# Synthesis and Characterization of Some Novel Heterocyclic Discotic Mesogens

<sub>by</sub> Marichandran V

### A thesis submitted to the Jawaharlal Nehru University for the degree of

### Doctor of Philosophy

2022



Raman Research Institute Bangalore 560080 India

### DECLARATION

I hereby declare that this thesis is composed independently by me at Raman Research Institute, Bangalore under the supervision of Prof. Arun Roy and Prof. Sandeep Kumar. The subject matter presented in this thesis has not previously formed the basis of the award of any degree, diploma, associateship, fellowship or any other similar title. I also declare that I have run it through the Turnitin plagiarism software.

Signature of the Student

(Marichandran V)

Signature of the Supervisor

Prof. Arun Roy Raman Research Institute Bengaluru 560080 Signature of the Co-Supervisor

Prof. Sandeep Kumar Raman Research Institute Bengaluru 560080

### CERTIFICATE

This is to certify that the thesis entitled **Synthesis and Characterization of Some Novel Heterocyclic Discotic Mesogens** submitted by Marichandran V for the award of degree DOCTOR OF PHILOSOPHY of Jawaharlal Nehru University is his original work. This has not been published or submitted to any other university for any other degree or diploma.

Signature of the Supervisor

Prof. Arun Roy Raman Research Institute Bengaluru 560080 Signature of the Co-Supervisor

Prof. Sandeep Kumar Raman Research Institute Bengaluru 560080

Signature of the Director

Prof. Tarun Souradeep, Raman Research Institute, Bengaluru- 560080.

### Acknowledgment

This PhD has been a challenging but rewarding experience, and it would not have been possible without the help of many people.

First, I would like to express my sincere gratitude to Professor. Sandeep Kumar for his motivation, guidance, and constant support in completing this thesis. His immense knowledge, optimism, and encouragement made this PhD experience fun and exciting. The time and trust he invested in me require more than a thank you note. I also thank Prof. Arun Roy for his advice and timely help in taking care of my thesis. He played various roles from advisory committee member to supervisor throughout my PhD time at RRI, and I thank him for his support and all the discussions we had. Also, thank you to Prof. Pratibha for being a part of my advisory committee and taking the time to critique this thesis.

I would especially like to thank Prof. Raghunathan V A for his advice on X-ray diffraction studies. He is an excellent teacher and a friendly person. The times when I found myself out of place, Raghu was always there to put me back on track. It is always a pleasant conversation with him. I want to thank our collaborator, Dr. Dharmendra Pratap Singh, for his help in mobility measurements. He always makes himself available whenever we want to have any discussions. I am looking forward to learning more from him in the future. I am also grateful to other SCM faculty members for their support over the years.

I would also like to acknowledge Mrs. Vasudha, Dr. Srinivas, Dr. Vijayaraghavan, Yatheendran, Dhason, and Mani for their technical support throughout my PhD time. I have learned many aspects of various techniques from them, and without their expertise, things would have been much harder. I also thank Prof. Reji and Nancy for their help in emission studies. My sincere thanks to KRK, Amudha, Chaithanya, Murali, Raja, and Venkatesh, for your help whenever I needed it.

Without my former and present lab members, I would not have been able to do as much as I accomplished. They brought excitement and enthusiasm to the lab. To Swamy, Avinash, Ashwath, Vinay, Siva, Vani, Alaka, Shikha, Tripti, Shaina, Reshmi, thank you for your input, assistance, and for making the lab a fun place to work. A special thanks to Swamy for being a fantastic friend and helping me get where I am today. Siva, thanks for sharing your experimental skills and the spices you bring.

