washed with dichloromethane to remove any physically adsorbed thiols on the surface. These electrodes were then cleaned with distilled water and finally rinsed with Millipore water and used for further characterisations.

**Electrochemical characterisation:** The cyclic voltammetric studies of the SAM modified electrodes were carried out using three different redox systems, namely 1 mM ferrocene, 10 mM ferrocyanide|ferricyanide and 1 mM hexaammineruthenium (II|III). Ferrocene, a hydrophobic redox probe was studied in a non-aqueous solvent, propylene carbonate with 0.1 M LiClO₄ acting as a supporting electrolyte in this medium. The other two redox probes were studied in aqueous solution. For potassium ferrocyanide|ferricyanide system, 1 M sodium fluoride (NaF) and for the hexaammineruthenium (II|III) system 0.1 M LiClO₄ were used as the supporting electrolytes. The cyclic voltammograms for the bare gold electrode were carried out in all these three redox systems for comparison at a scan rate of 50 mV/s. The electrochemical impedance studies were carried out at the half-peak potential of the redox system with an ac amplitude of 10 mV in a frequency range of 100 mHz to 100 kHz.

**Instrumentation:** Cyclic voltammetric studies were carried out using a potentiostat (EG&G model 263A) interfaced with a PC through GPIB (National Instruments). A conventional three electrode system was used for all the electrochemical characterisation, with a saturated calomel electrode (SCE) as the reference electrode and platinum foil as the auxiliary electrode. Either bare gold or the SAM modified electrodes were used as the working electrode. The electrochemical impedance spectroscopic studies (EIS) were performed using a Lock-in-Amplifier (Perkin Elmer Model 5210) along with the potentiostat interfaced to a PC. The EIS studies were carried out using Power Suite software (EG&G) and the equivalent circuit fitting by ZSimpWin software (EG&G). The FTIR spectrum of the monolayer-modified gold surface was carried out using Shimadzu FTIR model 8400 instruments at a grazing angle of 85° (FT-85, Thermo Spectra-Tech). The bare gold surface was used as a reference for the spectral studies.
5.3 Monolayers of Rod-like disulphides

Liquid crystalline materials have the orientational order of crystalline phase and the dynamic nature of liquid phase in the bulk under a definite temperature range. These mesogenic molecules, depending upon their orientation, may form different liquid crystalline phases like nematic, smectic and columnar phases that changes with temperature [8]. Self-assembled monolayers formed by these liquid crystalline materials are of great interest from the point of view of the orientation of the molecules on the surface [9]. There are several reports on the SAM formation of rod-like liquid crystalline materials on gold surface, especially of cyanobiphenyl thiols. Alloisio et al. have reported the 2-dimensional SAM formation on flat gold surface and 3-dimensional SAM formation on gold nanoparticles by diacetylenes functionalised disulphide [10]. They have shown that the nanoparticles stabilised by these disulphides are of two different sizes consisting of ~4.5 nm and ~21 nm in diameter. SAM formation by triphenylene substituted disulphides were studied in the literature using FTIR, quartz crystal microbalance (QCM) as well as AFM, where the studies show that the discotic cores lie in an edge-on configuration with respect to the gold surface [11]. The SAM formation of alkoxycyanobiphenyl thiols that show nematic phase in the bulk and its electrochemical characterisation have also been reported [12; 13].

In the present section, we describe the SAM formation by rod-like disulphides of alkoxycyanobiphenyl molecules that show a nematic phase in the bulk. The monolayers are characterised by electrochemical techniques like cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

5.3.1 Experimental Section

The cyanobiphenyl based disulphide molecules were synthesised as reported earlier by S. Kumar et al. [14], where DS\textsubscript{n} represents 4'-\{(n-(4'-Cyano[1,1'-biphenyl]-4yl)oxy)hexyl\}-disulphanylhexyl\}oxy\}[1,1'-biphenyl]-4-carbonitrile, with n being the alkyl chain length. A schematic diagram showing the synthesis of these molecules is shown in Figure 5.7. The molecules with lower alkyl chains show a nematic liquid crystalline phase, while higher homologous compounds show a smectic A phase at higher temperature near 100 °C. The electrochemical studies like cyclic voltammetry (CV) and electrochemical
Figure 5.7: The scheme for the synthesis of the cyanobiphenyl based disulphide molecules

Impedance spectroscopy (EIS) were carried out using two different redox systems, viz. ferrocyanide/ferricyanide and hexaammineruthenium(II/III) chloride systems. The EIS studies were performed at the half-peak potential of the corresponding redox system calculated from the CV studies.

