Chapter 6

Summary and Future Works

In this chapter we summarise the significant results and conclusions derived from the work described in the previous chapters. We also present here the scope for future investigations based on the outcome of our studies. Broadly, the thesis works can be classified as follows:

1. Electrochemical studies of redox probes in the columnar hexagonal phase of Triton X-100/water system.

2. Studies on dispersion of thiol-protected gold nanoparticles in the columnar hexagonal phase (H1 phase) of Triton X-100/water system and the reverse columnar hexagonal phase (H2 phase) of AOT.

3. Ionic conductivity studies of the H1 phase of Triton X-100/water system and the effect of different dopants on the ionic conductivity in these systems.

4. The electrical conductivity studies of the discotic liquid crystalline materials and the effect of addition of ferrocenium and chloroaurate dopants into the discotic matrix.

5. Self-assembled monolayers formed by rod-like cyanobiphenyl substituted disulphides and discotic triphenylene tethered thiols on gold surface and their electrochemical characterisation.
1. Electrochemical studies of redox probes in the columnar hexagonal phase of Triton X-100/water system

We have studied the electron transfer processes of a variety of redox probes in the columnar hexagonal phase of Triton X-100/water system. The polarising optical microscopic (POM) and small angle X-ray scattering (SAXS) studies revealed that the H1 phase of the Triton X-100/water system is retained even after the addition of the redox probes and the supporting electrolytes. The cyclic voltammetric studies show that the half-peak potential of the redox probes have shifted significantly in the H1 phase compared to the solvent phase. The nature and extent of the potential shifts have been explained on the basis of the interaction between the redox probe and the surrounding H1 phase. For the hexaammineruthenium (II/III) redox system, we have observed a negligible shift in the half-peak potential, which has been attributed to the outer-sphere electron transfer process in this system. On the other hand, the diffusion coefficient values of all the redox probes were found to be lower in the H1 phase than in the solvent phase. The extent of decrease was observed to be dependent on the interaction of the redox probes with the liquid crystalline system.

2. Dispersion of thiol-protected gold nanoparticles in the H1 phase and H2 phase

Hexanethiol and 10-CB thiol protected gold nanoparticles were dispersed in the lyotropic columnar hexagonal phase (H1 phase) of Triton X-100/water system and in the reverse columnar hexagonal phase (H2 phase) of AOT system. POM and SAXS studies were utilised for the characterisation of the dispersions. POM studies showed that the addition of gold nanoparticles did not disturb the liquid crystalline structure of these two systems. The SAXS studies have confirmed that the dispersions retain the liquid crystalline characteristics. Infact it was observed that the addition of gold nanoparticles have actually improved the columnar order in these two liquid crystalline systems with additional peaks in the SAXS, corresponding to the different lattice planes. The lattice parameters derived from SAXS studies are not altered by the addition of the nanoparticles.

3. Ionic conductivity studies of the H1 phase of Triton X-100/water system

We have observed that the ionic conductivity of the H1 phase of Triton X-100/water system is very high eventhough it is constituted of a non-ionic surfactant. The unexpectedly high ionic conductivity in the phase has been explained on the basis of Grotthus mechanism, according to which the ionic conductivity originates from the proton transfer between different
protonated water clusters like Zundel cations and Eigen cations. On the surface of the micelles of the Triton X-100/water system, the water molecules are arranged very close to each other and hence the proton transfer between the clusters is facile resulting in a very high ionic conductivity. We have observed that the addition of urea, a well known chaotropic agent decreases the ionic conductivity in contrast to that of gold nanoparticles which enhance the ionic conductivity. These observations are in good agreement with the Grotthuss mechanism of conductivity.

4. Electrical conductivity studies on the discotic liquid crystalline composites

We have studied the effect of dopants on the phase behaviour and the electrical conductivity of discotic liquid crystalline materials. For these studies, we have used ferrocenium tetrafluoroborate and chloroauroate as dopants in hexahexyloxytriphenylene and hexahexylthiotriphenylene which are the discotic molecules. The composites of different concentrations of the dopants were prepared with the discotic molecules. The POM, DSC and SAXS studies revealed that when the concentration of the dopants are low, they do not alter the columnar structure of the discotic molecules. The UV-visible spectral studies show that the ferrocenium ions form charge-transfer complex with the electron rich discotic molecules while the chloroauroate oxidises the triphenylene core of the discotic molecules resulting in the formation of triphenylene radical cations. Both the dopants enhance the DC conductivity of the discotic phase by almost million times while the chloroauroate-discotic composites show very high ionic conductivity due to the formation of radical cations. The chloroauroate-discotic composites show a significant absorption in the entire visible and NIR regions, which indicates that these composites can find potential applications in the field of solar cells. The DC conductivity of these composites were observed to decrease in the isotropic phase indicating that the observed high conductivity is due to the quasi-one-dimensional nature of the columnar hexagonal phase.

