Synopsis

Synthesis and Characterization of some Non-conventional Discotic Liquid Crystals

Introduction

Liquid crystals form a distinctive state of matter. Liquid crystals are considered as the fourth state of matter after solid, liquid and gas. Between the crystalline solid and isotropic liquid phases, some compounds demonstrate a distinctly different, intermediate state, also referred to as the fourth state of matter, or the mesophase (i.e. intermediate phase). They are unique functional soft materials combining both order and mobility on molecular, supramolecular and macroscopic levels. This is a true thermodynamic stable state of matter. The constituent which is responsible for mesophase formation is called mesogen. Mesogens can be organic (forming thermotropic and lyotropic phases), inorganic (metal oxides forming lyotropic phases) or organometallic (metallomesogens).

Liquid crystals are important in material science as well as in life science. Important applications of thermotropic LCs are electrooptic displays, temperature sensors and selective reflecting pigments. Lyotropic systems are used in cleaning process, and are important in cosmetic industries. They are used as templates for the preparation of mesoporous materials and serve as model systems for biomembranes. Lyotropic LCs are important in living matter also. Most important are the biological membranes. DNA can also form lyotropic mesophase.

Anisotropic fluid states of rigid polymers are used for processing of high strength fibers like Kevlar. LCs can potentially be used as new functional materials for electron, ion, molecular transporting, and sensory, catalytic, optical and bio-active materials. LCs are extremely diverse since they range from DNA to high strength synthetic polymers like Kevlar (used for bullet-proof vests, protective clothing, high performance composites for aircraft and automotive industries) and from small organic molecules like alkyl and alkoxy cyanobiphenyls used in liquid crystal displays (LCDs) to self-assembling amphiphilic soap molecules. Recently their biomedical applications such as in controlled drug delivery, protein binding, phospholipid labeling, and in microbe detection have been demonstrated. Apart from material science and bio-science, LCs are now playing significant role in nanoscience and nanotechnology such as synthesis of nanomaterials using LCs as template, the design of LC nanomaterials, alignment and self assembly of nanomaterials using LC phases and so on. Owing to their dynamic nature, photochemically, thermally or mechanically induced structure changes of liquid crystals can be used for the construction of stimuli-responsive materials. Although LCs have diverse applications such as temperature sensing, solvents in chemical reactions, in chromatography, in spectroscopy, in holography, etc., they are primarily known for their extensive exploitation in electrooptical display devices such as watches, calculators, telephones, personal organizers, laptop computers, flat panel television etc.

The geometric shape anisotropy of the constituent moiety, interaction anisotropy and microsegregation of the mismatching molecular parts are elementary necessities for any substance to exhibit mesomorphism. In the mesophase the molecules move all over the sample, at the same time they maintain short-ranged positional and/or orientational order. The ability of the molecules to move among the various lattice sites imparts fluidity to these structures, but since all directions within the phase are not identical, they are anisotropic rather than isotropic fluids. So liquid crystals combine the anisotropic properties of solids and fluidity of liquids.

Discotic liquid crystals are composed of rigid core which is surrounded by three or more flexible aliphatic chains. Any type of change in the rigid core and peripheral flexible chains controls their self-assembly in bulk as well as in solution. It is fairly understandable that discotic liquid crystals cannot compete with their calamitic counterparts in terms of electrooptic
Among all types of liquid crystals, discotic liquid crystalline materials are of fundamental importance not only as models for the study of energy and charge migration in self-organized systems but also as functional materials for device applications such as one-dimensional conductors, photoconductors, photovoltaic solar cells, light emitting diodes, gas sensors, thin film transistors 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.

One can get materials of interesting properties by combining more than one contrasting or different functionalities within a molecule. The structure and property of these materials deviate from ordinary or conventional LCs. These type of liquid crystals are called “Non-conventional liquid crystals”. A lot of combinations are possible e.g. thermotropic/lyotropic, hydrophilic/hydrophobic, non-polar/polar, hydrocarbon/fluorocarbon, rigid/flexible, disc/rod, electron donor/electron acceptor, mesogenic/dimeric, mesogenic/oligomeric, mesogenic/polymeric etc. Non-conventional mesogens bridge the gap between entirely different chemical or physical properties. The detailed study of novel non-conventional materials may result in knowledge about novel liquid crystalline phases and deeper insights in the driving forces of their self-organisation. It is well known that anisotropic molecular shape and space filling play vital role in self assembly of mesogens. However, nanoscale segregation of irreconcilable molecular parts i.e. micro segregation has also been realized to play an
important role in mesogenic self assembly, resulting in to new mesophase morphologies.\textsuperscript{7,8} On account of their astonishing self-assembly into complex soft materials, non-conventional liquid crystals are of massive interest at present.