5.3.2 Results and Discussion

5.3.2.1 Cyclic Voltammetry

Figure 5.8 shows the cyclic voltammograms of the monolayer modified electrodes in 10 mM ferrocyanide/ferricyanide system. The figure shows the CV for the bare gold electrode along with DS8, DS9, DS10 and DS12 modified electrodes. It is clear from the figure that the modified electrodes show a better blocking behaviour compared to the bare gold electrode. The electron transfer barrier property of the lower chain thiols is less and the blocking ability increases with increase in chain length. For the DS12 monolayer, the electron transfer process is almost fully blocked. It may be noted that the blocking behaviour of DS8 and DS9 modified electrodes are quite less as compared to the normal alkanethiol monolayer with similar chain lengths. The bulky cyanobiphenyl groups at the terminal positions of the monolayers prevents compact ordering of the monolayer on the surface, which results in a lower blocking ability.
Figure 5.8: Cyclic voltammograms in ferrocyanide/ferricyanide using a) bare gold electrode and b) DS8, c) DS9, d) DS10 and e) DS12 modified electrodes

Figure 5.9: Cyclic voltammograms in hexaammineruthenium(II/III) using a) bare gold electrode and b) DS8, c) DS9, d) DS10 and e) DS12 modified electrodes
Figure 5.9 shows the cyclic voltammograms of the bare gold electrode and the different disulphide modified electrodes in 1 mM hexaammineruthenium (II/III) chloride solution. It is observed that the bare electrode as well as the modified electrodes show a facile redox reaction in this medium. It has been proposed earlier that hexaammineruthenium(II/III) undergoes an outer sphere electron transfer reaction and the reaction rate is less dependent on the solvent environment for the electron transfer to occur [15]. As a result, direct contact between the redox site and the electrode is not essential for the redox reaction to occur which means that the monolayer offers no hindrance to the redox reaction. A similar behaviour was observed previously on other monolayer modified electrodes [16].

5.3.2.2 Electrochemical Impedance Spectroscopy

![Image of electrochemical impedance spectroscopy plots](image)

Figure 5.10: Real vs. imaginary plots from electrochemical impedance spectroscopy in ferrocyanide/ferricyanide system using a) bare gold electrode and b) DS8, c) DS9, d) DS10, and e) DS12 modified electrodes modified electrodes

We have carried out the electrochemical impedance studies in ferrocyanide/ferricyanide and hexaammineruthenium(II/III) redox systems using bare gold electrode as well as the dif-
Table 5.1: Values of the solution resistance ($R_u$), double layer capacitance ($C_{dl}$), charge-transfer resistance ($R_{ct}$), and Warburg impedance ($Z_w$) for the bare and DS SAM modified electrodes using ferrocyanide/ferricyanide reaction. *: $R(CR)$ circuit was used for the fitting.

<table>
<thead>
<tr>
<th></th>
<th>$R_u$ (Ω)</th>
<th>$C_{dl}$ (F/cm²)</th>
<th>$R_{ct}$ (Ω.cm²)</th>
<th>$Z_w$ (S.s¹/².cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAu</td>
<td>67.05</td>
<td>2.31×10⁻⁶</td>
<td>5.65</td>
<td>9.24×10⁻³</td>
</tr>
<tr>
<td>HDT</td>
<td>952.1</td>
<td>3.53×10⁻⁸</td>
<td>5.01×10⁵</td>
<td>1.75×10⁻⁶</td>
</tr>
<tr>
<td>DS8</td>
<td>12.81</td>
<td>2.44×10⁻⁶</td>
<td>75.72</td>
<td>0.0233</td>
</tr>
<tr>
<td>DS9</td>
<td>14.32</td>
<td>1.78×10⁻⁶</td>
<td>71.72</td>
<td>9.68×10⁻³</td>
</tr>
<tr>
<td>DS10</td>
<td>14.33</td>
<td>1.97×10⁻⁶</td>
<td>503.8</td>
<td>2.25×10⁻³</td>
</tr>
<tr>
<td>DS12*</td>
<td>2.73</td>
<td>1.86×10⁻⁶</td>
<td>1.03×10⁴</td>
<td>-</td>
</tr>
</tbody>
</table>

ferent disulphide monolayer modified electrodes. Figure 5.10 shows the real vs. imaginary components of the impedance for the electrodes in ferrocyanide/ferricyanide redox system. The bare gold shows a very small semi-circle while the diameter of the semicircle increases with increasing chain length of the disulphide monolayer except in the case of DS9, where it is similar to that of DS8. The diameter of the semicircle corresponds to the charge-transfer resistance of the redox reaction. The impedance data were fitted using Randles equivalent circuit and the fitting parameters are presented in Table 5.1. From the table, it is observed that the $R_{ct}$ values increase correspondingly and the redox reaction gets slower with the increase in chain length. This observation is in accordance with the CV results.