5. Self-assembled monolayers of liquid crystalline disulphides and thiols on gold surface

We have formed self-assembled monolayers of two liquid crystalline compounds on the gold surface viz the rod-like cyanobiphenyl functionalised disulphides and the discotic triphenylene based thiols. These monolayer modified surfaces were characterised using electrochemical techniques like cyclic voltammetry and electrochemical impedance spectroscopy.
The studies show that the cyanobiphenyl substituted disulphides inhibit the electron transfer process for the ferrocyanide|ferricyanide reaction, while allowing the hexaammineruthenium(II/III) reaction to take place through the monolayer film. The facile electron transfer in the hexaammineruthenium(II/III) has been explained on the basis of outer-sphere electron transfer reaction mechanism. Electrochemical impedance spectroscopic studies have revealed that the barrier offered for electron transfer process by these monolayers are lower than that of typical alkanethiol monolayers. This is attributed to the loose packing of the monolayers which are formed owing to the bulky cyanobiphenyl groups at the terminal positions. The higher chain disulphide modified monolayers offer higher barrier to electron transfer process owing to better organisation of the monolayers on the surface due to hydrophobic-hydrophobic interactions. On the other hand, the triphenylenethiol modified monolayers show poor blocking behaviour and the barrier to electron transfer process decreases for higher chain length. This has been explained on the basis of the disorganised structure of the longer chain length monolayers resulting from the π–π interaction between the electron rich triphenylene cores that leads to clustered packing, leaving out many voids on a polycrystalline gold surface.

Scope For Future Studies

In chapter 2, we have discussed the electron transfer reactions of several redox probes in the lyotropic columnar hexagonal liquid crystalline phase (H1 phase) of Triton X-100/water system. We have observed significant shifts in the half-peak potentials and large reduction in the diffusion coefficient of the redox probes in the H1 phase as compared to the solvent phase. At the same time, we have shown that the redox probes follow linear diffusion characteristics irrespective of the columnar arrangement of the cylindrical micelles near the electrodes. This provides a general basis for the study of several biological electron transfer reactions as the systems presented here can mimic the biological environment.

In chapter 3, we have discussed the dispersion of thiol-protected gold nanoparticles in the H1 phase of Triton X-100/water system and in the H2 phase of AOT, where we have shown that the dispersion of nanoparticles into the columnar phase does not alter the liquid crystalline phase behaviour. Such composites can be studied for several applications includ-
ing the targeted drug delivery. The interaction of the terminal groups of the ligands attached to the nanoparticles with the surfactant and the water molecules on the surface of the micelle plays a significant role on the \( d \) spacing of these dispersions as discussed in the chapter 3. Further studies have to be carried out for a better understanding of these phenomena. For example, the phase diagram of the nanoparticle-Triton X-100-water systems may be of fundamental interest for a better understanding of the behaviour of such dispersions.

The ionic conductivity of the H1 phase of Triton X-100/water system shows a surprisingly high ionic conductivity even though the constituent materials are non-ionic in nature. Interestingly, similar observations have been made on some protein surfaces as well as inside of the carbon nanotubes. A detailed experimental studies have to be carried out in this field, and the system that we presented here may become a model system for these experiments. In this context, the existence of different protonated water clusters needs to be probed and the kinetics of the proton transfer reactions have to be studied in detail.

The chapter 4 describes the electrical conductivity studies of the discotic liquid crystalline composites. We have shown that the electrical conductivity of the discotic materials can be enhanced by several orders of magnitude while the composites still retain the liquid crystalline order. The absorption of the chloroaurate-discotic composites over the entire visible and NIR region make them potential candidates for the solar cell applications. For this purpose the photocurrent measurements have to be carried out and should be compared with other solar cell devices. The efficiency of such solar absorbers can also be studied. The discotic-ferrocenium composite reported here opens a new area of discotic-organometallic composites of donor-acceptor couples. A study of similar composites with other organometallic compounds may lead to some novel composite materials with several interesting properties.

The self-assembled monolayers of disulphides, as described in the chapter 5, show that the electron transfer barrier properties of these modified electrodes are significantly lower than typical alkanethiol monolayers. This has been attributed to loose organisation owing to the bulky cyanobiphenyl groups at the terminal positions. Such monolayers can be further analysed using scanning tunneling microscopy and atomic force microscopy to establish the orientation of these molecules on the gold surface. The triphenylene thiols show abnormal behaviour in the electron transfer process as the blocking ability decreases with increase in
the chain length. This counterintuitive behaviour has been attributed to the formation of clusters by $\pi - \pi$ interaction between the triphenylene cores. Further surface studies using \textit{in situ} scanning tunneling microscopy and atomic force microscopy are necessary for a clear understanding of this behaviour. Moreover, such clusters on the electrode surface may exhibit some interesting properties as triphenylenes are well known for their quasi-one-dimensional electron transport in the bulk phase and therefore may be good candidate materials for molecular electronics.