This thesis deals with the synthesis and characterization of novel non-conventional mesogenic materials varying from imidazole-fused triphenylene discotics, triphenylene-benzene-based dimers to triphenylene-anthraquinone-triphenylene based trimers and materials for organic electronics, using traditional as well as modern synthetic methods (microwave heating). The thesis work spans across monomeric to trimeric discotic liquid crystals via monodisperse dimers, gemini discotic amphiphiles pure liquid crystalline compounds and composites, discotic liquid crystals with conventional and unconventional mesophase structures and room-temperature discotic liquid crystals with broad mesophase range and single mesophase structure with different electronic (electron rich or p-type and electron deficient or n-type) properties. A non-conventional approach has been applied to study the outcome of hybridization of more than one interesting and contrasting properties within a single system. All the synthesized materials have been characterized by nuclear magnetic resonance spectroscopy (NMR), ultraviolet spectroscopy (UV), infrared spectroscopy (IR), mass spectrometry (MS, HRMS, MALDI-ESI, MALDI-MS), elemental analysis, polarizing optical microscopy (POM), differential scanning calorimetry (DSC), X-ray diffractometry (XRD), scanning tunneling microscopy (STM) and conductivity studies etc.

Herein, this thesis describes new approaches to functional non-conventional discotic liquid crystals and shows how the molecular engineering of liquid crystals leads to the formation of a variety of new self-organized soft and nano 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 to liquid crystals in general like their classification and their important significance in material science, life science, nanoscience and their dominance in electrooptical display devices. The chapter focuses in greater detail on the physical properties of discotic liquid crystals, making them ideal candidates for various optical and electronic devices such as optical compensation films, photocopiers, laser printers, photovoltaic cells, light emitting diodes, field effect transistors, gas sensors and holographic data storage.\textsuperscript{9} Beginning with an overview of thermotropic liquid crystals and their brief history, this chapter mainly focuses the major classes of columnar mesophases formed by discotic liquid crystals, their efficient and elegant synthetic procedures, photo and electrical conductivity, macroscopic alignment of columnar phases, relevant mesomorphic and physical properties and finally, some applications and perspectives in material science, nanoscience and molecular electronics.

CHAPTER 2

This chapter describes a non-conventional approach to the synthesis of liquid crystalline materials. Here, we have adopted two main themes of dimer preparation; one is the effect of \textit{flexible-rigid}-mixed spacer and the other is relative orientation of mesogenic groups on the mesomorphic properties. The length of methylene spacer and the type of linkage group has also been varied in order to examine the structure–property relationships (Scheme 1 & 2).

Scheme 1. Synthetic route for dimers of ester series.
Scheme 2. Synthetic route for dimers of ether series.

Flexibility of methylene spacer gets disturbed due to the insertion of benzene ring in the spacer and finally stacking of triphenylene cores become difficult. As a consequence of the above phenomenon these dimers were non-mesomorphic but on doping with TNF, an electron acceptor, they gave a hexagonal columnar phase with distinct optical texture, which was further confirmed by X-ray diffraction.
CHAPTER 3

With their inimitable set of properties not attainable by other materials, ionic liquids have gained awesome interest over the past years. This opens up opportunities in a great variety of industrial applications. Ionic liquid crystals are the result of hybridization between liquid crystals and ionic liquids. These materials combine the properties of liquid crystals and ionic liquids. Some of the properties of the ionic liquid crystal differ considerably from that of conventional liquid crystals because of ionic property. Ionic conductivity is typical behaviour of ionic liquid crystals. Considerable research effort is currently being focused on the interplay between ionic conduction property of ionic liquids and anisotropic behavior of liquid crystals. Ionic molecules are known to form amphitropic liquid crystals.

Chapter 3 deals with a non-conventional approach towards mesomorphic imidazolium/ammonium salts. This discusses synthesis and liquid crystalline behavior of the first example of novel liquid crystalline discotic gemini amphiphiles. The initial part of the chapter deals with triphenylene-imidazole-imidazole-triphenylene based gemini salts with bromide as counter ion. A series of six compounds has been synthesized with the help of microwave dielectric heating (Scheme 1).