Figure 5.11 shows the impedance spectroscopic results for the bare gold and different DS modified electrodes in hexaammineruthenium(II/III) system and the fitting parameters using Randles equivalent circuit is presented in Table 5.2. Here the $R_{ct}$ values are very less for all the modified electrodes, which is contrary to the results with the ferrocyanide/ferricyanide system. As discussed earlier, this is due to the outer sphere electron transfer reaction of the hexaammineruthenium system. The electron tunneling from the electrode surface to the redox site through the monolayer can also contribute to the low barrier properties [15]. Even though the $R_{ct}$ values in general are less, they increase with the chain length of the molecules. As the chain length increases, the barrier to electron transfer also increases due to the better
packing of the monolayers which acts as an insulating layer between the electrode and the electrolyte.

We have observed that the barrier to electron transfer for the disulphide SAMs are less compared to alkanethiol SAMs of similar chain length. This shows that the packing of the monolayers are poor with the presence of a large number of pinholes and defects. These defects mainly arise due to the presence of bulky cyanobiphenyl terminal groups that are attached to the thiol molecules. The modified electrodes show very low impedance towards the redox reaction of hexaammineruthenium reaction irrespective of the chain length. This can be attributed to the fact that hexaammineruthenium undergoes an outer sphere reaction mechanism and the reaction may take place by through-bond tunneling of electrons between the electrode and the redox probes.
Table 5.2: Values of the solution resistance ($R_s$), double layer capacitance ($C_{dl}$), charge-transfer resistance ($R_{ct}$), and Warburg impedance ($Z_W$) for the bare and DS SAM modified electrodes using hexaammineruthenium(II/III) reaction

<table>
<thead>
<tr>
<th></th>
<th>$R_s$ (Ω)</th>
<th>$C_{dl}$ (F/cm²)</th>
<th>$R_{ct}$ (Ω.cm²)</th>
<th>$Z_W$ (S.s$^{1/2}$.cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAu</td>
<td>69.64</td>
<td>1.59x10$^{-6}$</td>
<td>4.586</td>
<td>5.19x10$^{-3}$</td>
</tr>
<tr>
<td>HDT</td>
<td>3.47x10$^4$</td>
<td>3.55x10$^{-8}$</td>
<td>5.14x10$^5$</td>
<td>1.64x10$^{-6}$</td>
</tr>
<tr>
<td>DS8</td>
<td>76.13</td>
<td>5.4x10$^{-7}$</td>
<td>4.21</td>
<td>1.94x10$^{-3}$</td>
</tr>
<tr>
<td>DS9</td>
<td>102.9</td>
<td>1.49x10$^{-6}$</td>
<td>21</td>
<td>1.21x10$^{-3}$</td>
</tr>
<tr>
<td>DS10</td>
<td>93.72</td>
<td>1.99x10$^{-6}$</td>
<td>29.06</td>
<td>1.89x10$^{-3}$</td>
</tr>
<tr>
<td>DS12</td>
<td>126.5</td>
<td>1.61x10$^{-6}$</td>
<td>372.1</td>
<td>2x10$^{-3}$</td>
</tr>
</tbody>
</table>

5.3.2.3 Capacitance Measurements

The double layer capacitance values of the bare gold electrode as well as the SAM modified electrodes were measured by the electrochemical impedance spectroscopy in 1 M NaF solution. The capacitance was calculated from the imaginary part of the impedance using the equation [17]

$$C_{dl} = \frac{1}{\omega Z''}$$

Where $C_{dl}$ is the double layer capacitance, $\omega$ the angular frequency ($=2\pi f$, $f$ being the frequency) and $Z''$ is the imaginary part of the impedance. Table 5.3 represents the double layer capacitance values measured for the different disulphide SAM modified electrodes. The values indicate that the capacitance has decreased to a large extent for the modified electrodes compared to the bare gold electrode but not in proportion to the chain length of the molecules. It may be noted that the capacitance values of the modified electrodes are more or less of the same range for different chain lengths. This indicates that the double layer structure of all the monolayer modified electrodes is similar. Normally the double layer capacitance values of alkanethiol SAMs are <1 µF/cm² while for the disulphide SAMs presented here, the capacitance values are several µF/cm² [6]. This is due to the higher permeability of the ions through the monolayer, which originates from the less compact structure of the molecules on the surface.
Table 5.3: Double layer capacitance values for the bare gold surface and the disulphide monolayer modified surfaces in 1 M NaF calculated from electrochemical impedance spectroscopy

<table>
<thead>
<tr>
<th>System</th>
<th>Capacitance (F/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAu</td>
<td>6.4 × 10⁻⁶</td>
</tr>
<tr>
<td>DS8</td>
<td>1.34 × 10⁻⁶</td>
</tr>
<tr>
<td>DS9</td>
<td>2.56 × 10⁻⁶</td>
</tr>
<tr>
<td>DS10</td>
<td>1.98 × 10⁻⁶</td>
</tr>
<tr>
<td>DS12</td>
<td>2.44 × 10⁻⁶</td>
</tr>
</tbody>
</table>

In summary, we have presented the electrochemical characterisation of the cyanobiphenyl functionalised disulphide SAMs on gold surface. The SAM modified electrodes with lower chain length of the monolayer show lower barrier for electron transfer, which however increases with increase in chain length. In general, the barrier to electron transfer process is less compared to the alkanethiol monolayers, since the monolayers of disulphides are less compact owing to the bulky cyanobiphenyl groups at the terminal position. The double layer capacitance values of these monolayers are quite high due to the less compact monolayer and the presence of polar cyano groups.

