Chapter 4

Electrical Conductivity Studies on the Discotic Liquid Crystals and its Composites

Liquid crystals, as mentioned earlier, are the intermediate phases between the crystalline and liquid phases. They have the orientational order of crystalline phases and the dynamic nature of liquid phases. The different properties of these phases have already been discussed in the chapter 1. The present chapter deals with the electrical conductivity studies on the thermotropic columnar liquid crystalline phases formed by triphenylene based discotic molecules and some of its composites. The discotic composites are prepared using two different acceptor systems, ferrocenium tetrafluoroborate and chloroauric acid. The composites were characterised using different techniques like POM, DSC, SAXS, spectral studies and cyclic voltammetry. The electrical conductivity of these composites were observed to be enhanced by several orders of magnitude compared to the pure discotic systems. The electrical conductivity studies of a series of pyridinium tethered triphenylene derivatives which form ionic liquid crystals are also part of this chapter.
4.1 Introduction

Columnar liquid crystalline phases are formed by the aggregation of disc like molecules which stack one over the other to form columns [1]. These columns can aggregate to form different phases like columnar rectangular, columnar hexagonal, columnar plastic and columnar oblique phases. Typically, these molecules consist of an aromatic core and flexible aliphatic chains. Several cores have been used for the synthesis of discotic molecules. The different strategies involved in the synthesis of molecules possessing columnar phases have been reviewed recently [2]. Some of the most studied electron rich discotic cores are benzene, naphthalene, anthracene, triphenylene, hexabenzocoronene and phthalocyanine. A typical electron deficient core is that of anthraquinone. Due to the strong $\pi-\pi$ interaction between the cores, the typical core-core distance in the columnar phase is $\sim 0.35$ nm. The column-column distance may be $\sim 2-4$ nm depending on the length of the aliphatic substitution on the core groups. These alkyl chains should be of sufficient length in order to provide necessary flexibility for the discotic molecules to form columnar phases.

Due to the strong core-core and weak column-column interactions, the discotic molecules show a quasi-one-dimensional behaviour in the electrical conductivity. This one-dimensional conductivity has been suggested to be important for a variety of applications in the areas including solar cells [3], molecular electronics [4], photovoltaic cells [5], organic light emitting diodes (OLED) [6] and field effect transistors (FET) [7]. The efficiency of such devices depends on the band gap of the materials, which is typically about 4 eV for the discotic liquid crystals. This high band gap of the discotic molecules makes them behave as insulators under normal conditions. On the other hand, they show semiconducting behaviour on doping with either electron rich or electron deficient molecules into the supramolecular order of the liquid crystalline phase. The important point to be noted here is that the concentration of the dopant is critical in order that the liquid crystalline phase is not disrupted. At the same time, the amount of dopants should be sufficient enough to introduce electrons or holes into the liquid crystalline medium to increase the conductivity.

The conductivity of the pure discotic systems have been studied by several groups. Triphenylene, hexabenzocoronene and phthalocyanine based columnar phases are the most studied systems. Either the conductivity ($\sigma$) or the related charge carrier mobility ($\mu = \sigma/ne$) were
measured using different methods for these systems. For the measurement of mobility, two methods have been widely used in the literature. The first method is based on the time of flight (TOF) experiments [8; 9], while the second method is based on the pulse radiolysis-time resolved microwave conductivity (PR-TRMC) method [10; 11]. In the TOF method, the time taken by the excited charge carriers to travel a known distance is measured, from which the mobility is calculated using the following equation

$$\mu = \frac{d}{t_T F}$$

where \(d\) is the distance between the two electrodes and \(F\) is the applied electric field. The transit time \(t_T\) can be obtained at the intersection of the two tangents for the two relaxation processes in the current-time profile from the TOF experiment [9]. In the PR-TRMC method, a microwave radiation of particular power is irradiated on the sample, which generates charge carriers and hence the conductivity of the sample increases. The current response of the cell is measured as a function of time and from these values the mobility of the charge carries can be estimated [10]. TOF measures the long-range mobility of the sample which means that the mobility is averaged out over a large distance between the two electrodes which may be several microns, in a millisecond to microsecond time scale. On the other hand, the PR-TRMC measures the mobility over a small distance of the order of thickness of a few molecules in a time period of a few nanoseconds. Two points may be noted here. Due to the small distance involved, mobility values from PR-TRMC are more fundamental while TOF gives the bulk charge-carrier mobility. Secondly, due to the larger distance involved, the mobility obtained from TOF will be smaller than the values from PR-TRMC. This is due to the fact that the bulk of the sample will be disordered with multidomains and un-aligned columns that results in defect structures which will contribute to scattering of charge carriers. Therefore the defect contributions to the TOF experimental values is quite significant, while for the PR-TRMC the contributions from these defects will be less [12].

In our work, we have focused on the electrical conductivity measurements, which is related to charge carrier mobility by the formula \(\sigma = ne\mu\) where \(\sigma\) is the conductivity, \(n\) is the charge carrier density, \(e\) is the charge of electrons and \(\mu\) is the mobility of the charge carriers. The electrical conductivity studies provide information on the effect of doping in the transport properties of charge carriers. As a result of the very high band gap, the discotic
materials have very low electrical conductivity of the order of $10^{-12}$ S/m along the column and $10^{-15}$ S/m perpendicular to the column. One route to enhance the conductivity of these supramolecular systems is the addition of a small quantity of either electron donors or electron acceptors. This doping can introduce electrons or holes into the discotic matrix and as a result, the conductivity can be enhanced by several orders of magnitude. Trinitrofluorenone, TNF[13; 14], iodine[15], aluminium chloride, AlCl$_3$ [16; 17; 18], nitrosonium tetrafluoroborate, NOBF$_4$ [19] and gold nanoparticles [20; 21] are some of the most studied dopants in the columnar liquid crystalline matrix. These dopants at low concentrations retain the columnar phase with enhancement in the electrical conductivity by several orders of magnitude. For AlCl$_3$ and NOBF$_4$ doped systems, it has been shown that they form charge-transfer complexes with the discotic molecules. This results in the oxidation of the aromatic core of the discotic moiety with the formation of radical cations that enhances the electrical conductivity of the composites. For the NOBF$_4$ dopants, they may even intercalate within the column and can form a 1:1 complex [22]. These complexes have better liquid crystalline order compared to the pure systems, that results from the strong electron donor-acceptor interactions within the column due to the sandwich type structure. In other systems, the doping will increase the entropy of the system that reduces the temperature range of liquid crystalline phase and therefore at higher concentrations of the dopants, the liquid crystalline order collapses.

