INTRODUCTION

The liquid crystalline state is an intermediate state of matter between that of a crystalline state with three-dimensional order and a completely disordered liquid state. When molecular crystals are heated to their melting point, they usually change directly into the liquid state. The periodic structures of the lattice as well as the orientational ordering of the molecules are destroyed simultaneously. However, if the constituent molecules have a pronounced anisotropy of shape, such as rod or disc, the melting of the lattice may precede the disappearance of the orientational ordering leading an intermediate phase composed of molecules which are more or less parallel to each other but at the same time exhibiting a certain degree of fluidity. The molecules can slide over one another while still preserving their parallelism. The fluid is therefore anisotropic; it is turbid and, like a crystal, shows optical birefringence and dielectric anisotropy. At a higher temperature, there is orientational melting and the anisotropic fluid transforms into the ordinary isotropic clear liquid. Such intermediate (or meso) phases are referred to as liquid crystals [1, 2]. They combine both, order and mobility. The fundamental requirement for any substance to exhibit a liquid crystalline phase is the shape anisotropy of the constituent molecules.

Liquid crystals are one of the most important families of materials in the general area of consumer electronics. They have found wide commercial applications in electro-optical display devices such as watches, calculators, telephones, personal organizers, laptop computers, etc. Such applications, which are numerous and varied, have been treated in a book series [1]. Among all types of liquid crystals, discotic liquid crystalline materials (disc-shaped) are of fundamental importance not only as models for the study of energy and charge migration in
organized systems but also as functional materials for device applications such as one-dimensional conductors, photoconductors, photovoltaic solar cells, etc. The negative birefringence films formed by polymerized nematic discotic liquid crystals have been commercialized as compensation foils to enlarge the viewing angle of commonly used twisted nematic liquid crystal displays.

This thesis deals with the synthesis and characterization of some novel liquid crystalline materials.

**CHALLENGES OF THIS THESIS**

Recently, soft materials have become more important as functional materials because of their dynamic nature. Although soft materials are not as highly durable as hard materials, such as metals, ceramics, and engineering plastics, they can respond well to stimuli and the environment. The introduction of order into soft materials induces new dynamic functions. Liquid crystals are ordered soft materials consisting of self-organized molecules and can potentially be used as new functional material for electron or ion transporting, sensory, catalytic, optical and bio-active materials. For this functionalization, unconventional materials design is required. In the past few years, besides the synthesis of new mesogens, molecular engineering of these unconventional liquid crystals such as, liquid crystalline dimers, oligomers and polymers has become increasingly important. These materials exhibit combination of macromolecular characteristics such as mechanical stability and ease of processability, with the anisotropic properties of low molar mass liquid crystals. Liquid crystalline oligomers and polymers have considerable application potential in a range of advanced electro-optic and semiconductor technology [3, 4].
However, the potential of these intriguing materials could not be fully explored primarily due to the difficulties in preparing functionalized liquid crystals [5, 6].

The focus of this thesis is mainly the preparation of a number of terminally functionalized calamitic and discotic molecules. These molecules have been used to prepare novel dimeric, oligomeric, polymeric and ionic liquid crystals. Ionic discotic liquid crystalline monomers, dimers and polymers based on triphenylene moiety have been studied extensively for the first time. Terminally thiol-functionalized calamitic and discotic molecules have been utilized to prepare self-assembled monolayers on gold and gold nanoparticles. Several rod-disc mesogenic liquid crystals have been synthesized to search the biaxiality in the nematic phase. A number of new derivatives of these molecules were prepared using classical and modern synthetic tools. All the synthesized materials have been characterized by nuclear magnetic resonance spectroscopy, ultraviolet spectroscopy, Infrared spectroscopy, elemental analysis, Polarizing optical microscopy, differential scanning calorimetry, X-ray diffractometry, transmission electron microscopy, scanning tunneling microscopy and atomic force microscopy.

Herein, this thesis describes new approaches to the functionalization of liquid crystals and show how the design of liquid crystals formed by supramolecular assembly and nano segregation leads to the formation of a variety of new self-organized functional materials. In what follows, we have briefly described some of the significant results and conclusions derived from our experimental work.

