SYNOPSIS

Synthesis and Characterization of Some Discotic Amphiphiles

Self-assembly is the spontaneous organization of building blocks into ordered structures without any external influence. During self-assembly, the molecules organize through non-covalent interactions such as dipole dipole , van der Waals forces, hydrogen bonds etc (*1*); Liquid crystals are well known hybrid phases of matter characterized by the conglomeration of order as in solids and mobility as in liquids. They have been termed as fourth state of matter. Thanks to Reinitzer who initially observed this phase transition phenomenon in cholesteryl esters (*2*, *3*) and termed it as double melting . Later Vorlander extended the study of these compounds and found them to be associated with both order and mobility (*4*). Thermodynamically all systems have a tendency to attain a state of maximum entropy with minimum possible energy. It is this balance of two opposing forces which form the basis for extent of order or disorder in a system. Crystalline solids usually possess ordered structures and the constituent molecules display both positional and directional order. Positional order refers to the uniform arrangement of molecules or building blocks. Directional order refers to the arrangement of molecules or building blocks such that their anisotropic axes are oriented in the same direction in space. In the case of liquids the molecules are distributed randomly throughout its bulk and they possess neither positional nor directional order. Liquid crystalline (LC) materials generally possess a degree of order intermediate to those of solids and liquids (*5*). 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 (*6*). Liquid crystalline (LC) systems always exhibit directional order and sometimes positional order too.

Liquid crystalline materials are also called as mesomorphic materials. Liquid crystals can be broadly classified into Thermotropic LCs, whose mesophase formation is temperature (T) dependent, and lyotropic LCs, whose mesophase formation is solvent, concentration and temperature dependent. Thermotropic liquid crystals may be further divided into three types on the basis of the shape of the constituent molecules. These are ; i) Calamitic liquid crystals-which are obtained from rod-like or lath-like shape of the molecules, ii) Discotic liquid crystals-which are formed from disk-like molecules and iii) Banana-shaped liquid crystals-whose constituent molecules have a bent-core. The investigations carried out and described in this thesis are liquid crystalline compounds composed of discotic molecules.

Vorlander one of the pioneers in liquid crystal research proposed the possibility of mesomorphic behavior in flat shaped molecules (*7*). He proposed the Voltas column model for their packing behavior. Experimentally he did not observe any mesomorphic signatures on triphenylenes and perylenes. The first experimental report came from Raman Research Institute by prof. chandrashekar etal. They observed the hexagonal symmetry in benzene hexaesters. This report is considered to be the birth of discotic liquid crystals (*8*). From then there are various accounts on LC behaviour of various pi fused systems as discotic scaffolds (*9, 10*)

A general structure of discotic Lc molecules is shown in Fig1.It consists of a central rigid core surrounded by flexible aliphatic chains connected to the core directly or via linking atom or a group (**Figure1**).

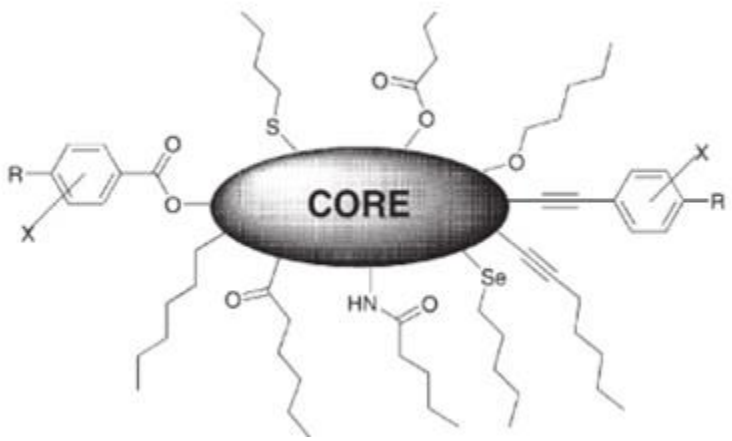


Figure1: General structure of discotic LC molecules (9)

DLCs generally form columnar mesophases probably due to intense π-π interactions of polyaromatic cores. The core–core separation in a columnar mesophase is usually of the order of 3.5 Å so that there is considerable overlap of π-orbitals. As flexible long aliphatic chains surround the core, the intercolumnar distance is usually 20–40 Å depending on the peripheral chain length (**Figure 2**). Therefore, interactions between neighboring molecules within the same column would be much stronger than interactions between neighboring columns(*11*). Consequently, charge migration in these materials is expected to be quasi one- dimensional. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than in the perpendicular direction. Thus the columns may be described as molecular wires. The supramolecular assemblies of disc-shaped molecules (Figure 2) have been extensively studied for the energy and charge migration in organized systems and their device applications such as, one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, field-effect transistors and gas sensors have been sought. The negative birefringence films formed by polymerized nematic DLCs have been commercialized as compensation foils to enlarge the viewing angle of commonly used twisted nematic liquid crystal displays. (*12*, *13*)