5.4 Monolayers of Triphenylenethiols

As mentioned in the previous section, there are several reports on the SAM formation by rod-like molecules on the metal surfaces. On the other hand, there are very few reports on the monolayer studies using discotic liquid crystalline compounds. Allinson et al. have studied the SAMs formed by different triphenylene based thiols on the gold surface using ellipsometry and STM studies, where they have shown that depending on the number and position of the thiols, the monolayer can have either vertical or horizontal arrangement [18; 19]. They have also shown that the SAMs based on these discotic molecules are less hydrophobic compared to the alkanethiol SAMs [18; 19]. Owens et al. have described the STM imaging of triphenylene based thiol monolayers on gold surface, where they have reported that the
2-dimensional ordering of these discotic molecules were improved after dipping the mono-
layer in a saturated solution of TNF, due to the charge-transfer complex formation between 
the triphenylene and trinitrofluorenone (TNF) molecules [20]. Charra et al. have shown that 
the chiral ordering of SAMs of discotic molecules on the surface can be tuned by chang-
ing the chain length of alkoxy groups [21]. Yamada et al. showed the one-dimensional 
and hexagonal arrangement of discotic modified gold nanoparticles induced by changing 
the solvent polarity [22]. The orientation of such discotic molecules as monolayer on the 
metal surface has also been studied, where it has been shown that the triphenylene based 
monolayers may form either a face-on or an edge-on structure on the surface [11]. In the 
face-on configuration, the triphenylene cores are parallel to the electrode surface whereas in 
the edge-on configuration the cores are perpendicular to the electrode surface. Recently it 
was shown that triphenylene functionalised thiols can be used for the stabilisation of gold 
nanoparticles [23].

From the literature, we have observed that there are only some scattered reports on the 
electrochemical studies on the SAMs formed by discotic molecules even though a few re-
ports are present on the self-organisation of such molecules on surfaces like HOPG or gold as 
described before. It is of great interest to study the electron transfer processes on the discotic 
molecules since they have very high one-dimensional conductivities and orientational order 
in the bulk. In this present work, we have carried out the electrochemical and FTIR char-
acterisations of three different discotic triphenylene based thiols, having chain length of 6, 
10 and 12 carbon atoms. These thiol modified SAMs were characterised by electrochemical 
methods like cyclic voltammetry, electrochemical impedance spectroscopy and capacitance 
measurements. The \( C_6 \)TP thiol SAM shows very good blocking behaviour towards the redox 
reaction of ferrocyanide|ferricyanide system, while thiols with higher chain length (contain-
ing 10 and 12) show lower barrier properties. Using hexaammineruthenium(II/III) as a redox 
probe, all the modified electrodes show a very little blocking behaviour. In an organic sol-
vent, we observe that due to disorganisation of the monolayers the electron transfer process 
is not inhibited significantly.
3.1 Experimental Section

Three triphenylene thiols having chain length of 6, 10 and 12 used in this study were provided by Prof. S. Kumar et al. and were synthesised by following the procedure as reported earlier [24; 23]. A schematic diagram of the synthesis of these molecules is shown in Figure 5.12. Dichloromethane (Rankem), potassium ferrocyanide (Loba), potassium ferricyanide (Qualigens), Sodium fluoride (S D fine-chem. limited), hexaammineruthenium (III) chloride (Alfa Aesar), ferrocene (Acros Organics), lithium perchlorate (Across organics) and ferrocenium tetrafluoroborate (Aldrich) were of analytical grade and used as received without further purification. Millipore water having a resistivity of 18 MΩ.cm was used for the preparation of all the aqueous solutions.

The monolayers were characterised using electrochemical techniques like cyclic voltammetry and electrochemical impedance spectroscopy and the experimental setup has been already described in the previous section. FTIR studies were carried out using Shimadzu FTIR model 8400 instruments at a grazing angle of 85° (FT-85, Thermo Spectra-Tech).