**CHAPTER 1**

This is an introductory chapter and mainly deals with the physical properties of discotic liquid crystals, making them ideal candidates for various optical and electronic devices such as photocopiers, laser printers, photovoltaic cells, light-emitting diodes, field effect transistors, and
holographic data storage. Beginning with an overview of liquid crystals, this chapter mainly focuses the description of major classes of mesophases formed by discotic liquid crystals, their efficient synthetic procedures, relevant mesomorphic and physical properties and finally, some applications and perspectives in materials science and molecular electronics.

CHAPTER 2
This chapter describes the synthesis and characterization of mesogens-decorated gold nanoparticles. Physical properties of nano-sized metal particles are very different from those of bulk material. For example, bulk gold is a very good conductor while GNPs of 1-2 nm size are only semiconducting. Recent advances in the chemistry of GNPs have generated a variety of organic-functionalized stable gold nanoparticles. These nanoparticles can be handled like simple organic materials. They can be dried of solvents and redissolved without core aggregation. Classical chemical reactions can be performed on functionalized gold nanoparticles. These organic-stabilized metal particles have potential applications in the field of catalysis, nonlinear optics, chemical and biological sensors, molecular recognition, nanotechnology, etc. A plethora of papers is available on the chemistry and physical properties of gold nanoparticles [7].

On the other hand, as described in the beginning, the dynamic properties of liquid crystals enable us to apply them not only to liquid crystal displays but also to various applications like optical switching, optical data storage, etc. Furthermore, the unique geometry of columnar mesophases formed by discotic liquid crystals is of great importance not only as models for the study of one-dimensional charge and energy migration in organized systems but also as functional materials for device application such as, one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, gas sensors, etc.
Hybridization of these two fields may lead to novel materials with interesting properties that will be useful for many device applications. With this in view, we have initiated this research programme to prepare gold nanoparticles covered with liquid crystalline materials by attaching thiol-terminated mesogens (both rod-shaped & disc-shaped) covalently to gold nanoparticles or by doping thiolate-protected gold nanoparticles in liquid crystalline medium. The challenge is to study and understand the soft self-assembly behaviour of nanoparticles functionalized with organic groups. Several parameters, like size of nanoparticles, shape of the nanoparticles, size of the attached organic molecules, shape of the attached molecules, number of attached molecules, characteristics of the attached molecules are very crucial in this self-assembly process. This chapter describes the influence of such parameters on the self-organization of gold nanoparticles wrapped with liquid crystals. The aim in this chapter is to provide a new resource of materials for applications in the nanosciences.

In this chapter, we describe the preparation of novel thiol functionalized alkoxycyanobiphenyls which have been used for the preparation of self-assembled monolayers (SAMs) on gold and gold nanoparticles (scheme 1). The chemical structures of these thiol-functionalized mesogens were characterized by $^1$H NMR, $^{13}$C NMR, IR, UV spectroscopy and elemental analysis. Their thermotropic liquid crystalline behaviour was investigated by polarizing optical microscopy, differential scanning calorimetry and X-ray diffractometry. Only the nematic phase was observed in all the members of the terminally thio-substituted cyanobiphenyl series. All the new thiol-terminated alkoxycyanobiphenyls form stable monolayers on gold surface and this has been studied through cyclic voltammetry and electrochemical impedance spectroscopy.

Gold nanoparticles fully covered with alkoxycyanobiphenyls (CNBP-GNPs) were characterized from $^1$H NMR, IR, UV and STM studies. The mean diameter of CNBP-GNP’s was
determined to be *ca.* 3 nm by STM measurement. The virgin CNBP-GNPs were found to be non-liquid crystalline.

This chapter also describes the inclusion of gold nanoparticles in the supramolecular order of discotic liquid crystals. This has been achieved via following three ways.