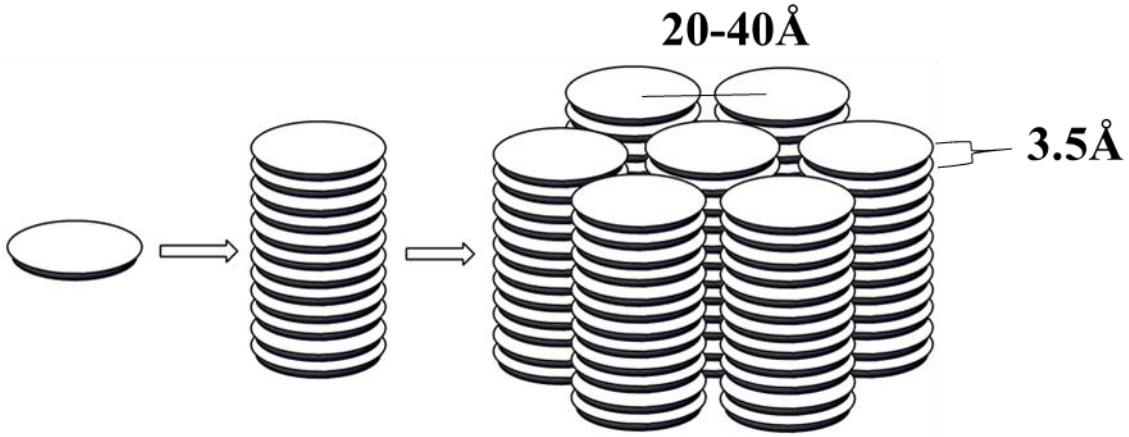


Figure 2 : Schematic of columnar assembly of discotics (*9*)

This thesis mainly involves study of influence of different hydrophilic moieties in mesomorphic behaviour of anthraquinones & triphenylenes

This thesis consists of following chapters.

Chapter 1: Introduction

This chapter explains the concept of liquid crystalline arrangement. Further it also describes structure property relationships in discotic materials followed by characterizing techniques which aid the information about the liquid crystalline arrangement. It also give some account on application of liquid crystals in fields ranging from material science to biology.

Chapter 2: Synthesis and mesomorphism of discotic polyelectrolyte surfactant complexes

This chapter gives details about synthesis of polyelectrolyte surfactant complexes (**Figure 3**) and their mesomorphic behaviour. The complexes have been prepared via ionic self-assembled approach with discotic cores such as anthraquinone and triphenylene as polyelectrolyte. The isolated complexes have been found to have good thermal stability. The complexes show lamellar

phase. Further the lyotropic behaviour of these complexes has also been explored. It was also found that they show lamellar phase with different water concentration.

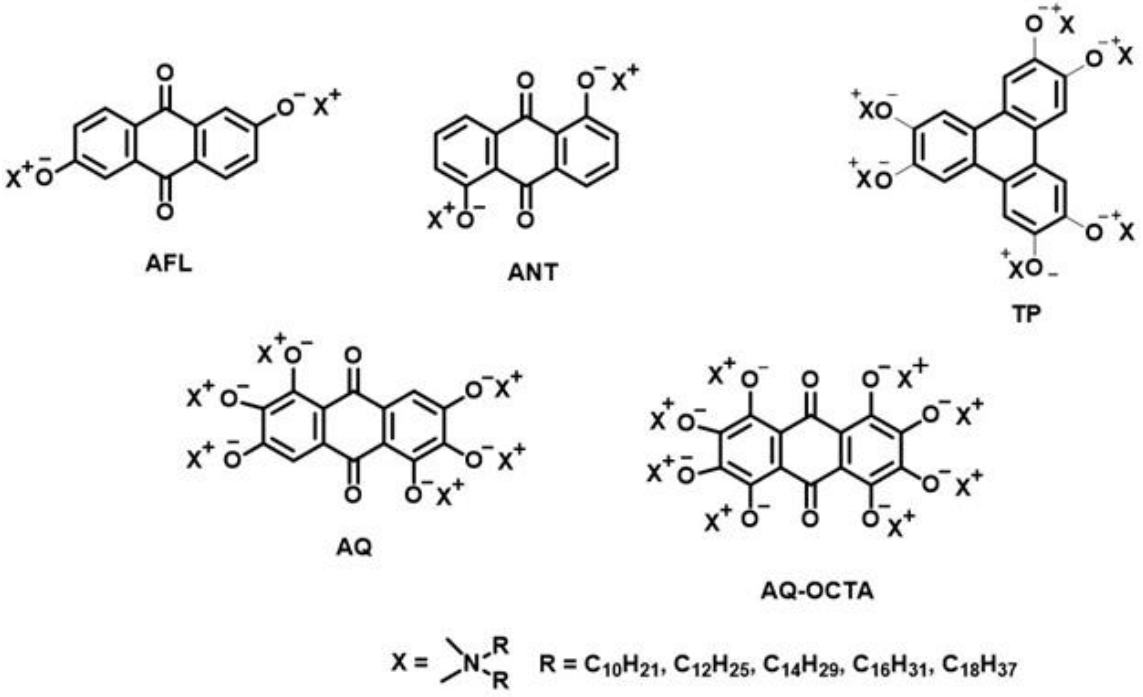
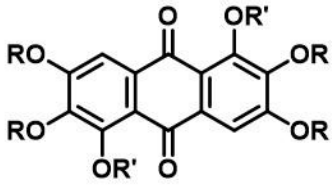