Figure 5.12: The scheme for the synthesis of the triphenylene-based thiol molecules
5.4.2 Results and Discussion

5.4.2.1 Cyclic Voltammetry

Figure 5.13: Cyclic voltammograms in 10 mM ferrocyanide/ferricyanide/1 M NaF/H₂O for a) bare electrode b) C₆TP, c) C₁₀TP and d) C₁₂TP modified electrodes

Figure 5.13(b-d) shows the cyclic voltammograms for the SAM-modified electrodes in 10 mM ferrocyanide/ferricyanide system containing 1 M NaF as the supporting electrolyte. The CV using the bare gold electrode is shown in Figure 5.13(a) for comparison. It can be seen from the figure 5.13(b) that the C₆TP has a better blocking property towards the ferrocyanide/ferricyanide system, while for C₁₀TP (Figure 5.13(c)) it is less and the C₁₂TP modified electrode (Figure 5.13(d)) behaves very similar to the bare gold electrode. This is contrary to the behaviour of typical alkanethiol SAM modified electrodes, where longer chain alkanethiol SAMs show better blocking behaviour to redox probes than shorter chain thiols. In alkanethiol monolayers, as the chain length increases, the packing will be more compact due to the hydrophobic-hydrophobic interaction among the hydrocarbon chains of the monolayers. In the present case, due to the π-π interaction of the discotic core, the
molecules can cluster together in different regions of the surface, which creates large number of voids within the monolayer surface as shown in Figure 5.14. This is more pronounced as the chain length of the thiol molecules increases due to higher flexibility of the alkyl chain of the thiol molecules. This allows the redox molecules to enter through the voids and undergo electron transfer reaction. A more quantitative study on these electron barrier properties based on the electrochemical impedance spectroscopy will be presented later in this chapter.

Figure 5.14: A schematic model of packing of the triphenylethiols on the gold surface

The cyclic voltammetric studies of the monolayer modified electrodes in 1 mM hexaammineruthenium (II/III) system were carried out and the plots are shown in Figure 5.15(b-d). The cyclic voltammogram on the bare electrode is also shown for comparison as Figure 5.15(a). As can be observed from the plots, even though \( C_6 \)TP and \( C_{10} \)TP modified electrodes show a good blocking behaviour towards the ferrocyanide/ferricyanide system (Figure 5.13(b-c)), all the three SAM modified electrodes show facile electron transfer towards the redox reaction of hexaammineruthenium (II/III) system (Figure 5.15(b-d)). A similar behaviour involving naphthalenethiol and alkanethiols was reported earlier [15; 16]. A further insight into this behaviour is provided in the following sections, where we discuss the results.
Figure 5.15: Cyclic voltammograms in 1 mM hexaammineruthenium(II/III)/0.1 M LiClO₄/H₂O for a) bare electrode b) C₆TP, c) C₁₀TP and d) C₁₂TP modified electrodes.

In order to study the effect of non-aqueous solvent on the blocking properties of the C₆TP SAM modified electrodes, the cyclic voltammetry in ferrocene system, a well-known redox probe in propylene carbonate medium was carried out. Figure 5.16 shows the cyclic voltammograms of bare gold and SAM modified electrodes when 1 mM ferrocene was used as the redox probe in propylene carbonate medium using 0.1 M LiClO₄ as the supporting electrolyte. As can be seen from the figure, all the three SAM modified electrodes show a facile redox reaction towards ferrocene. This can be attributed to the disorganisation of SAMs in the propylene carbonate medium. The disorganisation of the SAMs has been confirmed by cycling the same electrode modified with C₆TP in 10 mM ferrocyanide/ferricyanide system, where the blocking ability is only partial, contrary to a freshly prepared monolayer surface, which has an excellent blocking ability. The electrode was annealed at 60 °C for 1 hour and the cyclic voltammetry was repeated in the 10 mM ferrocyanide/ferricyanide system for the
Figure 5.16: Cyclic voltammograms in 10 mM ferrocene/1 M LiClO$_4$/propylene carbonate for a) bare electrode b) C$_6$TP, c) C$_{10}$TP and d) C$_{12}$TP modified electrodes

same electrode. The better blocking property shown by this annealed electrode confirms the existence of the monolayer, which rules out any possibility of desorption of the monolayer from the gold surface. The annealing process removes the trapped solvent molecules and organises the monolayer by making it more compact. This results in a better blocking ability. Quantitative studies on the barrier properties of the modified electrodes have been carried out by electrochemical impedance spectroscopy which is discussed below.

5.4.2.2 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopic studies can be used to get a detailed information about the processes occurring at the interface like the double layer capacitance charging, kinetics of the redox reaction, diffusion of the ions towards the electrode surface etc. Such studies are of great interest for the monolayer modified electrodes. In the presence of the redox species, from the impedance studies, the kinetics of the redox reactions and therefore the barrier to electron transfer process can be calculated. In the present study, we have carried
Figure 5.17: impedance plots in 10 mM ferrocyanide/ferricyanide/1 M NaF/H₂O for a) bare electrode b) C₆TP, c) C₁₀TP and d) C₁₂TP modified electrodes

Table 5.4: Values of the solution resistance (Rₛ, Ω), double layer capacitance (Cₗ, F/cm²), charge-transfer resistance (Rₑt, Ω.cm²), and Warburg impedance (Zₘ, S.s¹/₂.cm²) for the bare and SAM modified electrodes using ferrocyanide/ferricyanide reaction

<table>
<thead>
<tr>
<th></th>
<th>Rₛ</th>
<th>Cₗ</th>
<th>Rₑt</th>
<th>Zₘ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Ω)</td>
<td>(F/cm²)</td>
<td>(Ω.cm²)</td>
<td>(S.s¹/₂.cm²)</td>
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<td>BAu</td>
<td>13.59</td>
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<td>C₆TP</td>
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<td>C₁₂TP</td>
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<td>0.047225</td>
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</table>
out the impedance spectroscopic studies for all the three modified electrodes and for the bare gold electrode in three different redox systems at a potential corresponding to their formal potential calculated from the cyclic voltammetric studies.