1. Mixing monolayer protected gold nanoparticles and discotic liquid crystals
2. Mixed monolayer: attaching thiol-functionalized discotic liquid crystals to gold nanoparticles using exchange reaction
3. Discotic liquid crystals protected gold nanoparticles
First, we have synthesized three types of discotic liquid crystals to prepare GNP-DLC composites. They are hexahexylthiotriphenylene (HHTT) 7 displaying a highly ordered helical phase at lower temperature in addition to a hexagonal columnar mesophase, Hexahexyloxytriphenylene (H6T) 8 having ordered hexagonal columnar mesophase and hexakis[4-(4-methylnonyl)phenylethynyl]benzene 9 showing a discotic nematic phase at room temperature. Binary mixtures of hexanethiol protected GNPs 10 with DLCs were prepared by sonicating the two components in dichloromethane followed by removal of solvent in vacuum. Four compositions (by weight) of GNP:HHTT (7a; 1:4; 7b; 1:3; 7c; 1:2; 7d; 1:1), Five compositions (by weight) of GNP:H6T (8a; 1:3; 8b; 1:2; 8c; 1:1; 8d; 2:1; and 8e; 3:1) and 1:1
mixture GNPs-9 (9a) were prepared and analyzed by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

In all the composites (7a-7d, 8a-8e) increasing the amount of GNPs decreases the mesophase to isotropic temperature but the crystals to mesophase or mesophase to mesophase (helical phase to columnar phase) temperatures do not change significantly. This is logical as GNPs are expected to disturb core-core interaction and, therefore, disruption of cores i.e., mesophase to isotropic temperature would be most affected. Phase segregation is also visible upon increasing the amount of GNPs. While H6T (also HHTT) and hexanethiol-protected nanoparticle composites show mesophase, a clear phase separation was observed in the case of discotic nematic-GNP (1:1) composite (9a). In the nematic phase, there is only an orientational order without any positional order of molecules and therefore, the molecular interactions are not sufficient to hold the gold nanoparticles. On the other hand, in the columnar phases, the π-π interactions between aromatic cores are strong, which are likely to be responsible for retaining the nanoparticles in the column.

The inclusion of gold nanoparticles in the matrix of discotic liquid crystals increases the conductivity of these composites. We have measured the DC conductivity of the HHTT and HHTT:GNPs (1:1) composite by a four point probe. The results indicate 250 times enhancement in the conductivity of HHTT upon doping with GNPs. A steady increase in the current was observed upon increasing the temperature in the nanocomposites.

Secondly, to prepare mixed monolayer with discotic liquid crystals we have first synthesized thiol-functionalized triphenylene 17 as shown below (scheme 2).
Mixed monolayer covered GNPs (Scheme 3, 18) were prepared by mixing 10 (5 mg) and 17 (5 mg) in dichloromethane followed by removal of solvent in vacuum. $^1$H NMR analysis of the product indicates the presence of triphenylene and hexanethiol moieties in 1:1 ratio.

Thirdly, gold nanoparticles fully covered with triphenylene-based discotic liquid crystals 19 were synthesized as shown in scheme 4 and dispersed in a columnar matrix. These discotic functionalized gold nanoparticles were found to be highly soluble in common organic solvents. $^1$HNMR, IR, UV spectra fully support the formation of triphenylene-capped gold nanoparticles. The size of the gold nanoparticles was obtained from its TEM image. A regular hexagonal self-
assembly can be seen in the TEM image. The triphenylene ligands play a crucial role in the self-assembly process.

Scheme 3

The virgin TP-GNPs were found to be non-liquid crystalline. However, their doping in columnar phase forming triphenylene-based DLCs does not disturb the nature of the mesophases. Binary mixtures of TP-GNPs and hexaheptyloxytriphenylene (H7TP) were prepared as follows. Three compositions (by weight) of TP-GNPs:H7TP (0.5% TP-GNPs, 1% TP-GNPS, 2% TP-GNPS) were prepared and the thermophysical properties of these nanocomposites studied using
polarizing optical microscopy, differential scanning calorimetry and small angle X-ray diffraction studies (SAXS), confirm their insertion into columnar matrix. The presence of gold nanoparticles in the triphenylene-based DLCs does not disturb the nature of the mesophase other than altering the transition temperatures. We propose that the gold nanoparticles are distributed between the domain gaps of the DLCs in random disordered manner. Interestingly, the DC conductivity measurements show an enhancement of the electrical conductivity by more than a million times upon doping of the discotic liquid crystals with the 1% triphenylene-capped nanoparticles under ambient conditions.