### 4.1.1 Mechanism of Electrical Conductivity

The quasi-one-dimensional conductivity on discotic liquid crystalline phases was first reported in 1985 using triphenylene based systems [23]. Further studies were carried out on several triphenylene derivatives and their composites, which indeed demonstrated that the conductivity of these supramolecular systems can be enhanced by several orders of magnitude [18; 24]. After this, a number of reports have appeared in the literature on the quasi-one-dimensional conductivity of the columnar phase formed by triphenylene, benzocoronene [25; 26; 27; 28; 29], phthalocyanine [12; 30] and perylene derivatives [31; 32; 33] either in their pure state or in the presence of dopants. In all these systems, it was shown that the electrical conductivity is very much higher in the columnar phase compared to the crystalline phase. In many systems, the low frequency ionic conductivity decreased again in
the isotropic phase. This clearly indicates that the conductivity in these systems is mainly
governed by the columnar hexagonal arrangement of the disc-shaped molecules.

The ionic conductivity values are frequency dependent at higher frequency ranges, while
being independent of frequency at lower frequency ranges. Boden et al. have shown that the
conductivity at higher frequencies follows the form [16]

$$\sigma(\omega) = \sigma(0) + A\omega^{0.8}$$

The frequency independent part has been modelled by the Fickian diffusion, which is based
on the concentration-independent Fick's law of diffusion, and can be expressed by the
Nernst-Einstein equation given by [16]

$$\sigma(\omega) = \frac{ne^2}{kT} D(\omega)$$

where

$$D(\omega) = \frac{L^2}{2d} \Delta_{rms} \lambda$$

with $\lambda$ being the inverse of mean hopping time ($\lambda = 1/\bar{t}$) and $\Delta$ the mean hopping distance.

This provides the frequency-independent conductivity at low frequencies where only the
slowest motions, the non-localised or long-range hops, of the charge-carriers are dominated.
In other words, the system is in the frozen state or the fully ordered state with single hopping
rate between the sites. This diffusion was also observed to be independent of the carrier
concentration [16].

Boden et al. have discussed the frequency dependency of the ionic conductivity in detail
[16]. They have shown that the frequency independent conductivity observed at low fre-
quencies originates from the charge-migration between the discotic columns of the domains,
that are present due to the absence of perfect alignment of the columns. The frequency
dependency of the conductivity arises from the following equation,

$$D(\omega) = \frac{L^2_{rms}}{2d} \frac{i\omega(1 + i\omega/\lambda)^{-v-1}}{1 - (1 + i\omega/\lambda)^{-v-1}}$$

where $\Delta$ is the mean hopping distance, $v$ is an arbitrary parameter, $d$ is the distance between
neighbouring sites. Fitting of the experimental ionic conductivity data using this equation
revealed the following points:

1) The frequency independent conductivity that dominates at low frequency region arises due
to the charge-migration between columns of different domains. Normally, these different domains are formed due to the imperfect alignment of the discotic columns.

2) The fitting parameters in the columnar hexagonal as well as in the isotropic phases are very close to each other, which indicates that the molecular stacks or the columns retain at least partially even in the isotropic phase.

3) For the frequency dependent conductivity at high frequencies, the best fitting value for $v$ is $\sim 0.8$, which explains the $\omega^{0.8}$ dependency of the ionic conductivity at high frequencies. This is reported to be typical of hopping transitions with a distribution of hopping probabilities. For the columnar liquid crystalline systems, this originates from the disorder in the stacking of the disc-like molecules.

The conductivity of the system is related to the mobility ($\mu$) of the charge-carriers by the relation $\sigma = ne\mu$, where $n$ is the density of charge-carriers which can be estimated from the ESR measurements and $e$ is the charge of electrons. The conductivity in the parallel and perpendicular directions are related to the mobility in the same manner [19]. The mean hopping time of charge-carriers within the column is related to the measured mobility by the equation

$$\tau = \frac{ed^2}{2kT\mu}$$

where $d$ is the average separation between the aromatic cores within a column. For triphenylene derivatives, this corresponds to $\sim 0.35$ nm.

The conductivity in the crystalline phase is very less, mainly due to the restricted charge-carrier migrations in the phase. The different carrier sites have frozen structure with defects. In the isotropic phase, the columns persist to some extent. The total hopping length is given by the length of the molecular stacks, which is $\sim 200$ nm at a temperature close to the columnar-isotropic phase transition temperature. This length decreases as the temperature increases and the conductivity falls down. It may be noted however that close to the phase transition temperature, the conductivity may increase due to the facile temperature-dependent charge-carrier migration [16].

The conductivity perpendicular to the columns is more complex as the charge-carriers have to cross a longer distance. The typical core-core distance between adjacent columns in discotic systems is 2-4 nm and hence typical quantum-mechanical tunneling can not explain the observed conductivity. Inter-columnar charge-carrier transport at low temperatures may
take place through the defects or dislocations. At high temperature, the process may involve many-phonon assisted tunneling process [34]. Assuming the hopping rate is of the form

\[ W_\perp \approx W_0 e^{-2\alpha \bar{R}} \]

where \( \alpha \) is the inverse decay length of the wavefunction and \( \bar{R} \approx 20 \, \text{Å} \) is the column-column distance in the liquid crystalline phase for HAT6. Comparing this with the \( W_\parallel \),

\[ \sigma_\parallel / \sigma_\perp = W_\parallel / W_\perp \approx 10^6 \]

The molecular diffusion coefficient perpendicular to the columns, \( D_\perp \), is measured to be around \( 5 \times 10^{-11} \, \text{m}^2 \text{s}^{-1} \), which is comparable to the mobility of the charge-carriers perpendicular to the column. This indicates that the \( \sigma_\perp \) may be dominated by the dislocations of these disc shaped molecules in between the adjacent columns which is ionic transport [35].

### 4.1.2 Role of the Electrodes

Boden et al. have studied the effect of electrode materials on the conductivity of discotic systems [36]. They have used indium tin oxide (ITO) electrodes as well as aluminium (Al) electrodes as symmetric and antisymmetric combinations. With a cell separation of about 5 \( \mu \text{m} \) and above, they have shown that the bulk resistance of the material dominates over the surface resistance and hence the influence of surface resistance can be neglected. In the bulk, under such a condition, the conductivity may be due to electron or the hole mobility. The hole mobility is temperature independent. The electron mobility follows the form

\[ \mu_\parallel \sim \mu_0 e^{-E_a/kT} \]

where \( E_a \) is the activation energy, and has values close to 0.5 V. In the symmetric ITO electrodes, ie. ITO/HAT6/ITO, it has been shown that hole conduction dominates due to the presence of intrinsic p-type impurities and a lower work function of ITO compared to HAT6. On the other hand, for the Al/HAT6/Al combination, the electron conduction is observed to be dominated.