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Scheme 1. Synthesis of triphenylene-imidazole-based ionic dimmers. (i) Br(CH\(_2\))\(_n\)Br, NaH, DMF; (ii) N-methylpyrrolidone, microwaves.

Their mesomorphic properties have been investigated with the help of DSC, POM and XRD. Out of the six gemini salts, four display hexagonal columnar phase over a wide range of temperature. Shorter spacer length is in favor of liquid crystalline property in these symmetrical gemini dimers. Ac conductivity of some of these dimers in their liquid crystalline temperature range was found to be in the range of 10\(^{-6}\) to 10\(^{-5}\) S/m. The direct current photo conductivity was also measured and was of the order of 10\(^{-4}\) S/m. The synthesized gemini dimers tend to form monolayer at the air-water interface.

The later part of the chapter deals with non-conventional approach to incorporate ammonium-based gemini amphiphiles in the supramolecular order of discotic liquid crystals by attaching two triphenylene moieties to diammonium. The synthesis and characterization of a series of two novel triphenylene-ammonium-ammonium-triphenylene diads consisting of two ammonium moieties as lyotropic ionic part, connected with two thermotropic triphenylenes via methylene spacer has been described here (Scheme 2). The peripheral chain length around triphenylene and the length of linker connecting triphenylene with ammonium moiety have been varied.
Scheme 2. Synthesis of triphenylene-ammonium-based ionic dimers. (i) Toluene, 80 °C, 48 hrs; (ii) NaBF$_4$, 10% aq Methanol, rt, 3 hrs.

The chemical structure of these two compounds was confirmed by $^1$H NMR, $^{13}$C NMR, MS and elemental analysis. The mesophase behavior of these two compounds was examined by POM and DSC. The mesophase structure was established by XRD. Both gemini discotic salts were identified to exhibit hexagonal columnar phase. A combination of longer spacer connecting triphenylene to ammonium part and longer peripheral alkyl chain length around triphenylene is in favour of liquid crystallinity in this system.

As expected, the intercolumnar distance increases on increasing the spacer length. Study of such kind of thermotropic-lyotropic hybrid systems provides greater insight into the subtle intra and intermolecular interactions involved in the self-assembling process of soft condensed matter.
CHAPTER 4

Rufigallol is a molecule of both biological and materials science interest. Rufigallol derivatives are one of the most primitive systems accounted to form columnar mesophases. Elongated core with a 2-fold symmetry axis, coloured in appearance, existence of important polymorphism, thermal stability of the core and fairly easy chemistry of the core make rufigallol a fascinating material. Additionally, by the virtue of quinonoid ring in the center, the anthraquinone skeleton is electron-deficient in nature. The importance of anthraquinone skeleton in liquid crystal field gets significance because of the fact that most of the discotic liquid crystals are made of electron rich (p-type) cores and only a few electron deficient (n-type) discotics are known. A careful literature survey of liquid crystals constructed from discotic compounds reveals that unexpectedly very little work has been focused on rufigallol core. Recently there have been tremendous efforts to achieve both p-type (hole conducting) and n-type (electron conducting) properties in organic semiconducting materials which are crucial for molecular electronics. One elegant approach for such materials is to covalently link electron donor and electron acceptor components at molecular level. These kinds of materials are expected to behave as intrinsic, non-composite p/n-type semiconductors.

Chapter 4 describes microwave assisted facile synthesis of triphenylene-anthraquinone-triphenylene based symmetrical liquid crystalline trimers. Our molecular design is such that it contains the well studied electron rich triphenylene moiety and electron deficient

\[ 13 \text{ S. Kumar, Phase Transitions, 81, 113, 2008.} \]
anthraquinone\textsuperscript{9} as the hole and electron transporting components, respectively. Stacking of similar core one on the top of other results in formation of molecular wire which may play an important role in design of electronic devices. These molecular double-cables, owing to their incommensurate core sizes, may stack one on top of the other in the columns to give columnar versions of double cable polymers,\textsuperscript{14} which could eventually provide side-by-side percolation pathways for electrons and holes in solar cells. To the best of our knowledge, these are the first donor-acceptor-donor triads in which all the three components represent discotic mesogenic moiety. All attempts to etherify the intramolecularly hydrogen bonded C-1 and C-5 positions with bulky ω-bromo-substituted triphenylene were failed under classical thermal heating conditions even by using strong basic conditions and prolonged reaction times (Scheme 1).