The dispersion of discotic-capped nanoparticles in the liquid crystalline matrix can provide a route for synthesizing similar other composites of varying properties that may find applications in many device developments.

**CHAPTER 3**

This chapter presents phase transitions in novel disulfide-bridged alkoxycyanobiphenyl dimers. Although the first examples of liquid crystalline dimers were reported by Vorlander in 1927 [8], they attracted particular attention during the 1980s. Griffin and Britt showed that a liquid crystalline dimer, a precursor to main chain polymeric liquid crystals, can be prepared by coupling two mesogenic units with an aliphatic spacer [9]. Subsequently, several classes of dimeric liquid crystals have been prepared and studied extensively [10]. The interest in these materials stems not only from their ability to act as model compounds for semi-flexible main chain liquid crystalline polymers but also from their quite different properties to conventional low molar mass mesogens [10]. Dimers containing two calamitic units show interesting mesomorphic behavior depending on the length of the spacer and structure of the linking group. For example, dimesogenic compounds having oligosiloxyl group form smectic mesophases
regardless of the nature of the terminal substituent whereas same type of compounds having methylene spacer form only nematic phases [11, 12]. An ether linkage between the mesogenic unit and the central polymethylene spacer usually produce nematogens whereas ester linkage induces smectogenic properties in the system [12]. Effects of methylene, ethylene oxide and siloxane spacers on mesomorphic properties of symmetrical as well as unsymmetrical liquid crystalline dimers containing alkoxy cyanobiphenyl have been studied by Creed et al. [13].

The formation of self-assembled monolayers (SAMs) by thiols, disulfides and thioethers on metals, particularly on gold, is well documented. SAMs provide a convenient, flexible and simple system for studies in nanoscience and nanotechnology. A variety of thiols and disulfides have been used to prepare SAMs [14]. Literature survey reveals that while disulfide-bridged discotic dimers have been synthesized and used to prepare SAMs, alkoxy cyanobiphenyl-based calamitic dimesogenic compounds having disulfide-bridge in the linking unit have not yet been explored. In chapter 2 we have described the synthesis and characterization of mesogenic thiol-functionalized alkoxy cyanobiphenyles and their self-assembled monolayers on gold. In order to study the effect of sulfur atoms in linking unit on mesomorphism and SAMs, we prepared the first examples of disulfide-bridged mesogenic alkoxy cyanobiphenyl dimers. Their synthesis and mesomorphic behaviour is described in this chapter. The synthesis of disulfide-bridged alkoxy cyanobiphenyl 5 is outlined in scheme 5.

All the chemical structures of the disulfide-bridged alkoxy cyanobiphenyl dimers 5 were confirmed by \(^1\)H NMR, \(^{13}\)C NMR, IR, UV spectroscopy and elemental analysis. The thermal behaviour of these mesogens was investigated by polarizing optical microscopy, differential scanning calorimetry and X-ray diffractometry. The dimers with a shorter spacer exhibit only the nematic phase while dimers with a longer spacer display nematic as well as smectic phases. X-
Ray diffraction experiments reveal the intercalated structure of the SmA phase of these dimers and the presence of short range SmA-like order in the N phase (cybotactic nematic) of all the compounds, except the one with the shortest spacer.

\[ \text{Scheme 5} \]

**CHAPTER 4**

This chapter focused the synthesis, characterization and mesomorphic properties of novel triphenylene-based ionic discotic liquid crystals. As mentioned in the introduction, discotic liquid crystals are renowned for their one-dimensional transportation of charge, ion and energy. On the other hand ionic liquids [15] are functional isotropic liquids exhibiting high ionic conductivity. Recently, they have been intensively investigated based on their remarkable properties such as chemical stability, incombustibility, non-volatility etc. Hybridization of self-organizing triphenylene discotics with imidazolium and pyridinium ionic liquids may lead to novel materials with interesting properties that are useful for many device applications. With this in mind we have initiated this research program to incorporate imidazolium-based and
pyridinium-based ionic liquids in the supramolecular order of discotic liquid crystals by attaching triphenylene discotics covalently to the imidazolium and pyridinium salts and study the effects of counter ions, spacers and peripheral substitution in these materials. The design strategy here is to modify ionic liquids to prepare simpler columnar assemblies that exhibit fluid ordered states, maintaining both of high ionic conductivities and liquid crystalline states at reasonable temperature ranges. In this chapter we describe the synthesis of novel pyridinium and imidazolium bromides containing hexaalkoxytriphenylene units and their thermotropic liquid crystalline properties. The synthesis of triphenylene substituted pyridinium and imidazolium salts is outlined in scheme 6 and 7 respectively.