Since the hole mobility is almost independent of temperature, the temperature dependency of the conduction at higher temperatures has to be either due to defect ionisation of
the trapped impurities or due to the external injection of charge carriers. Theoretical formulation of the defect ionisation would result $\sigma_{\text{defect}} \to 0$ as $T \to 0$. Experimentally it was observed that the conductivity levels off at low temperature instead of approaching zero. This means that the defect ionisation is not the dominant factor for the temperature dependency of conductivity. The experimental results can be explained on the basis of external injection of charge-carriers [36].

Some of the general trends in the conductivity of discotic liquid crystalline phase are as follows:

1. The conductivity in the columnar hexagonal phase is higher than that of crystalline and isotropic phases. In the crystalline phase the conductivity is less due to the defect structures at the electrode/discotic interface as well as in the bulk, that can not be cured. In the isotropic phase, the liquid crystalline order is collapsed. This results in the decrease in the mean free path, where the charge-carriers are trapped, and should normally lead to a decrease in conductivity.

2. As the chain length of the discotic molecules increases, the core-core distance increases which results in a lower coupling between the cores. It is also observed that the work function for the discotic system increases as the chain length increases. Due to these two reasons the conductivity decreases with increase in chain length.

3. The ionic conductivity shows a frequency-independent constant value at low frequencies and varies as $\omega^{0.8}$ at higher frequencies. The low frequency limiting value is attributed to the charge-migration between different columns or due to long-range hopping of charge-carriers while at high frequencies it is due to the charge-migration within the columns.

### 4.1.3 Alignment of Discotic Systems

The quasi-one-dimensional conductivity of the liquid crystalline phase originate from the stacking of the discs in columns and the transport of charge-carriers along these columns. Since the typical column length is only a few tens of nanometers while the separation between the electrodes is at least a few microns, the alignment of the discotic system is important for the observation of anisotropic conductivity. For the device applications, this alignment has a major role. For example, for the solar cell and photovoltaic cell applications, the
columns perpendicular to the surface is preferred while for the field effect transistor (FET) applications, the columns should be parallel to the surface. This means that all the columns should be aligned in the same direction so that the net carrier transport is a one-dimensional property. The alignment of the columns may be either parallel or perpendicular to the electrode surface as represented in the Figure 4.1. If the alignment of the columns is parallel to the surface, it is known as homogeneous alignment and in this case, the measurement of conductivity between the two electrodes gives the conductivity perpendicular to the columns ($\sigma_\perp$). On the other hand, if the columns are aligned perpendicular to the electrode surface, which is the homeotropic alignment, the conductivity parallel to the columns ($\sigma_\parallel$) can be measured between the electrodes.

Eventhough the alignment of calamitic liquid crystals are easy by the surface modifications or by the application of electric fields, these methods are not very effective for the alignment of discotic systems and several other methods have been proposed for this purpose [37]. One of the most common methods is the application of magnetic field. The discotic systems have negative magnetic susceptibility. Due to this, while cooling from the isotropic phase, the discs will align parallel to the field or the column axis will align perpendicular to the applied magnetic field. Hence applying a magnetic field perpendicular to the electrode surface will result in the homeotropic alignment of the sample [18]. Magnetic field of strength $\sim 2-5$ T is observed to be sufficient for a nearly perfect alignment of the samples [16]. Similarly homogeneous alignment can be achieved by a magnetic field parallel to the electrode surface. Applying mechanical forces have been shown to align the discotic materials, especially for the highly viscous phases. The mechanical shear will align the columns perpendicular to the applied shear field [38; 39]. Alignment of liquid crystals by surface modification is a common method in calamitic liquid crystals, but is not a very successful
method for the discotic systems, although it has been shown that glass surfaces coated with electron rich molecules results in the homeotropic alignment [40]. Hexaphenol, mellitic acid, hexahydroxytriphenylene and rufigallol have been utilised for this purpose. A slow cooling of the discotic molecules from the isotropic phase in an ITO coated cell with a small cell thickness has shown to produce homeotropically aligned samples. This is one of the easiest and most common method for the alignment of discotic molecules. Hexaalkoxytriphenylene can be homeotropically aligned easily using this method [8; 13; 14; 37; 41]. The typical cell thickness used for this purpose is \( \sim 5 \, \mu m \). In general, the aligned samples can be easily distinguished from a non-aligned sample using polarising optical microscopy. For an aligned sample, since the domains are all in the same direction, the sample will not show any birefringence whereas in the unaligned samples the birefringence originates from the defects from the different domains.

In the present chapter, we discuss the electrical conductivity measurements of triphenylene based columnar hexagonal liquid crystalline phases. The first part describes the ferrocenium doped HAT6 and HHTT composites, while the second part describes about the chloroauric acid-HAT6 composites. The composites were characterised using a variety of techniques and the electrical conductivity of these composites were observed to be enhanced by several orders of magnitude compared to the pure discotic systems. The last part of the chapter deals with the ac conductivity studies on ionic columnar hexagonal liquid crystals that are formed by pyridinium tethered triphenylene molecules.

### 4.2 Experimental Section

#### 4.2.1 Chemicals

Two triphenylene derivatives, hexaaxyloxytriphenylene (HAT6) and hexahexylthiotriphenylene (HHTT), which show columnar hexagonal phase, were used for the preparation of composites. The molecular structure of these two compounds are shown in Figure 4.2 and were synthesised by S. Kumar following the method described earlier [42]. The high purity dopants, ferrocenium tetrafluoroborate (FcTFB) was from Aldrich and chloroauric acid, HAuCl4 was from Spectrochem and were used without further purification.
4.2.2 Preparation of the Composites

The discotic molecules were dissolved in dichloromethane, to which appropriate amount of dopants were added and sonicated for 5 minutes. A slow evaporation of the solvent with simultaneous stirring of the mixture resulted in the formation of the composites. Composites of different dopant-discotic ratios were prepared that includes 1 % FcTFB/HAT6, 10 % FcTFB/HAT6, 50 % FcTFB/HAT6 using HAT6 and FcTFB, 1 % FcTFB/HHTT, 10 % FcTFB/HHTT, 50 % FcTFB/HHTT using HHTT and FcTFB and 0.1 % HAuCl₄/HAT6, 1 % HAuCl₄/HAT6, and 5 % HAuCl₄/HAT6 using HAT6 and HAuCl₄.