Figure 3: Structure of synthesized discotic polyelectrolyte surfactant complexes

Chapter3: Synthesis and mesomorphism of anthraquinone based bolaamphiphiles:

In this chapter we have reported synthesis of ethyleneoxy derivatives functionalized anthraquinones (**Figure 4**). We have studied the structure property relationship by changing both the length of hydrophilic i.e ethyleneoxy chains and the hydrophobic chains i.e alkyl chains. It was found that the lower homologue **4a** was non mesomorphic whereas the higher ones show columnar phase as typical of discotic compounds. Further lyotropic behavior of these compounds with

respect to water have been studied. Except **4a** all the other compounds show columnar phase as typical of chromonic systems.



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4a-1: R = C_6H_{13} R' = EGMME
4a-2: R = C_6H_{13} R' = DEGMME
4a-3: R = C_6H_{13} R' = TRIEGMME
4a-4: R = C_6H_{13} R' = TETRAEGMME
4b-4: R = C_8H_{17} R' = TETRAEGMME
4c-4: R = $C_{10}H_{21}$ R' = TETRAEGMME

Figure 4: Structure of bolaamphiphiles functionalized with glycol chains

Chapter 4: Synthesis and characterisation of cholestrol functionalised amphiphilic anthraquinones

This chapter is all about synthesis of cholesterol functionalized anthraquinone discs with ethylene glycol (EG) spacers (**Figure 5**). The influence of mesomorphic properties as a function of length of ethylene glycol spacer is studied. The compound **6a** was non mesomorphic. Whereas the compounds **6b & 6c** show cubic phase and they were found to be having clearing point around 50^0C. The compound **6d** was non- mesomorphic and highly viscous. These compounds were explored for lyotropic behavior with respect to water and formamide. The water based systems were found to be nonmesomorphic. On the other hand the formamide based systems were found to be gels.

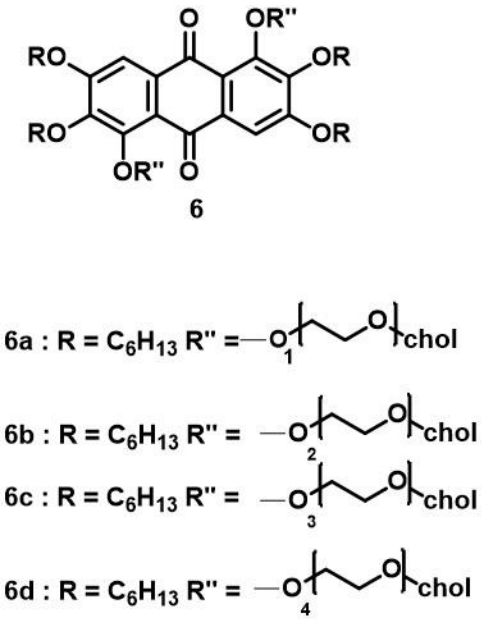

Figure 5: Structure of cholesterol functionalized anthraquinones

Chapter 5: Synthesis and characterization of amphiphilic anthraquinones with glycerol head groups

This chapter contains compounds involving glycerol functionalisation in anthraquinone scaffold (**Figure6**). It was found that the racemic compound **5a** was found to be non mesomorphic and corresponding chiral derivatives **5b & 5c** show columnar hexagonal phase. The higher chain homologues **5d &5e** show columnar phase too. It was further noticed that the pre final compounds **4a - 4e** were also mesomorphic. All the compounds were found to have good thermal stability. The final compounds were analyzed for lyotropic behavior with respect to water and Formamide. formamide based systems were found to be mesomorphic whereas the aqueous based were not.