**Ferrocyanide/ferricyanide reaction:** The impedance plots of the three SAM modified electrodes in 10 mM ferrocyanide/ferricyanide/1 M NaF/H₂O system are shown in the Figure 5.17. The impedance plot for the bare gold electrode is also shown for comparison. We have observed from the plots that the C₆TP SAM modified electrode shows the highest blocking properties among the three modified electrodes. This is in accordance with the behaviour exhibited in the cyclic voltammetric studies. The plots were fitted with a modified Randles circuit containing the double layer capacitance, Cdl in parallel to a series combination of the charge transfer resistance Rct and the Warburg impedance (Zw). The solution resistance (Rs) was modeled in series to the above circuit. From the fitting of the plots we have calculated the charge-transfer resistance (Rct) values for the ferrocyanide/ferricyanide reaction and the results are presented in Table 5.4. From the table, it can be seen that C₆TP and C₁₀TP thiols have higher Rct values, which shows that the kinetics of the reaction is slower over these electrodes, a result in accordance with the cyclic voltammetric studies. For the C₁₂TP SAM, a very low Rct value was observed, which shows that the reaction is highly facile on this modified electrode. This is also supported by cyclic voltammetric studies of the same system as shown in Figure 5.13, where higher current similar to behaviour of the bare gold electrode is observed. As stated before (section 5.4.2.1), this can be attributed to the clustering of the discotic molecules on the gold surface for higher chain length thiols, leaving large number of voids on the surface, through which the redox molecules can access the surface.

**Hexaammineruthenium (II/III) system:** The Nyquist plots of the impedance studies in 1 mM hexaammineruthenium (II/III) system are shown in Figure 5.18 using the SAM modified electrodes as well as the bare gold electrode. The Rct values for the systems were calculated from the plots by fitting with the modified Randles circuit and are presented in Table 5.5. It can be seen from the table that the charge-transfer resistance values for these systems are very low, which means that the electron transfer process is not inhibited over the SAM modified electrode, a result in accordance with the cyclic voltammetric studies. The very low Rct values for the redox system also imply that the monolayer does not block hexaammineruthenium electron transfer reaction unlike ferrocyanide reaction. This behaviour
Figure 5.18: Impedance plots in 1 mM hexaammineruthenium(II/III)/0.1 M LiClO₄/H₂O for a) bare electrode b) C₆TP, c) C₁₀TP and d) C₁₂TP modified electrodes

Table 5.5: Values of the solution resistance ($R_s$, Ω), double layer capacitance ($C_{dl}$, F/cm²), charge-transfer resistance ($R_{ct}$, Ω.cm²), and Warburg impedance ($Z_W$, S.s¹/².cm²) for the bare and SAM modified electrodes using hexaammineruthenium (II/III) reaction

<table>
<thead>
<tr>
<th></th>
<th>$R_s$</th>
<th>$C_{dl}$</th>
<th>$R_{ct}$</th>
<th>$Z_W$</th>
</tr>
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<tr>
<td>BAu</td>
<td>98.04</td>
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<td>1.86×10⁻³</td>
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<td>C₆TP</td>
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<td>240.2</td>
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</tr>
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<td>C₁₂TP</td>
<td>80.75</td>
<td>2.94×10⁻⁶</td>
<td>2.49</td>
<td>2.53×10⁻³</td>
</tr>
</tbody>
</table>
is attributed to the outer-sphere electron-transfer mechanism followed by the ruthenium redox system as shown earlier [15]. In an electron transfer reaction following the outer-sphere mechanism, the redox species need not have to be in contact with the counter species, here the gold surface, and hence the monolayer has no significant effect on the electron transfer process.

**Ferrocene system:** Figure 5.19(a-d) show the Nyquist plots of the impedance spectra for 1 mM ferrocene system in propylene carbonate medium for the bare gold and the modified electrodes. The $R_{ct}$ values for the reaction obtained by equivalent circuit fitting are shown in Table 5.6. It can be seen that the charge-transfer resistance values for these systems are very less in accordance with the cyclic voltammetric studies where it has been shown that the reaction is highly facile towards the ferrocene system. The results of the impedance studies support the fact that the SAMs of the $C_n\pi$TP thiols disorganise in the propylene carbonate medium and therefore does not block the electron transfer process efficiently.