4.2.3 Characterisation of the Composites

The composites were characterised using a variety of techniques like polarising optical microscopy, differential scanning calorimetry, small angle X-ray scattering, UV-visible spectroscopy, photoluminescence spectroscopy and electrical conductivity measurements. Polarising optical microscopy was carried out using Olympus POM instrument coupled with a Mettler heater. The samples were sandwiched between a glass-slide and a coverslip. The textures were imaged while cooling from the isotropic phase. The transition temperatures and associated enthalpy changes were determined by differential scanning calorimetry (DSC; Perkin-Elmer, model Pyris 1D) at a scan rate of 5 °C min⁻¹ for both heating and cooling. The apparatus was calibrated using indium (156.6 °C) as a standard. Small-angle X-ray scattering studies were carried out using an X-ray diffractometer (Rigaku, UltraX 18) operating at 50 kV and 80 mA using Cu Kα radiation having a wavelength of 1.54 Å. Samples were
prepared by filling a capillary (Hampton Research, USA) with either the pure discotic systems or the composites and then sealed it. All scattering studies were carried out at 80 °C, and the diffraction patterns were collected on a two-dimensional Marresearch image plate. A model SD 2000 spectrophotometer (Ocean Optics, Dunedin, FL) or Perkin Elmer (USA) fitted with a tungsten lamp source and a cell having a path length of 1 cm was employed to measure the UV-visible absorbance spectra.

The DC conductivity studies of the samples were carried out in ITO-coated glass sandwich cells (10 mm × 5 mm area) with a thickness of either 60 μm or 4 μm. A schematic representation of the setup is shown in Figure 4.3. A Keithley picoammeter (model 480) along with a constant DC voltage source and a temperature controller was used for current measurements. The ionic conductivity measurements were conducted using a lock-in amplifier (Stanford Research Systems model SR830) at 1 kHz frequency on cooling from the isotropic phase. The frequency dependency for the conductivity of the composites were measured using the lock-in-amplifier at 80 °C, where the samples are in the liquid crystalline phase. A Howland constant current circuit, as shown in Figure 4.3 was used for the temperature measurements, where the terminals from the platinum thermal resistor were connected as the load resistance (LR). A precision operational amplifier (CA3140) was used in the circuits.

4.3 Results and Discussion

4.3.1 Discotic-Ferrocenium Composites

This section deals with the experimental results using the composites of FcTFB with the two discotic molecules viz. HAT6 and HHTT.

4.3.1.1 POM studies

Polarising optical microscopic studies provide an easy assessment of the different liquid crystalline phases formed by the materials. Figure 4.4 shows one of the polarising optical micrographic textures obtained for the 10 % FcTFB/HAT6, which is typical of the columnar hexagonal phase. A similar texture was also obtained for the other FcTFB composites. As is clear from the figure, all the composites retain the columnar hexagonal (Col₆) phase.
Figure 4.3: Schematic diagram of the experimental setup used for a) DC conductivity b) ac conductivity and c) temperature measurements. LR represents the load resistance from the platinum thermal resistor.
Figure 4.4: Polarising optical micrographic texture obtained for the 10 % FeTFB/HAT6 composite

of the pure discotic molecules. At very high concentrations of the dopant (for example, 50 % FeTFB) a phase separation was observed in both the discotic systems. The phase transition temperatures of the composites have been found to be a function of the ferrocenium concentration.

4.3.1.2 DSC studies

Figure 4.5: DSC traces for a) pure HAT6, and the composites b) 1 % FeTFB HAT6 and c) 10 % FeTFB HAT6

The composites were characterised by DSC analysis for the measurement of the phase transition temperatures and the enthalpies of the transitions. Figures 4.5 and 4.6 show the
DSC traces for the the pure discotic systems and the composites of HAT6 and HHTT, respectively. It is clear from the plots that the phase transition profiles are similar to the pure systems even after the addition of ferrocenium ions at low concentrations. It was observed that the Col$_h$ phase becomes destabilised at very high concentrations of FcTFB, which is in accordance with the POM results. The phase transition temperatures were shifted to lower temperature and the enthalpy of the phase transition decreases with increasing dopant concentration. At very high concentration of the dopants, for example, 50% FcTFB/HAT6, the Col$_h$ phase was not observed. The highly electron-deficient ferrocenium ions form a charge-transfer complex with the electron-rich triphenylene core, as is evident from the UV-visible spectroscopic studies. The formation of the complex reduces the electron density in the columns. In addition, the steric hindrance of the ferrocenium ions is the major destabilising factor in the composite systems, eventhough charge-transfer complex formation of ferrocenium with the electron-rich triphenylene core may enhances the stability at lower concentrations. This is further supported by the fact that the enthalpy of the phase transition decreases with increasing ferrocenium concentration.
Figure 4.7: Scattering vector, q vs. intensity profiles obtained from small-angle X-ray scattering studies for (a) 10% FcTFB/HAT6 and (b) 10% FcTFB/HHTT composites. The insets show enlargements of the $1/\sqrt{3}$ and $1/\sqrt{4}$ peaks from the main plot.

### 4.3.1.3 SAXS Studies

Small-angle X-ray scattering studies of the samples were carried out in 1 mm capillary tubes at 80 °C, and all of the scattering studies were performed during cooling from the isotropic phase. The SAXS patterns support our conclusions from the POM and DSC studies that 1% and 10% FcTFB composites with both HAT6 and HHTT systems retain the Col$_h$ phase. The typical patterns obtained for the samples are shown in Figure 4.7. The $d$ spacings calculated from the SAXS patterns are summarised in Table 4.1. The $d$ values of 20.15 Å for HAT6 and 18.02 Å for HHTT as calculated from the SAXS patterns are in good agreement with the values reported in the literature [43]. The main scattering peak in the pattern shown here corresponds to the 2D plane having Miller indices of (1,0) of the Col$_h$ phase. The other two peaks of lower intensity are shown in the inset of the figure. The ratio of the $d$ values corresponding to the three peaks is $1:(1/\sqrt{3}):(1/\sqrt{4})$ which is typical for the hexagonal order.

As is clear from the table 4.1, the doping of FcTFB in the discotic matrix has not disturbed the lattice parameters as there was a negligible change in the $d$ spacing. We have shown that gold nanoparticles occupy the interdomain spacing without altering the $d$ spacing of the columns in a discotic matrix [20]. In a similar manner, the ferrocenium molecules can occupy the interdomain spacing in the columnar architecture. The dopant, FcTFB may not occupy the intercolumnar spacing because of the relatively larger size of ferrocenium ions as compared to, for example, iodine [15]. This is supported by the $d$ values, which is almost
the same even after the doping.