All the pyridinium and imidazolium salts were purified by repeated recrystallisation and isolated as solids or semi-solids upon the addition of diethyl ether to the solution of pure material. They were filtered, washed with cold dry ether and dried under high vacuum for longer time. All the final compounds and their intermediates were characterized from their $^1$H NMR, $^{13}$C NMR, IR, UV-vis, and elemental analysis. The thermophysical properties of all pyridinium and imidazolium ionic salts were investigated through polarizing optical microscopy, differential scanning calorimetry and X-ray diffractometry. Increasing the number of carbon atoms on the peripheral chains of the triphenylene core stabilized the columnar phase while increasing the spacer length connecting the triphenylene unit with the pyridine moiety destabilized the mesophase. The variation of counter ion from Br$^-$ to BF$_4^-$ destroys the liquid crystalline property of these salts. These are the first known thermotropic ionic liquid crystals based on triphenylene. These salts are not only important for a new possibility of organic molten salts in materials science, but also contribute to the development of novel anisotropic soft materials for directional ion conductivity and charge transport.
Scheme 6
Chapter 5 addresses the chemistry of novel triphenylene-based ionic discotic liquid crystalline dimers and polymers. One of the recent advances in the molecular electronics is to search for the elusive ion-conductive materials, to be used at a molecular level, for which the ion conductivity should be anisotropic, which means that the ion conductivity depends on the direction in which it is measured. Ionic liquid crystals [16] are the most promising candidates to design anisotropic ion-conductive materials because they have an anisotropic structural organization and also they
contain ions as charge carriers. Moreover, the long alkyl chains of mesogenic molecules can act as an insulating sheet for the ion conductive channel. Liquid crystals with a columnar mesophase can be used to prepare a material for one dimensional ion-conduction. Triphenylene derivatives are the archetypal discotic liquid crystals. Highly ordered columnar mesophase formed by triphenylene-based ionic liquid crystals [17] may give a high anisotropy of the system which may be responsible for tremendous ion conduction. Obviously, they will be the good candidates in molecular electronics. To make these types of materials on the basis of ionic liquid crystals that keep their anisotropic ion conductivity for a long time it is necessary to stabilize the ordered molecular arrangement of the liquid crystalline monodomain. Ionic dimeric and polymeric liquid crystals are the representatives of this type of systems.

To the best of our knowledge ionic liquid crystalline dimers based on imidazolium moiety containing two mesogenic groups and ionic discotic liquid crystalline polymers based on triphenylene has not yet been explored in literature. Hybridisation (scheme 8) of two different types of mesogens with imidazolium moiety may lead to novel materials with interesting properties.

Scheme 8
With this in mind, we have initiated this research programme to incorporate imidazolium-based ionic liquids in the supramolecular order of calamitic and discotic liquid crystals by attaching two calamitic, two discotic and hybrid of both the moieties, to imidazole. Microwave dielectric heating was used to prepare these dimers. The quaternization of imidazole-substituted mesogens under classical reaction conditions failed to produce the desired quaternary salts. Similarly, we have prepared ionic discotic polymer for the first time which is very useful for unidirectional transport of ion and energy at nanoscale. This chapter describes the synthesis, characterization and thermal properties of these dimers and polymers. The synthesis of calamic-calamitic ionic dimers is shown in Scheme 9 whereas calamitic-discotic and discotic-discotic ionic dimers are presented in Scheme 10. Polarizing optical microscopy and X-ray diffraction experiments showed smectic and columnar phases of the calamitic-calamitic and discotic-discotic hybrids, respectively.