There are several people that I've had the support of and have been an inspiration to me throughout my PhD time. The blend of RK, JK, and Madhukar is the finest I have experienced; a perfect company that inspires, challenges, and motivates. I thank Chaithra, Nishanth, and Giri for their care and friendship. Nomaan, I see you too. Swamy, Jaggu,

Surya, Asha, Chandan, Venu, Amith, Archana, Anindya, Subodh, Ayush, Sreeja, Niranjan, Saichand, Shreyas, Sebanti, Vardhan, Arun, Sumanth, Vishnu, Arsalan, Abhishek, Manju, KP sir, thank you for making my time wonderful and for bearing with me for so long. I thank GB sir, for introducing me to some finest of Bangalore and the memorable musical evenings. It is my pleasure to have met you all, and I thank you for all the late-night tea parties, early morning treks, and never-ending arguments that made me see things differently. Your friendship and honesty kept me sane through most of these years. It is no exaggeration to say that I have been fortunate to have all your support.

I thank the RRI admin, library, hostel staff, sports committee, canteen, and E&B for providing a beautiful and friendly environment. To describe my experience at RRI is almost impossible to do within a few sentences. I will just say that it was a pleasure to have participated.

Huge thanks to Geetha and Magendran; you are the best people I have got back home, and your kindness and support have given me the courage to go further.

Without my parents, none of this would have been possible. They always believed and stood by me when I needed them the most. To Amma and Appa, thanks a lot for being there for me.

#### SYNOPSIS

### Synthesis and Characterization of Some Novel Heterocyclic Discotic Mesogens

Self-assembly is the process of arrangement of objects in an orderly fashion driven by noncovalent interactions(1). The non-covalent interactions are generally comprised of dipolar quadrupolar interactions, van der Waals forces, and hydrogen bond, etc; This self-assembly process is omnipresent at all scales ranging from subatomic particles to macromolecules(2). The degree of order in a system is the result of the balance of two thermodynamic properties i.e entropy and free energy. Molecules in any condensed phase generally possess two types of orders (3).

• Positional order: Positional order may be defined as the tendency of molecules to occupy fixed positions. It gives regular distances between molecules.

• Orientational order: It may be defined as the tendency of molecules to orient in a particular direction. This means that groups of molecules lie in the same direction.

Crystalline solids have both positional and orientational order, that is, they occupy their fixed positions and are also aligned along a particular direction. In liquid, molecules are randomly oriented and hence liquids have neither positional nor orientational order. Liquid crystal has orientational order and reduced positional order. Liquid crystals are different from plastic crystals as follows, a plastic crystal possesses long-range positional order but is orientationally completely disordered(4). The type of liquid crystal phase formed by a mesomorphic material is essentially dependent on the molecular architecture, that is, polarity, polarizability and topology of a molecule(5). Based on the observations reported we can generalize the prerequisites for inducing the liquid crystallinity of a molecule as follows (6).

- a. Simple geometrical form of the molecule: rods, discs or balls, which facilitates closer packing in their mesophase regime.
- b. An intramolecular contrast, i.e (rigid and flexible motifs in the structure) which causes microsegregation of different parts of the molecules

Liquid crystals (LCs) can be classified broadly into two types.

Thermotropic LCs, whose mesophase formation is the temperature (T) dependent(7), and lyotropic LCs (8), whose mesophase formation is solvent, concentration and temperature-dependent.

Thermotropic liquid crystals may be further divided into three types based on the shape of the constituent molecules (9).

### 1. Calamitics (Rod-shaped)

- 2. Discotics (Disc-shaped systems)
- 3. Bent core liquid crystals( Banana shaped systems)

The investigations carried out and described in this thesis are liquid crystalline compounds composed of discotic molecules.

Vorlander, one of the trailblazers of liquid crystal research proposed the speculation of mesomorphic behavior in flat-shaped molecules such as triphenylenes and perylenes(10). He projected 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 et al. They reported columnar order by benzene hexaesters. This report forms the genesis of discotic liquid crystals (DLCs)(11). It is worth mentioning here regarding the report in the early 1960s, where the anisotropic mesophases with nematic features have been documented in the pyrolysis of graphitizable substances(12)(13). They have been termed as carbonaceous mesophases.