Table 4.1: The $d$ spacing (in Å) for the $Col_a$ phases of HAT6 and HHTT measured from the SAXS studies before and after doping

<table>
<thead>
<tr>
<th>sample</th>
<th>pure</th>
<th>10% FcTFB</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAT6</td>
<td>20.15</td>
<td>18.16</td>
</tr>
<tr>
<td>HHTT</td>
<td>18.02</td>
<td>18.47</td>
</tr>
</tbody>
</table>

4.3.1.4 UV-visible Spectroscopy

UV-visible absorbance spectral studies of the pure samples and the composites were carried out in dichloromethane medium. The solution was sonicated for 5 min, and the absorbance of the solution was recorded immediately with pure dichloromethane as a reference. Figure 4.8 shows the absorbance spectra for different composites, in addition to those of pure FcTFB and ferrocene. It is clear from the figure that for the composites, there is a blue shift in the absorbance of the ferrocenium group, which is due to the formation of a charge-transfer complex. There is a shoulder peak in the 400-500 nm region. Since ferrocenium is a very strong electron acceptor, charge transfer from the electron-rich discotic molecules occurs, resulting in the formation of donor-acceptor pairs. Pure ferrocenium ions absorb at $\sim$600 nm, whereas pure ferrocene absorbs at $\sim$460 nm. In the present systems, a blue shift was observed in the absorption, which can be explained due to the charge transfer from triphenylene to ferrocenium ion in the composites. It is known that ferrocenium ions are unstable in an electron-rich environment such as highly polar solvents [44]. The extent of the blue shift was shown to be dependent upon the concentration of Fc$^+$ ion and the polarity of the solvent. In the present study, the absorbance had a larger blue shift at lower concentrations for both HAT6 and HHTT composites, as shown in the Figure 4.8. The 1%, 10% and 50% FcTFB composites with HAT6 show absorbances at wavelengths of 358 nm, 362 nm, and 383 nm, respectively, whereas pure HAT6, absorbs at 277 nm [45]. This may be due to the fact that, at lower concentrations of Fc$^+$, complete charge transfer between the donor and acceptor molecules occurs. Similar behaviour was observed for the Fc$^+$/HHTT composites.
Figure 4.8: UV-visible absorbance spectra for a) 1% FcTFB/HAT6, b) 10% FcTFB/HAT6, c) 50% FcTFB/HAT6, d) pure ferrocene and e) pure FcTFB as well. The absorbance in ferrocenium species is a result of the charge transfer from the e\textsubscript{1u} bonding ligand level to the empty e\textsubscript{2g} metal level [46].

4.3.1.5 Conductivity Studies

Figure 4.9: DC conductivity vs. temperature plots for a) 1% FcTFB/HAT6 and b) 10% FcTFB/HAT6 unaligned samples, c) 1% FcTFB/HAT6 and d) 10% FcTFB/HAT6 aligned samples

The DC conductivity studies of the composites were carried out in 60 μm thick ITO-coated glass sandwich cells. The conductivity measurements were also carried out using a 4 μm thickness cell. A slow cooling from the isotropic phase in the 4 μm cell results in the homeotropic alignment of the sample. This method of cooling from the isotropic phase
Figure 4.10: DC conductivity vs. temperature plots for a) 1% FcTFB/HHTT and b) 10% FcTFB/HHTT unaligned samples

in sandwiched cells has proven to be an effective method for the homeotropic alignment of discotic liquid crystals [34; 36; 37]. In the present study, the alignment was confirmed using polarising optical microscopy, where the aligned samples do not exhibit the characteristic birefringent textures. The conductivity values of both aligned and unaligned samples show a similar trend even though the aligned sample shows a larger electrical conductivity because of its facile electron transport through the well-aligned columns as compared to that of the unaligned sample.

The DC conductivity values of the samples were measured as a function of temperature while cooling from the isotropic phase. Figures 4.9 and 4.10 show the plots of conductivity as a function of temperature for the HAT6 and HHTT systems respectively, after doping. Both HAT6 and HHTT have very low DC conductivities in their pure state (of the order of $10^{-12}$ S/m) which is well below the accurate detection limit of our measurement system. There is a large increment in the conductivity values of the systems after doping. This can be explained by the charge transport that takes place after the addition of FcTFB to the discotic phase. It can be seen that the conductivity increases by several orders of magnitude after doping. The extent of increase depends up on the concentration of the dopant. A similar trend was observed for the aligned sample in the direction of column axis for the HAT6 system, as is obvious from Figure 4.9. The HHTT system also was found to exhibit similar behaviour as shown in Figure 4.10. The conductivity values of the HHTT composites were found to be higher than that of HAT6 composites, a trend similar to the higher conductivity
Figure 4.11: a) DC and b) ac conductivity plots for 10 \% FcTFB/HAT6 on cooling from the isotropic phase of HHTT over HAT6.

The ionic conductivity of the composites were studied by ac measurements for all of these samples. Figure 4.11 shows a plot for the comparison of ionic conductivity with the DC conductivity values for the 10 \% FcTFB/HAT6 composite. From the graph, the ionic conductivity was found to be about 2 orders of magnitude less than the DC conductivity. This indicates that the mechanism operating in these systems is mainly electron transport rather than ion transport by the ferrocenium ions or the $\text{BF}_4^-$ counterions. This is in accordance with the argument that the dopant ions will be trapped in between the alkyl chains of the discotic molecules in a frozen state and their contribution to the ionic conductivity will be less [16].

Ferrocene has an iron(II) ion sandwiched between the two cyclopentadienyl units, and this organometallic compound obeys the 18-electron rule [47]. On the other hand, the ferrocenium cation has 17 electrons and therefore acts as a strong electron acceptor. The $a_{1g}$ molecular orbital of the ferrocenium ion has an unpaired electron, which explains its high electron-accepting nature. After the charge transfer from triphenylene, the composite forms an electron-hole pair, which enhances the DC conductivity of the composites. Even though the electron-accepting properties of ferrocenium have been well studied in different solvent systems, its behaviour in discotic liquid-crystalline systems is of greater interest as such systems form quasi-one-dimensional molecular wires.
We have calculated the mole fractions of the composites by taking 0.35 nm as the core-core distance and 18.3 Å as the d spacing for the discotic molecules. For 10 % FcTFB/HAT6 composition, the molar ratio of ferrocenium ions to discotic molecules was estimated to be about 1:3, which is much higher than the corresponding weight ratio. On the other hand, the volume fraction of ferrocenium ions to discotic molecules was calculated to be about 1:200 from the known molecular volumes of HAT6 and ferrocenium[48; 49]. This explains the fact that no significant change in the d spacing and no disruption of the hexagonal order occurs even after the doping of ferrocenium up to the extent of 10 %. For the 50 % composite, the molar ratio is too large, so that there is a disruption of the columnar phase.