Scheme 1: Synthesis of triphenylene-anthraquinone triads. (i) Cs\(_2\)CO\(_3\), NMP, MW. TATa Series (n = 12): OR = H (TATa0); R = n-C\(_6\)H\(_{13}\) (TATa6); R = n-C\(_7\)H\(_{15}\) (TATa7); R = n-C\(_8\)H\(_{17}\) (TATa8); R = n-C\(_{10}\)H\(_{21}\) (TATa10); R = 3,7-dimethyloctyl (TATa10'); R = n-C\(_{14}\)H\(_{29}\) (TATa14); TATb Series (n = 10): R = n-C\(_6\)H\(_{13}\) (TATb6); R = n-C\(_7\)H\(_{15}\) (TATb7); R = n-C\(_{10}\)H\(_{21}\) (TATb10); R = 3,7-dimethyloctyl (TATb10'); R = n-C\(_{12}\)H\(_{25}\) (TATb12); R = n-C\(_{14}\)H\(_{29}\) (TATb14).

Mesophase behavior of the symmetrical trimers was studied by polarizing optical microscopy and differential scanning calorimetry. They exhibit columnar mesophase over a wide range of temperature. Hexagonal columnar structure of the mesophase of these donor-acceptor-donor triads was established by X-ray diffraction studies. Longer spacer length,
smaller peripheral alkyl chain length and branching in peripheral alkyl chain of anthraquinone are in favor of liquid crystalline property in these symmetrical trimers.

CHAPTER 5

It is possible to have broad mesophase range as well as improved conductivity by a suitable balance between the size of rigid discotic core and peripheral insulating chains. This small chapter tells about unsymmetrical examples of triphenylene-imidazole-fused derivatived for the effect of extention of discotic core on the mesomorphic behavior and charge carrier mobility in their liquid crystalline phase.

Molecular shape is one of the most imperative factors which determines the self-assembly of molecules into mesomorphic phases. Expansion of triphenylene ring is expected to lead to dramatic changes in phase behaviour, since the extension of aromatic ring would, in effect, give rise to a mesogen with a core that is both much larger and of a different shape. These supramolecular macro discotics are anticipated to be mesomorphic over broad temperature ranges\textsuperscript{15} and exhibit high charge carrier mobilities\textsuperscript{16} in their columnar phases. Hydrogen bonding caused by imidazole ring plays an important role in the formation of supramolecular mesomorphic aggregates. Imidazole moiety functions both as proton donor as well as proton acceptor.\textsuperscript{17} There have been reports of design and construction of supramolecular mesomorphic assembly on the basis of imidazole moiety.\textsuperscript{18} However, most of the liquid crystalline materials based on imidazole skeleton come from the category of ionic.

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liquids, the mesomorphic materials based on molecular imidazole derivatives have been less investigated.

Chapter 5 depicts the extension of triphenylene ring with nitrogen containing heterocycle i.e. imidazole. We adopted this approach to increase π-electron conjugation as well as to reduce overall symmetry of triphenylene ring. We discuss the synthesis, characterization and mesomorphism of novel triphenylene-imidazole-fused mesogens. The number peripheral alkyl chains around triphenylene have been varied between 5 and 6.

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\begin{align*}
6TPOH & \quad \text{(i)} \quad \text{CAN, CH}_3\text{CN, rt, 2 min (yield = 65.33 %)}; \\
6TPCO2 & \quad \text{(ii)} \quad \text{R'CHO, CH}_3\text{COONH}_4, \text{CH}_3\text{COOH, refluxed, 5 hrs (yield = 26.69 %)}. \\
\end{align*}
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Scheme 1. Synthesis of triphenylene-imidazole-fused mesogens. (i) CAN, CH\textsubscript{3}CN, rt, 2 min (yield = 65.33 %); (ii) R'CHO, CH\textsubscript{3}COONH\textsubscript{4}, CH\textsubscript{3}COOH, refluxed, 5 hrs (yield = 26.69 %).