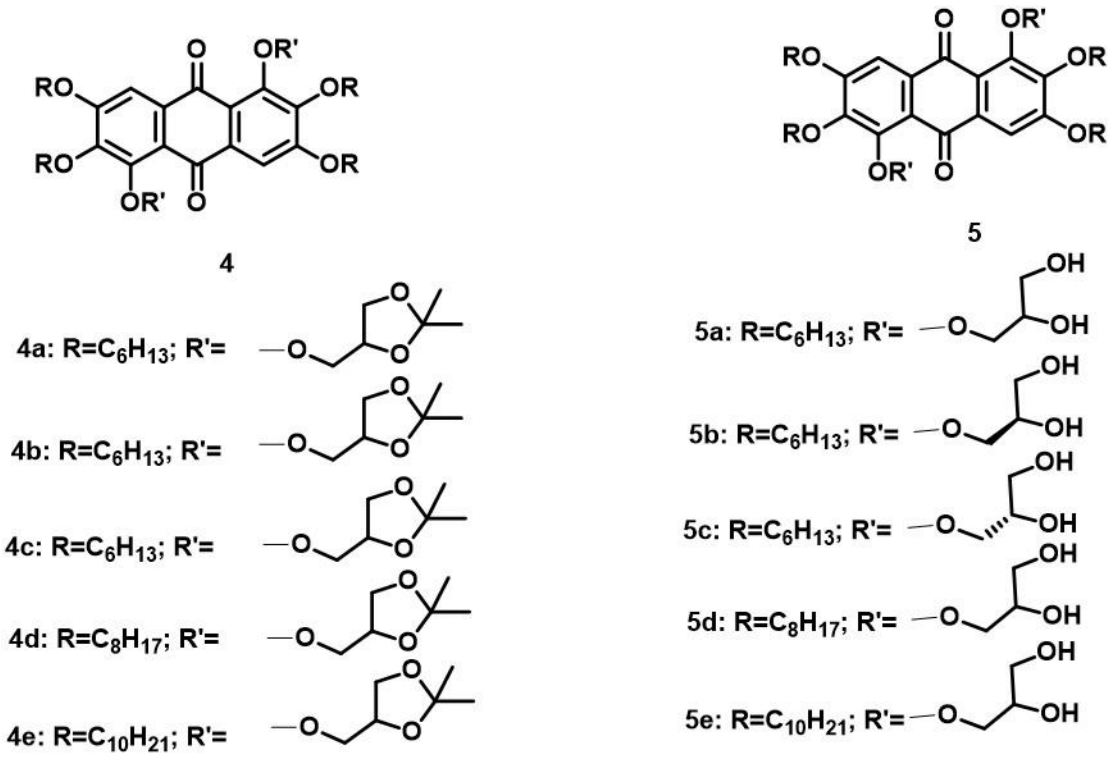

Figure 6: General structure of glycerol functionalized anthraquinone molecules

Chapter 6: Summary

This chapter summarises the whole dissertation which revolves around the topic synthesis and characterisation of some discotic amphiphiles .We briefly discuss the diverse possibilities and scope for future work based on the results obtained.

Publications:

The results presented in this thesis are reported in the following papers (published / to be published)

1. Synthesis and mesomorphism of ionic self-assembled complexes of anthraquinones

   K.Swamynathan, V.A Raghunathan & Sandeep Kumar*, Liquid crystals, 2017, 2311-2318

2. Mesomorphic triphenylene based polyelectrolyte surfactant complexes (manuscript under preparation)

   K.Swamynathan, Sreeja Sasidharan, V.A.Raghunathan & Sandeep Kumar*

3. Synthesis and mesomorphsim anthraquinone based bolaamphiphiles (manuscript under preparation)

   K. Swamynathan, Irlasivakumar, V.A. Raghunathan &Sandeep Kumar*

4. Synthesis and characterization of cholesteryl functionalized amphiphilic anthraquinones (manuscript under preparation)

   K. Swamynathan, Irlasivakumar, V.A.Raghunathan &Sandeep Kumar*

5. Synthesis and characterization of amphiphilic anthraquinones with glycerol head groups

   (manuscript under preparation)

   K.Swamynathan, Shikha Singh, V.A.Raghunathan & Sandeep Kumar*

The present author was involved in other projects as well but the results obtained are not described in this thesis and published in the following journals:

1. Novel annulated triphenylene discotic liquid crystals generated by Pictet Spengler cyclization

   Marichandran Vadivel, Irlasivakumar, K. Swamynathan, Raghunathan.V.A,

   Sandeep Kumar*, Chemistry select, 2018, 8763

2. Columnar self-assembly of novel benzylidene hydrazones and their diflouron complexes:

Structure-property correlations

D.R Vinayakuamra, K. Swamynathan, Sandeep Kumar, Airody Vasudeva adhikari*

New J .chem. 2019, 43, 7099-7108

3. Optoelectronic exploration of novel non-symmetrical star shaped discotic liquid crystals based on cyanopyridine

D.R Vinayakuamra, K. Swamynathan, Sandeep Kumar, Airody Vasudeva adhikari*

New J .chem. 2019, 43, 7099-7108

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