From the cyclic voltammetry shown in Figure 4.12, we have calculated the oxidation potential of HAT6 to be -0.356 V vs. ferrocene/ferrocenium reference couple. The lower oxidation potential of HAT6 compared to ferrocene indicates that the electron transfer from HAT6 to the ferrocenium is energetically facile in the mixture and therefore their role as donor-acceptor pair. The electronic conductivity occurs by the hopping mechanism where the electron-rich triphenylene core donates an electron to the electron-deficient ferrocenium ion, thereby forming an electron-hole pair. The hopping conductivity of the electron-hole pair under the action of an applied DC electric field brings about the electronic conductivity. A very low dependence of the conductivity on temperature in the columnar phase supports the hopping mechanism as the dominant charge-carrier mechanism in the present systems. It has been reported that the electron tunneling mechanism depends more on the tempera-
Figure 4.13: Polarising optical micrographic texture obtained for the composite 1 % HAnCl4/HAT6 on cooling from the isotropic phase

ture while the hopping mechanism is weakly dependent on the temperature [36]. A similar mechanism was also reported in discotic liquid crystalline systems doped with TNF, iodine and gold nanoparticles [15; 20; 50].

4.3.2 Discotic-Chloroaurate Composites

This part describes the characterisation of HAT6-chloroaurate composites. As mentioned before, composites of three different ratios of HAnCl4 with HAT6 were prepared, 0.1 % HAnCl4/HAT6, 1 % HAnCl4/HAT6 and 5 % HAnCl4/HAT6. These composites were characterised using POM, DSC, SAXS, UV-visible spectra, photoluminescence spectra and conductivity studies.

4.3.2.1 POM Studies

Figure 4.13 shows the polarising optical micrographic texture obtained for the composite 1 % HAnCl4/HAT6 and similar textures were obtained for other compositions also. The focal conic textures show that the composites retain the columnar hexagonal liquid crystalline phase. At high concentrations of HAnCl4 (for example, the 5 % HAnCl4/HAT6 composite), a phase separation was observed. We have noticed that higher concentration of HAnCl4 leads to the total disruption of the liquid crystalline order.
4.3.2.2 DSC Studies

The DSC traces as shown in Figure 4.14, show that the phase transition temperatures shift to lower temperature with increasing the dopant concentration. As expected, the enthalpy of the phase transition decreases as the dopant concentration increases. This is due to the fact that the dopants increase the entropy of the liquid crystalline phase and when its concentration is high, the liquid crystalline phase disrupts. Moreover, as the concentration of HAuCl₄ increases, the concentration of HAT₆ radical cation also correspondingly goes up, which weakens the \( \pi - \pi \) interaction within the column that acts as another major factor for the destabilisation of the liquid crystalline order. As clear from the figure, the enthalpies of phase transition is high for the pure HAT₆ and for the composites up to the concentration of 1 % HAuCl₄/HAT₆.

4.3.2.3 SAXS Studies

The liquid crystalline structure of the composites were further characterised by small-angle X-ray scattering (SAXS) studies. The studies were carried out in 0.7 mm diameter capillary tubes at 80 °C, while cooling from the isotropic phase. Figure 4.15 shows plot of intensity
vs. scattering vector for 0.1 % HAuCl₄/HAT6 and 1 % HAuCl₄/HAT6 composites. It is observed that the inter-columnar separation is not disturbed by the addition of the dopants at lower concentrations. The $d$ values were calculated from the SAXS pattern using the equation

$$d = \frac{2\pi}{q}$$

The $d$ values for the composites were similar to the values obtained for the pure HAT6 and with ferrocenium doping, which is already shown in the table 4.1. The $d$ values follow the ratio $1:(1/\sqrt{3}):(1/\sqrt{4})$ indicating that both the samples retain the columnar hexagonal order. It is clear that the addition of HAuCl₄ has not affected the $d$ values and the columnar arrangement at lower concentration of the dopants in accordance with the POM and DSC studies.

4.3.2.4 Spectral Studies

UV-visible absorbance studies of all the composites were carried out in dichloromethane medium with pure dichloromethane as the reference sample. Figure 4.16 shows the spectra of 0.1 %, 1 % and 5 % HAuCl₄/HAT6 composites. The peaks at 430 nm, 580 nm, 630 nm and 830 nm are clear and can be attributed to the presence of HAT6 radical cation formed by the oxidation of HAT6 by AuCl₄⁻ ions as shown below, which is similar to the oxidation of the discotic core by AlCl₃ reported earlier [45].

$$\text{AuCl}_4^- + 2(\text{HAT6}) \rightarrow \text{AuCl}_2^+ + 2(\text{HAT6})^+ + 2\text{Cl}^-$$

The spectral bands described above, have been attributed to the symmetrically allowed transitions in the discotic molecules [42]. A strong band was observed at 360 nm and another peak at 280 nm. The peak at 280 nm is assigned to the electronic transitions in pure HAT6 molecule corresponding to a band gap of about 4.4 eV. It may be noted that these composites have absorption throughout the visible range.

Both photoluminescence (PL) emission and excitation spectra of the composites were taken in dichloromethane medium. First the emission spectra were taken at an excitation wavelength of 360 nm which is the highest intensity peak in the UV-vis spectra for the pure HAT6. The PL emission spectra are shown in Figure 4.17. The emissions were observed at three wavelengths, 383 nm, 406 nm and 433 nm. The intensity among these three was found
Figure 4.15: Intensity vs. scattering vector plot from the small-angle X-ray scattering studies for a) HAT6 b) 0.1 % HAuCl₄/HAT6 and c) 1 % HAuCl₄/HAT6.

Figure 4.16: UV-visible spectra for the composites a) 0.1 % HAuCl₄/HAT6, b) 1 % HAuCl₄/HAT6 and c) 5 % HAuCl₄/HAT6. Absorbance is in arbitrary units.
to be highest for the 406 nm peak. The excitation spectra for the 406 nm band were taken and are shown in Figure 4.18. Three excitation wavelengths were observed at 361 nm, 353 nm, 340 nm and a weak shoulder band at 300 nm that correspond to a band gap of 3.43 eV, 3.51 eV, 3.64 eV and 4.08 eV. The peaks can be assigned to the \( S_0 \rightarrow S_1 \), \( S_0 \rightarrow S_2 \), \( S_0 \rightarrow S_3 \) and \( S_0 \rightarrow S_4 \) transitions. It has been shown that the photo-excitation spectral lines like \( S_0 \rightarrow S_1 \) and \( S_0 \rightarrow S_2 \) are symmetrically forbidden for the single discotic molecule, while the aggregation of the molecules makes them symmetrically allowed [51]. This indicates that there are small aggregates of the discotic molecules in the solution.