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(14) (Figure 1).



Figure 1: General structure of discotic LC molecules

DLCs generally form columnar mesophases probably due to intense  $\pi$ - $\pi$  interactions of polyaromatic cores(15). The  $\pi$ - $\pi$  stacking interactions between discotic cores often constitutes the weakly attractive stacking forces in columnar mesophases, in addition to that, linking groups may play an important role if they engage in dipole-dipole interactions (e.g. carbonyl groups) or Hbonding (e.g. amide groups). The surrounding side- chains have two functions: they lower melting points and increase fluidity and they induce microphase segregation between cores and sidechains, which significantly promotes columnar stacking. The columnar arrangement of these discogens is due to the strong  $\pi$ - $\pi$  interaction between the aromatic cores which are separated by about 3.5 Å in general and lead to the crystal-like ordering of discs(16). The peripheral aliphatic chains induce the fluidity in these systems and also are electrically insulating in nature. Owing to these properties, the discotic liquid crystals are known to be conducting, upon doping with suitable dopants, along the columns and insulating between the columns. It has been observed that conductivity along the column axes in columnar mesophases to be several orders of magnitude greater than in the perpendicular direction (17)(18) The core-core separation in a columnar mesophase is usually of the order of 3.5 Å so that there is considerable overlap of  $\pi$ -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(19). 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(*9*).

The mesomorphic potential of a discotic compound depends on three factors

- a. Nature of central core
- b. Nature of peripheral chains
- c. Nature of linking groups



Figure 2: Schematic of the columnar assembly of discotics

The nature of the central core is one of the backbones for the orderly arrangement of discogens. In the aromatic cores, the p orbitals of the adjacent atom can overlap that results in the formation of extensible pi molecular orbitals above and below the plane of the core causing extensive delocalization of electrons. With this argument we can think about increasing the core size, which in turn increases the delocalization larger, and, therefore, can improve charge-transporting behavior due to shorter core-core seperation(20). In the case of extending the core by fusing with heteroatom introduces strong polar interactions owing to their electron density. This can make the cores electron-deficient and could be of great use in semiconducting applications(21).

This thesis attempts to study the design, synthesis and mesomorphic properties of some of the derivatives of nitrogen and oxygen-containing heterocyclic systems

This thesis contains the following chapters

#### **Chapter 1. Introduction**

This chapter gives details about the concept of liquid crystals, their history, classification, and characterization techniques. Further, this chapter also gives a brief account of discotic liquid crystals, structure-property relationships of discotic systems and their applications.

#### Chapter 2. Synthesis and Characterization of Novel Naphthophenanthridine DLCs

#### 2.1 Synthesis and Characterization of Novel 5-Phenylnaphthophenanthridine DLCs

This chapter gives an account of the synthesis of 5-Phenylnaphthophenanthridine derivatives achieved through Pictet-Spengler cyclization of hexaalkoxytriphenylene-1-amine with benzaldehydes and its methoxy analogs (**Figure 3**). These derivatives showed a columnar hexagonal phase. Among the four compounds, 6a and 6b show enantiotropic and the other two are forming monotropic mesophases. Compound 6a was found to show the plastic columnar phase in addition to the hexagonal phase.



6a;  $R_1 = R_2 = R_3 = H$ 6a;  $R_2 = OCH_3$ ,  $R_1 = R_3 = H$ 6c;  $R_1 = R_2 = OCH_3$ ,  $R_3 = H$ 6d;  $R_1 = R_2 = R_3 = OCH_3$ 

Figure 3. Structure of 5-Phenylnaphthophenanthridine derivatives.

#### 2.2 Synthesis and Characterization of Novel 5-alkylnaphthophenanthridine DLCs

This chapter gives an account of the synthesis of naphthophenanthridines through the Pictet Spengler pathway involving amino triphenylenes and aliphatic aldehydes (**Figure 4**). All the compounds exhibit enantiotropic columnar hexagonal phase. These compounds show mosaic and dendritic textures under POM suggests the columnar nature. The X-ray diffraction data validates the columnar order in these compounds comprising of hexagonal symmetry.