It is worth mentioning here that the molecules used for the monolayer studies contains a triphenylene group with attached alkoxy groups and thiol groups bound to the electrode surface. For the $C_{12}\pi$TP, where the alkyl chain length is more, it is difficult for the molecule to have a perfect vertical orientation because of the bulky triphenylene groups on the top. Moreover the trace amounts of solvent and electrolyte species trapped between the monolayer molecules will also lead to a poor blocking behaviour of the electrodes.

The disorganisation of SAMs is exhibited normally only in the non-aqueous solutions. Since ferrocene is insoluble in water, we have carried out cyclic voltammetry and impedance studies using ferrocenium tetrafluoroborate, which is water soluble in order to probe the monolayer in aqueous medium. Figure 5.20 shows the typical cyclic voltammogram and the impedance plot in this medium using $C_{12}\pi$TP modified electrode. It has been observed that the redox reaction of $Fc^+$ species is blocked on the SAM modified electrode in aqueous medium as compared to the ferrocene reaction in propylene carbonate medium. This clearly shows that the disorganisation of the SAMs is a direct consequence of the cycling in the organic solvent. The above results confirm that the $C_{12}\pi$TP SAM is better organised in aqueous medium than in the propylene carbonate.
Figure 5.19: Impedance in 10 mM ferrocene/1 M LiClO₄/propylene carbonate for a) bare electrode b) C₆TP, c) C₁₀TP and d) C₁₂TP modified electrodes

Table 5.6: Values of the solution resistance ($R_s$, $\Omega$), double layer capacitance ($C_{dl}$, F/cm²), charge-transfer resistance ($R_{ct}$, $\Omega$.cm²), and Warburg impedance ($Z_W$, S.s$^{1/2}$.cm²) for the bare and SAM modified electrodes using ferrocene reaction

<table>
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<tr>
<th></th>
<th>$R_s$ (\Omega)</th>
<th>$C_{dl}$ (F/cm²)</th>
<th>$R_{ct}$ (\Omega.cm²)</th>
<th>$Z_W$ (S.s$^{1/2}$.cm²)</th>
</tr>
</thead>
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<tr>
<td>BAu</td>
<td>411.5</td>
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<td>6.32</td>
<td>2.37×10$^{-3}$</td>
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<tr>
<td>C₆TP</td>
<td>419</td>
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<td>7.21</td>
<td>2.25×10$^{-3}$</td>
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<tr>
<td>C₁₀TP</td>
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<td>C₁₂TP</td>
<td>438.8</td>
<td>2.92×10$^{-6}$</td>
<td>21.34</td>
<td>1.78×10$^{-3}$</td>
</tr>
</tbody>
</table>
5.4.2.3 Capacitance Measurements

Table 5.7 shows the double layer capacitance values measured for the SAM modified electrodes using EIS. As expected, the capacitance for the bare gold is highest among these systems. The C₆TP and C₁₀TP SAM modified electrodes show a lower capacitance values, due to the formation of monolayer. In contrast, the C₁₂TP thiol SAM shows a higher capacitance than the other two thiols, but it is lower than the value for bare gold. The higher capacitance is due to the very poor organisation of the thiol over the gold surface. The ions and solvent molecules enter through the monolayer thereby effectively increasing the dielectric constant and reducing the monolayer thickness resulting in an increase in the interfacial capacitance.

These results are in agreement with the cyclic voltammetric studies in the presence of redox probes, where we have observed that SAMs formed by C₆TP and C₁₀TP thiols have better blocking properties compared to bare gold electrode and C₁₂TP SAM modified electrode. The lower capacitance for the C₆TP and C₁₀TP modified electrodes can be further explained due to the hydrophobic nature of the electrodes. In these cases, due to the better orientation of the molecules, the highly hydrophobic alkyl chains make the outer surface of the monolayer more hydrophobic and less permeable to ions. A more compact monolayer has a lower dielectric constant and therefore lower double layer capacitance. It has been reported that the
Table 5.7: Double layer capacitance values for the bare gold surface and the monolayer modified surfaces in 1 M NaF calculated from electrochemical impedance spectroscopy

<table>
<thead>
<tr>
<th>System</th>
<th>Capacitance (F/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAu</td>
<td>7.10 × 10⁻⁶</td>
</tr>
<tr>
<td>C₆TP</td>
<td>1.22 × 10⁻⁶</td>
</tr>
<tr>
<td>C₁₀TP</td>
<td>1.02 × 10⁻⁶</td>
</tr>
<tr>
<td>C₁₂TP</td>
<td>3.25 × 10⁻⁶</td>
</tr>
</tbody>
</table>

Triphenylene based thiol monolayers exhibit more hydrophilic surface compared to normal alkanethiol SAM modified surfaces and hence higher capacitance values [18; 19].