### 4.3.2.5 Conductivity Studies

Figure 4.19 shows the DC conductivity of the composites as a function of temperature while cooling from the isotropic phase. The electrical conductivity of pure HAT6 is about \( 10^{-12} \) S/m as mentioned in the previous section. The plots in Figure 4.19 show the variation of electrical conductivity with temperature for 0.1 % HAuCl₄/HAT6 and 1 % HAuCl₄/HAT6. It is observed that the conductivity increases by several orders of magnitude after the doping. This is similar to the ferrocenium composite with HAT6 which is explained in the previous section. It can be noted that there is a clear and significant change in the electrical conduc-
Figure 4.19: DC electrical conductivity plots for the composites a) 0.1 % HAuCl₄/HAT₆ and b) 1 % HAuCl₄/HAT₆ as a function of temperature

tivity at the temperatures corresponding to the phase transitions. The conductivity of the crystalline phase is very much lower than the columnar hexagonal phase. In the isotropic phase, the conductivity again decreases due to the disruption of the columns indicating that the major contribution of the conductivity comes from the columnar hexagonal order of the composites. Such a behavior has not been reported for the DC conductivity in the literature earlier.

Figure 4.20 shows the ac conductivity of the composites as a function of temperature. The ac conductivity values are higher than the corresponding DC conductivity values. It has been previously observed that the addition of dopants like AlCl₃ and iodine increases the ionic conductivity of the columnar phase by about million times [16; 34]. The present systems show a similar trend in ionic conductivity with a simultaneous enhancement in the DC conductivity. Figure 4.21 shows a frequency independent ionic conductivity in the lower region while at high frequencies it increases rapidly. The conductivity follows a \( \omega^{0.8} \) relation at high frequencies and this can be attributed to the hopping or tunneling mechanism of conductivity within the columns while the frequency-independent conductivity is attributed to the slowest transition rates due to the structural defects in the columns or hopping between different columns as discussed in section 4.1.1 [16; 35].

The DC conductivity enhancement can be attributed to the formation of radical cations with the retention of columnar phase that provides a facile transport of charge carriers along
the columns. The enhancement in the ac conductivity can be attributed either due to the
presence of ionic dopants or due to the formation of radical cations in the discotic matrix.
Previously, using AlCl₃/HAT6 composites, it has been proposed that the contribution of the
counter ions to the ionic conductivity will be very less compared to the electronic migra-
tions, since the counter ions will be almost frozen between the alkyl chains of the discotic
molecules [16]. We have observed that doping with FcTFB has not increased the ionic
conductivity even at higher concentrations of dopants even though they form charge-transfer
complex with the discotic molecules. In the present system, the dopants form charge-transfer
complex with the formation of radical cations of the discotic molecules. Comparing these
observations, the very high ionic conductivity of the present composites can be attributed to
the formation of HAT6 radical cations.

From the cyclic voltammetric studies as shown in Figure 4.12, the oxidation of HAT6 is
observed to be at -0.356 V while for gold it is at 0.64 V vs. ferrocene/ferrocenium reference
electrode. This shows that the formation of HAT6 radical cation is energetically favoured
due to the reduction of Au³⁺ to Au⁺ ions. On the other hand, the absence of any surface
plasmon band in the UV-vis spectra rules out the possibility of the complete reduction to
gold nanoparticles, even though small clusters of gold may be formed due to the aggregation
of gold atoms formed by disproportionating the Au⁺ ions.

The conductivity values of the HAuCl₄/HAT6 systems are comparable with conductivity
of HAT6 composites doped with ferrocenium ions as described in the previous section. The values are also comparable with discotic systems doped with gold nanoparticles [20; 21]. The DC conductivity of discotic systems can be attributed to either hopping mechanism or to the electron tunneling mechanism. Due to the facile formation of the radical cations of HAT6 and a weak temperature dependence on the conductivity in the liquid crystalline phase, we have concluded that hopping mechanism rather than electron tunneling mechanism is responsible for the DC conductivity in HAuCl₄/HAT6 composites [36].

The HAuCl₄/HAT6 composites in the columnar hexagonal phase show a high ionic conductivity that is comparable to the DC conductivity values. Systems with very high electronic and ionic conductivity may provide several promising advantages over systems with only electronic or ionic conductivity. The photon absorption of the present system in the full visible region makes it an interesting candidate for the solar cell applications. A higher absorption in the near IR region of the photons is more promising as the sun emits a major flux in this region, which increases the external quantum efficiency for the solar cell and photovoltaic device applications [52; 53; 54]. Since the high conductivity of the present system originates from the columnar arrangement present in the columnar hexagonal phase under normal conditions, the system may find diverse applications and overcomes the major disadvantage of the quenching of charge carriers by moisture as observed in many other discotic systems.
The increase in electrical conductivity of HAuCl₄/HAT6 systems after the addition of ferrocenium as well as tetrachloroaurate highlight several interesting aspects. They can be considered as model systems for the study of the interactions of donor-acceptor species. One can derive informations on interactions of other organometallic compounds in discotic systems, π–π interactions between donor-acceptor moieties, and similar interactions. In the present systems, the dopants occupy the interdomain spacing as confirmed by the SAXS studies, and in this way they differ from many of the other reported dopants such as iodine or potassium, which occupy the intercolumnar space [15; 50].

4.4 Electrical Conductivity Studies of Ionic Liquid Crystals

This section deals with the ionic conductivity studies of a series of pyridinium tethered triphenylene based discotic liquid crystalline compounds. Eventhough the discotic systems are quasi-one-dimensional conductors with very low conductivity in their pure state, the conductivity can be enhanced by the addition of dopants into the columnar matrix as described in the previous sections. Other approaches to increase the conductivity of these materials are i) attachment of donor or acceptor molecules that may form intra-molecular charge-transfer complexes with the discotic molecules or ii) attachment of ionic groups in the side chains. In this section, we describe the second approach for the preparation of highly conducting discotic phases. Kato et al. have studied a series of pyridinium substituted phenyl derivatives with different spacer groups [39; 55; 56; 57]. They have shown that these ionic liquids form columnar hexagonal phase over a wide range of temperature and have studied the quasi-one-dimensional conductivity as a function of temperature. These ionic liquids possess very high ionic conductivity that are in the order of 10⁻² S/m at temperatures close to the isotropic phase. The addition of LiBF₄ has shown to increase the $\sigma_\parallel$ without significantly increasing the $\sigma_\perp$, which indicates that the lithium ions have occupied the centre ionic part of the columns, that also enhanced the liquid crystalline order [39]. This effectively increases the anisotropy in the conductivity. Here we describe the ionic conductivity of a series of pyridinium substituted triphenylene based discotic ionic liquid crystalline materials.
4.4.1 Experimental Section