Figure 4. Structure of naphthophenanthridine derivatives.

## 2.3 Synthesis and Characterization of Novel chromophore-coupled Naphthophenanthridine DLCs

In this chapter, the synthesis of a series of four compounds each bears a chromophore moiety covalently attached to the naphthophenanthridine discotic liquid crystals are discussed (**Figure 5**). Pyrene, anthracene, phenothiazine, and triphenylamine moieties were used as chromophores. The effect of these chromophores in the thermal and structural arrangement of these discotic cores have been explained. All the molecules show columnar liquid crystalline phase. Particularly the pyrene functionalized phenanthridine derivative was found to be liquid crystalline at room temperature.



Figure 5. Structure of  $\pi$ - Extended napthophenanthridines

#### Chapter 3. Synthesis and Characterization of Novel Triazacoronene DLCs

This chapter discusses the synthesis of triazacoronene based discotic liquid crystals and their structural and mesomorphic behavior (**Figure6**)We have synthesized 1,5,9-triaminotriphenylene and coupled it with aliphatic aldehydes to give triazacoronene derivatives as a yellow solid. The compounds are characterized by spectral and elemental analysis.



**Figure 6. Structure of triazacoronene derivatives** 

These compounds are non-liquid crystalline in nature possibly due to the imbalance in the amount of rigid and flexible units in the structure. The above prediction was validated when we replaced the alkyl chains in the periphery with the alkoxy substituted phenyl rings, the compounds were found to be mesomorphic (**Figure 7**). All the compounds show liquid crystalline behavior for a wide temperature range. Compound 4b is liquid crystalline at room temperature and till 160°C. Diffraction data of the compounds suggests the hexagonal order of the mesophase.



Figure 7. Structure of triphenyl triazacoronene derivatives

## Chapter 4. Synthesis and Charecterization of Novel Chromenonaphthophenanthridine DLCs

In this chapter, we studied the effect of the incorporation of heteroatoms and the extension of the ring system on the mesomorphic properties. We have synthesized pi extended N and O incorporated discotic molecules (1,2,5,6,9-pentaalkoxychromeno{4,3,2-gh]naphtho[1,2,3,4-lmn]phenanthridine). The disc composed a core which is an extension of triphenylene with pyridine and benzopyrano groups. The core is surrounded by five flexible alkoxy chains (**Figure 8**). All the compounds were characterized using spectral and elemental analysis. The liquid crystalline property of these compounds was studied as a function of increasing peripheral alkoxy chain length.



Figure 8. Structure of benzopyrano extended phenanthridine derivatives

### **Chapter 5: Summary**

This chapter summarizes all the experimental work done and the results discussed in the thesis. This thesis mainly focuses on the design and synthesis of new liquid crystalline materials with an extended heterocyclic pi-conjugation. This chapter also gives a summary of promising possible extensions towards diverse applications.