In the second portion of this chapter we describe novel imidazolium-based ionic discotic liquid crystalline polymers. The chemical structure of the polymer 14 was characterized by $^1$H NMR, IR, and GPC. The thermotropic liquid crystalline behaviour was investigated from POM, DSC, and X-ray diffractometry. X-ray diffraction study indicates the columnar order is small in the polymer compare to monomer. GPC showed that the polymer is actually a mixture of low molecular weight oligomers. Such ionic discotic polymers are not only important as polymeric molten salts in materials science, but also contribute to the development of novel anisotropic soft materials for directional ion conductivity and charge transport. The chemical synthesis is outline in scheme 11.
Scheme 9

5a: n = m = 7
5b: n = 7, m = 2
5c: n = 7, m = 4
5d: n = 7, m = 8

Scheme 10

9: n = 4, R = C4H9
This chapter discusses microwave-assisted synthesis of novel rufigallol-based rod-disc mesogens. One of the most active areas of research in liquid crystal science in recent years has been the search for the elusive biaxial nematic phase, where the unique axes of the molecules arranged not only in a common direction (known as director) but also there is a correlation of the molecules in a direction perpendicular to the director \[1^{18}\]. Theoretical studies have shown that mixtures of rods and discs can exhibit the biaxial nematic phase in which long axes of the rods arranged perpendicularly to the short axes of the discs and hence, the system has two directors \[1^{19}\]. In these simulations an attractive interaction is required between the rods and discs to prevent phase separation into two uniaxial nematic phases and in real systems phase separation
does indeed occur. To overcome this difficulty a number of authors have attached rod-like and
disc-like units via flexible alkyl spacers. In all these systems one, two or three rods have been
attached to a single disc. We have extended this approach and report here the synthesis and
characterization of a series of molecules in which one, two, four, five and six rod like
cyanobiphenyl moieties are attached to a central rufgallol core via flexible alkyl spacers.
(Scheme 12). Synthesis, characterization and thermal behavior of these discotic-calamitic
hybrids are presented in this chapter.

\[ \text{Scheme 12} \]

\[ \text{a: } R = R_2 = C_{n}H_{2n+1}, R_1 = X \]
\[ \text{b: } R = C_{n}H_{2n+1}, R_1 = R_2 = X \]
\[ \text{c: } R_1 = R_2 = H, \ R = X \]
\[ \text{d: } R_1 = H, \ R = R_2 = X \]
\[ \text{e: } R_1 = R = R_2 = X \]

\text{CHAPTER 7}

The thesis is concluded with a chapter, which summarizes results presented in all the above
chapters. Some of these results have been published/communicated in the following international
journals.

with a triphenylene moiety

[2] Ionic discotic liquid crystals: synthesis and characterization of pyridinium bromides
containing a triphenylene core
[3] The first examples of terminally thiol-functionalized alkoxycyanobiphenyls

[4] Discotic-decorated gold nanoparticles


[6] Self-assembled monolayers (SAMs) of alkoxycyanobiphenyl thiols on gold-A study of
electron transfer reaction using cyclic voltammetry and electrochemical impedance spectroscopy

and their insertion into a columnar matrix

[8] Synthesis of monohydroxy-functionalized triphenylene discotics: green chemistry approach

[9] Phase transitions in novel disulphide-bridged alkoxycyanobiphenyl dimers
(This work has been featured on the cover page of the journal)

[10] Dispersion of thiol stabilized gold nanoparticles in lyotropic liquid crystalline systems

[11] Self-assembled monolayers (SAMs) of alkoxycyanobiphenyl thiols on gold surface using
a lyotropic liquid crystalline medium

[12] Twist Viscoelastic coefficient of novel thiol terminated alkoxy cyanobiphenyl nematic liquid crystals

[13] Films of novel mesogenic molecules at air-water and air-solid interfaces

[14] Green chemistry approach to the synthesis of liquid crystalline materials


[16] Novel triphenylene-based ionic discotic liquid crystalline polymers (Communicated).

**REFERENCES**


Signature of the Research Fellow

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