The pyridinium tethered triphenylene molecules were synthesised by S. Kumar et al. and the synthesis and phase behaviour of these molecules have been reported previously [58]. The structure of these molecules are shown in the Figure 4.22 with the following alkyl chain lengths:

- C4Py: R=C5H11; n=2
- C5Py: R=C5H11; n=3
- C6Py: R=C5H11; n=4
- C7Py: R=C5H11; n=5
- C11Py: R=C5H11; n=9

In these CnPy compounds, the spacer group between triphenylene and pyridinium group used was alkyl chain length (n) with 4,5,6,7 and 11 carbon atoms. All these molecules show columnar hexagonal phase. The phase behaviour of C5Py is as follows:

On heating: SS 75.7 (6.3) SS 96.2(5) Col 112.2 (2) col 121.2 (2.4) I
On cooling: I 118.7 (2.3) col 107.4 (2) Col

where SS = solid state Col=columnar phase and I=isotropic phase. For the ionic conductivity studies, the sample was inserted between two ITO coated glass plates. The thickness of these conductivity cells were \(~60 \, \mu m\) while the area was \(~10 \, mm \times 5 \, mm\). The sample was inserted into the cell at the isotropic phase by the capillary action. The cells were then cooled, connected with the electrical contacts and used for the conductivity measurements.
The ionic conductivity was measured using a temperature controller and a lock-in-amplifier (Stanford Research Systems, USA, model SRS 830) at 1 kHz frequency.

4.4.2 Results and Discussion

Figure 4.23 shows the plots of the variation of ionic conductivity with temperature for the above mentioned ionic liquid crystalline compounds. It is clear that the conductivity of these systems is very high in the liquid crystalline phase. In this phase, it can be seen that as the temperature increases, there is a sharp increase in the conductivity. The conductivity values are retained even in the isotropic phase. The conductivity of C4Py is less compared to the other homologous series. The conductivity is higher for C5Py especially in the columnar and isotropic phases. C6Py and C7Py shows very similar conductivity in the entire temperature range studied. For the C11Py with an alkyl spacer length of 11 carbon atoms, the conductivity decreases.

The samples C4Py and C5Py show a very high temperature dependent ionic conductivity in the liquid crystalline phase, which indicates a large contribution of electron mobility to the charge-migrations. The activation energy $E_a$ for the electron mobility was calculated using the equations $\sigma = ne\mu$ and

$$\mu = \mu_0 e^{-E_a/kT}$$

A linear fit of the observed values of conductivity vs. inverse of temperature provide an
$E_0$ value of 0.63 eV which is quite close to 0.5 eV as reported in the literature [39]. A higher value in the present system may be due to more substitutions in the side chains of the discotic core, which increases the core-core distance. In all other samples, the temperature dependence is less, which may be due to lesser involvement of electron mobility towards the charge-migration compared to the hole mobility. As the chain length increases, the core-core interaction decreases and the work function of the molecules increases. This increase in the lower electron mobility makes the electron tunneling process more difficult. This results in the lower electron mobility and the measured hole migration. Hopping conductivity may be favoured under such conditions through different vibrational couplings of the discotic molecules [16].

The conductivity increases with alkyl chain length of the spacer group from 4 to 7 carbon atoms while for C11Py with alkyl chain length of 11 carbon atoms, the conductivity decreases. It has been reported that the higher the chain length, the lower will be the core-core interaction since at higher core-core distance within a column there is more probability of defects in the stacking. This leads to a lower coupling strength between the cores, resulting in the decrease in conductivity. Moreover, the area occupied by each column on the surface will be more for molecules with higher chain length in the homeotropically aligned sample. This reduces the surface area available for the charge-injection to the discotic matrix, that contributes to a lower conductivity [36].

It is clear that the conductivity of these ionic liquids are several orders of magnitude higher than the same triphenylene cores without any pyridinium substitution. The conductivity of hexaalkoxytriphenylenes is of the order of $10^{-12}$ S/m while for the pyridinium tethered triphenylenes the conductivity is $10^{-6}$ S/m an enhancement by six orders of magnitude.

4.5 Conclusion

In this chapter, we have discussed the electrical conductivity studies of composites formed between discotic liquid crystals as donor and either ferrocenium tetrafluoroborate or chloroauric acid as dopants which act as acceptors. The presence of donor-acceptor pairs with the electron rich discotic molecules have been demonstrated. In the case of chloroauro-
rate, the dopants oxidises the triphenylene core to form HAT6 radical cations which is con-
firmed by the UV-visible spectroscopy and cyclic voltammetry. These radical cations show significant absorbance throughout the visible and near IR region, indicating that these composites may act as potential candidates for solar cell applications. Both the dopants enhance the DC electrical conductivity of the composites by several orders of magnitude as compared to the pure discotic system. Interestingly the chloroaurate complex enhances the ionic conductivity of the systems to almost the same extent as that of DC conductivity. Eventhough both the dopants, FcTFB and HAuCl₄ enhance the conductivity by several orders of magnitude, the concentration levels of both the dopants are different. Chloroaauric acid (HAuCl₄) is strong enough to enhance the conductivity even at a concentration as low as 0.1 % while 1 % FcTFB is necessary for a similar enhancement. It is also observed that even a 5 % doping of HAuCl₄ has an adverse effect on the phase behaviour of the discotic systems and therefore doping above this level has been found to disrupt the liquid crystalline phase. Doping with FcTFB, on the other hand, provides a better stability at least up to 10 %. Higher doping of FcTFB also results in the disruption of the liquid crystalline phase. The main reason for this behaviour is due to the fact that the HAuCl₄ is a more powerful oxidising agent than FcTFB, eventhough in both cases, the dopants form charge-transfer complexes with the discotic molecules, which is clear from the UV-visible spectral studies.

The ionic conductivity studies of the pyridinium tethered triphenylene based discotic liquid crystals have shown that the ac conductivity of these systems have been enhanced by several orders of magnitude as compared to the system without pyridinium moiety. This indicates that the ionic conductivity of the discotic systems can be enhanced by attaching ionic groups to the side chain of the aromatic core of the discotic molecules. The conductivity is shown to be due to electron mobility for lower chain lengths while for higher homologous series, hopping mechanism dominates.
Bibliography