### **References:**

- 1. J. W. Steed, J. L. Atwood, P. A. Gale, in *Supramolecular Chemistry: From Molecules to Nanomaterials* (2012).
- 2. G. M. Whitesides, Self-Assembly at All Scales. *Science* (80-. ). **295**, 2418–2421 (2002).
- 3. S. Mohanty, Liquid crystals The 'fourth' phase of matter. *Resonance*. **8**, 52–70 (2003).
- 4. Chapman.D, in *Liquid crystals and plastic crystals Vol -1*, P. A. W. G.W.Gray, Ed. (Ellis Horwood, 1974).
- 5. I. W. Hamley, *Introduction to Soft Matter–Revised Edition* (John Wiley & Sons, Ltd, Chichester, UK, 2007; http://doi.wiley.com/10.1002/9780470517338).
- 6. O. D. Lavrentovich, *Liquid Crystals* (Oxford University Press, 2017; http://oxfordhandbooks.com/view/10.1093/oxfordhb/9780199667925.001.0001/oxfordhb-9780199667925-e-3), vol. 1.
- 7. A. Ramamoorthy, *Thermotropic Liquid Crystals* (Springer Netherlands, Dordrecht, 2007; http://link.springer.com/10.1007/1-4020-5354-1).
- 8. G. Tiddy, Surfactant-water liquid crystal phases. *Phys. Rep.* 57, 1–46 (1980).
- 9. B. Bahadur, M. Tilton, Liquid Crystals Applications and Uses. J. Soc. Inf. Disp. 2, 63 (1994).
- 10. D. Vorlander, Investigation of the molecular form by means of crystalline liquids. *Zeitschrift für Phys. Chemie* (1923).
- 11. S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, Liquid crystals of disc-like molecules. *Pramana*. **9**, 471–480 (1977).
- 12. J. D. Brooks, G. H. Taylor, The formation of graphitizing carbons from the liquid phase. *Carbon N. Y.* (1965), doi:10.1016/0008-6223(65)90047-3.
- 13. J. E. Zimmer, J. L. White, in *Mol Cryst Liq Cryst* (1976).
- 14. S. Kumar, *Chemistry of discotic liquid crystals: From monomers to polymers* (CRC press, New York, 2011).
- 15. S. Kumar, Self-organization of disc-like molecules: chemical aspects. *Chem. Soc. Rev.* **35**, 83–109 (2006).

- 16. S. Kumar, Playing with discs. Liq. Cryst. (2009), doi:10.1080/02678290902755549.
- 17. V. S. K. Balagurusamy *et al.*, Quasi-one dimensional electrical conductivity and thermoelectric power studies on a discotic liquid crystal. *Pramana*. **53**, 3–11 (1999).
- 18. N. Boden *et al.*, Transient Photoconductivity and Dark Conductivity in Discotic Liquid Crystals. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A. Mol. Cryst. Liq. Cryst.* **261**, 251–257 (1995).
- 19. S. Sergeyev, W. Pisula, Y. H. Geerts, Discotic liquid crystals: a new generation of organic semiconductors. *Chem. Soc. Rev.* **36**, 1902 (2007).
- 20. A. Gowda, M. Kumar, S. Kumar, Discotic liquid crystals derived from polycyclic aromatic cores: from the smallest benzene to the utmost graphene cores. *Liq. Cryst.*, 1–28 (2017).
- M. Stępień, E. Gońka, M. Żyła, N. Sprutta, Heterocyclic Nanographenes and Other Polycyclic Heteroaromatic Compounds: Synthetic Routes, Properties, and Applications. *Chem. Rev.* 117, 3479–3716 (2017).

Signature of the Student

(Marichandran V)

Signature of the Supervisor

Prof. Arun Roy Raman Research Institute Bengaluru 560080 Signature of the Co-Supervisor

Prof. Sandeep Kumar Raman Research Institute Bengaluru 560080

### **List of Publications**

- 1. Vadivel, M., Kumar, I. S., Swamynathan, K., Raghunathan, V. A. & Kumar, S. Novel Annulated Triphenylene Discotic Liquid Crystals Generated by Pictet-Spengler Cyclization. *ChemistrySelect* **3**, 8763–8769 (2018).
- Vadivel, M., Singh, S., Singh, D. P., Raghunathan, V. A. & Kumar, S. Ambipolar Charge Transport Properties of Naphthophenanthridine Discotic Liquid Crystals. *J. Phys. Chem. B* 125, 10364–10372 (2021).
- 3. Vadivel, M., Raghunathan, V. A. & Kumar, S. Highly ordered columnar liquid crystalline triazacoronene: An electron-deficient core and novel addition to the discotic family. (Manuscript under preparation)
- 4. Vadivel, M., Raghunathan, V. A. & Kumar, S. Chromenonaphthophenanthridine: Benzopyrano fused Nitrogen-containing heterocyclic discotic Mesogens. (Manuscript under preparation)
- 5. Vadivel, M., Kumar, S. Synthesis and mesomorphic properties of chromophore-coupled naphthophenathridine discotic liquid crystals. (Manuscript under preparation)