The chemical structure of both compounds was confirmed by $^1$H NMR, UV spectra, MS and elemental analysis. The mesomorphic behaviour of these two triphenylene-imidazole-fused unsymmetrical derivatives was confirmed by polarizing optical microscopy and differential scanning calorimetry. They exhibit columnar mesophase over a wide range of temperature. Hexagonal columnar structure of the mesophase of these compounds was recognized by X-ray diffraction studies. Addition of one alkyl chain to the periphery of non-conventional triphenylene core (compare 6TPIM\textsubscript{6} vs 6TPIM\textsubscript{0}) results in expansion of hexagonal columnar lattice. We observed reasonable increment in mesophase range and improvement in DC electrical and DC photoconductivity after fusion of triphenylene ring with imidazole nucleus.
CHAPTER 6

The thesis is concluded with a chapter, which summarizes some the important results and conclusions derived from this thesis work, which deals with ‘synthesis and characterization of some non-conventional discotic liquid crystals’. We briefly discuss the diverse possibilities and scope for future work based on the results obtained from our experimental work.

Some of the findings of this thesis have been published/communicated in the following international journals.

1. The first examples of discotic liquid crystalline gemini surfactants,
   Sandeep Kumar, Satyam Kumar Gupta.

2. Novel Benzene-Bridged Triphenylene-Based Discotic Dyads,
   Satyam Kumar Gupta, V. A. Raghunathan, V. Lakshminarayanan, and Sandeep Kumar.

3. Microwave-assisted facile synthesis of discotic liquid crystalline symmetrical donor–acceptor–donor triads,
   New J. Chem., 2009, 33, 112–118,
   Satyam Kumar Gupta, V. A. Raghunathan and Sandeep Kumar.

4. Stress-strain relation in the collapse of Langmuir monolayer of a dimer of disk shaped moiety,
   The Journal of Chemical Physics 133, 044701-2010,
Bharat Kumar, K. A. Suresh, **Satyam K. Gupta** and Sandeep Kumar.

5. **Popular article**

Hot Article: **Microwaves only for novel discotic LC trimers** [NJC News]

**Satyam Kumar Gupta**, V. A. Raghunathan, Sandeep Kumar,

New J. Chem., 2008,


DOI: 10.1039/b808750d

6. Novel imidazole-fused triphenylene discotics,

Manuscript under preparation,

**Satyam Kumar Gupta** and Sandeep Kumar.

7. Synthesis and chemistry of triphenylene-ammonium-ammonium-triphenylene diads,

Manuscript under preparation,

**Satyam Kumar Gupta** and Sandeep Kumar.

Signature of the Research Fellow
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Synthesis and Characterization of Novel Discotic Liquid Crystal Porphyrins for Organic Photovoltaics. Xiaoli Zhou. Quan Li.Â Mechanic and Electro-Optical Properties of Non-conventional Liquid Crystal Systems. Guangxun Liao. Antal Jakli.Â Liquid Crystals Containing the Dibenzopyran Nucleus: Synthesis and Mesomorphic Properties of 3-(4-n-Alkoxybenzylidene-amino) Dibenzo[b,d]Pyran. Sundar Subramanyam. Derry Fishel. New ionic and polymerizable discotic liquid crystals based on the commercial dye tetraazaporphyrin are presented in Chapters 4 and 5. Both areas have been given little attention despite their importance for the preparation of stable films for devices. Tetraazaporphyrins containing azide and acetylene groups at the end of aliphatic spacers have been prepared and crossâ€linked by cycloaddition (click chemistry). Some derivatives form columnar mesophases and could be thermally crossâ€linked in their columnar mesophase and their copper catalyzed crossâ€linking in Langmuir and Langmuir-Blodgett layers...Â 6 1.6 Characterization of Discotic Liquid Crystalline Phases . Discotic liquid crystals compounds. Ali H Dawood* and Nasreen R Jber. Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq. INTRODUCTION. Liquid crystal is a state of matter in which the. degree of molecular order is intermediate. between the perfect three dimensional, long-. range positional and orientational order found. in solid crystals and the absence of long-range. order found in isotropic liquids, gases, and. amorphous solids. Recommended Citation. Li, Yuzhan, "Synthesis and characterization of liquid crystalline epoxy resins" (2014). Graduate Theses and Dissertations.Â Liquid crystalline epoxy resins (LCERs) are a unique class of thermosetting materials formed upon curing of low molecular weight, rigid rod epoxy monomers, resulting in the retention of a liquid crystalline (LC) phase by the three dimensional networks. LCERs exhibit a polydomain structure, thereby combining the outstanding properties of liquid crystals and thermosets.Â In addition, liquid crystals possess properties that can be controlled by external fields, greatly improving the design flexibility. These attractive features make LCERs good candidates for polymer matrices in high performance composites.