5.4.2.4 Gold Oxide Stripping Analysis

Gold oxide stripping analysis provides a qualitative picture about the coverage of the SAM over the gold surface. The modified electrode was cycled in 0.1 M HClO₄ solution in a potential window of 0.2 V to 1.4 V vs. SCE. During the forward sweep, the gold surface is oxidised and on the reverse scan, it is reduced to Au, as represented in Figure 5.21. The charge measured by integrating the reverse peak provides information about the amount of gold oxide reduced which is a measure of the surface area of the gold exposed to the electrolyte. Therefore from the ratio of the charge value with that of the bare gold surface, the coverage of the thiol on the gold surface can be estimated using the equation

\[ \theta = 1 - \frac{Q_{SAM}}{Q_{Au}} \]

Where \( Q_{SAM} \) and \( Q_{Au} \) are the integrated area under the reverse peak for the SAM modified electrode and for the bare gold electrode respectively and \( \theta \) is the surface coverage. \( Q_{SAM} \) corresponds to the charge value due to exposed gold to the electrolyte with the remaining region covered with the monolayer. It has been reported that the surface area for the bare gold surface corresponds to a charge of 410 μC/cm² [7].

For the C₆TP the surface coverage is measured to be 0.595 while for the C₁₀TP and C₁₂TP the values are 0.615 and 0.692 respectively. The surface coverage values obtained by
Figure 5.21: Cyclic voltammograms of a) bare gold electrode and b) C6TP modified electrode in 0.1 M HClO₄

this method are contrary to the cyclic voltammetric and impedance studies in the presence of redox probes like ferrocyanide/ferricyanide system. Moreover the coverage values calculated by this method varies significantly from that calculated from the impedance in the presence of redox probes. The coverage of the monolayer on the surface is given by

$$\theta = 1 - \frac{R_{ct}'}{R_{ct}}$$

where $R_{ct}'$ and $R_{ct}$ are being the charge transfer resistance on the bare gold and the SAM modified electrodes. For example, for the C₆TP modified surface, the impedance calculation gives coverage of 0.996 and for C₁₀TP and C₁₂TP the values are 0.995 and 0.655 respectively. The lesser coverage values obtained from the stripping analysis is due to the better permeability of the smaller ions, in this case OH⁻ ions, through the monolayer surface.
Figure 5.22: Grazing-angle FTIR spectroscopic profile for the C₆TP modified gold electrode

5.4.2.5 Grazing Angle Fourier Transform Infrared Spectroscopy

Figure 5.22 shows the GA-FTIR spectrum of the C₆TP SAM over the gold surface. Bare gold surface was used as a reference to get the spectra of the SAM modified sample. From the spectra, the peaks at 1625 and 1701 cm⁻¹ are attributed to the aromatic core of triphenylene. Peaks at 2891, 2914, and 2947 are due to the asymmetric stretching vibrations of CH₂ groups. Peaks at wave numbers of 3057, 3085 and 3114 cm⁻¹ are due to the symmetric stretching vibrations of the CH₂ groups. The absence of any S-H vibrations in the spectra shows that all the thiols are adsorbed by chemisorption forming Au-S bonding as expected for any thiol monolayer over the gold surface.

In summary, the monolayers of three triphenylene-based thiols with different chain lengths have been formed on the gold surface and are characterised by electrochemical and FTIR analysis. The lower chain thiols show better barrier properties for the electron transfer to the redox probes in the solution, which is contrary to the typical alkanethiol monolayers.
5.5 Conclusion

The self-assembled monolayers of cyanobiphenyl based thiols have been formed and were characterised using electrochemical techniques like cyclic voltammetry and electrochemical impedance spectroscopy. The studies show that the coverage of these monolayers on the evaporated gold surface is less when compared to that of alkanethiol SAMs of similar chain length. This is due to the poor packing of the bulky cyanobiphenyl groups that are present as the terminal groups. The electron transfer barrier properties of higher homologous series of these monolayers are better than the lower chain thiols. This is similar to the trend in the alkanethiol monolayers and arises due to the better organisation of the aliphatic chains on the surface after adsorption. The capacitance values of these monolayers are higher compared to the alkanethiol SAMs, which is due to the terminal polar cyano groups which allow ions to enter into the film and the poor organisation due to repulsion among negatively charged polar cyano groups.

The self-assembled monolayers of triphenylene substituted thiols on the gold surface and their electrochemical behaviour indicate that the electron transfer barrier properties of these thiols decrease with the chain length. This is contrary to the behaviour of typical alkanethiol monolayers. We attribute this to the cluster formation of the triphenylene core on several regions of the monolayer surface which creates large number of pinholes and defects. As the chain length increases, the interaction of the triphenylene cores on the surface also increases due to the flexibility of these molecules on the surface. This leads to the lowering of electron transfer barrier properties. The capacitance values of these modified electrodes are in general very high compared to the typical alkanethiol monolayers.
Bibliography