Signature of the Student

(Marichandran V)

Signature of the Supervisor

Prof. Arun Roy Raman Research Institute Bengaluru 560080 Signature of the Co-Supervisor

Prof. Sandeep Kumar Raman Research Institute Bengaluru 560080

### **Table of Contents**

### **Chapter 1: Introduction**

1. Liquid crystals	2
1.1. Brief history of liquid crystals	3
1.2. Classification of liquid crystals	.4
2. Discotic liquid crystals	7
2.1. Classification of discotic liquid crystals	9
2.1.1. Nematic mesophases of discotic mesogens	10
2.1.2. Columnar mesophases of discotic mesogens	12
2.2. Classes of compounds used for discotic liquid crystals	17
2.2.1. Polycyclic aromatic hydrocarbons (PAH) based DLCs	17
2.2.2 Heterocyclic DLCs	20
2.3. Characterization of discotic liquid crystals.	22
2.4. Applications of discotic liquid crystals	25
3. References	30

### Chapter 2: Synthesis and Characterization of Novel Naphthophenanthridine DLCs

Introduction	
2.1. Synthesis and Characterization of Novel 5-Phenylnaphthophenanthridine DLCs	46
2.1.1. Results and discussion	47
2.1.1.1. Synthesis	47
2.1.1.2. Mesophase characterization	48
2.1.1.3. Photo physical properties & DFT studies	55
2.1.2. Conclusion	58
2.1.3. Experimental section	58
2.1.3.1. Reagents and Instruments	58

2.1.3.2. Synthetic procedures and spectral data	59
2.1.4. Spectral data	63
2.2. Synthesis and Characterization of Novel 5-Alkylnaphthophenanthridine DLC	Cs73
2.2.1. Results and discussion	74
2.2.1.1. Synthesis	74
2.2.1.2. Mesophase characterization	75
2.2.1.3. Photo physical properties & DFT studies	81
2.2.1.4. Charge transport properties	
2.2.2. Conclusion	
2.2.3. Experimental section.	86
2.2.3.1. Reagents and Instruments	86
2.2.3.2. Synthetic procedures and spectral data	87
2.2.4. Spectral data	
2.3 Synthesis and Characterization of Novel Chromophore-coupled Naphthe	onhenanthridine
DLCs	
2.3.1. Results and discussion	
2.3.1.1. Synthesis	94
2.3.1.2. Mesophase characterization	
2.3.1.3. Photo physical properties & DFT studies	101
2.3.2. Conclusion	103
2.3.3. Experimental section.	105
2.3.3.1. Reagents and Instruments	105
2.3.3.2. Synthetic procedures and spectral data	105
2.3.4. Spectral data	
2.4. Deferences	117
2.4. References	110

### Chapter 3: Synthesis and Characterization of Novel Triazacoronene DLCs

3.1. Introduction	
3.2. Results and discussion	136

3.2.1. Synthesis	136
3.2.2. Mesophase characterization	138
3.2.3. Photo physical properties & DFT studies	145
3.3. Conclusion	148
3.4. Experimental section	148
3.4.1. Reagents and Instruments	148
3.4.2. Synthetic procedures and spectral data of compounds 6a and 6b	148
3.4.3. Synthetic procedures and spectral data of compounds 4a-d	150
3.5. Spectral data	154
3.6. References	168

### Chapter 4: Synthesis and Characterization of Novel Chromenonaphthophenanthridine DLCs

4.1. Introduction	176
4.2. Results and discussion	
4.2.1. Synthesis	183
4.2.2. Mesophase characterization	184
4.2.3. Photo physical properties & DFT studies	191
4.3. Conclusion	193
4.4. Experimental section	193
4.4.1. Reagents and Instruments	193
4.4.2. Synthetic procedures and spectral data of compounds 6a-d	193
4.5. Spectral data	196
4.6. References	200

### **Chapter 5: Summary**

Summary	207
List of Publications	209

### **Chapter 1**

### Introduction

Supramolecular chemistry is an extensively interdisciplinary area of science that deals with the chemical, physical and biological aspects of chemical components. In addition to molecular chemistry based on covalent bonds, supramolecular chemistry attempts to generate highly complex chemical systems that interact through non-covalent intermolecular forces. The classic definition of supramolecular chemistry describes it as "Chemistry beyond the molecule." It substantially impacts materials research by manipulating the intermolecular forces leading to the design of smart functional materials<sup>1,2</sup>. The structure and performance of these functional supramolecular materials are often controlled by the nature of their constituents and the interactions between them that lead to self-assembly. Self-assembly and self-organization provide direct access to the supramolecular architecture that involves organized assemblies such as molecular crystals, liquid crystals (LC), micelles, phase-separated polymers, and colloids<sup>3,4</sup>. Several nanostructures have been developed through the self-assembly of chemically synthesized small molecules. Self-assembly provides a level of control over the selection and positioning of individual atoms or groups than the nanostructures formed by other methods of fabrication<sup>3</sup>. The interplay between enthalpic contribution due to the non-covalent interactions between neighboring molecules and the nonfavoring entropic values arises from the loss of long-range translational motion, and conformational changes play a vital role in the stability of these self-organized systems. In general, the large surface area that offers greater intermolecular forces of attraction favors self-assembly and self-organization. These self-organized systems may be distinguished into two cases depending on their fluid nature. A hard self-organized matter, for example, a crystal with minimal or no diffusion, and a soft self-organized system, for example, a liquid crystal with fluidity at least in one direction<sup>5</sup>. Liquid crystals, one of the delicate phases of matter, are self-organized intermediate phases between ordered crystal and isotropic liquid<sup>6–8</sup>. The molecules in liquid crystal phases have fluidity like in liquid, but they maintain a certain degree of positional and orientational order. This unique phase of matter is also referred to as mesophase, and the molecules exhibiting

them are said to be mesomorphic. Here we shall discuss some of the fundamental aspects of this state of matter after their brief introduction. We will also discuss the types of liquid crystals based on their molecular shape and self-organized structure. Furthermore, we will review the classifications of discotic liquid crystals, their synthesis, characterization techniques and applications.

### 1. Liquid crystals

Liquid crystals (LCs) are an important class of functional materials with both order and mobility on a molecular, supramolecular, and macroscopic level<sup>7,9–11</sup>. They stand between isotropic liquid and highly ordered crystalline solids, hence referred to as an intermediate phase or mesophase. Molecules or the constituent species that organize to form this type of mesophase are known as mesogens. One of the fundamental distinctions between liquid crystals and other states of matter emerges from their positional and orientational order. Crystals have three-dimensional long-range positional and orientational order, with molecules vibrating in their mean position. Liquids possess short-range order to some extent, but molecules are free to vibrate, rotate and diffuse. On the other hand, liquid crystals have the fluidity of liquid and short-range positional and orientational ordering like crystalline solid (**Figure 1.1**). The molecules that form the liquid crystalline phase have pronounced shape anisotropy like a rod or a disc<sup>12</sup>.



Temperature, mobility

**Figure 1.1.** Types of different states of matter and the change in their molecular order and mobility with temperature.

### **1.1 Brief history of liquid crystals**

While determining the melting point of cholesteryl benzoate (**Figure 1.2**), Friedrich Reinitzer observed the formation of cloudy liquid at 145 °C, which cleared at around 178 °C. He sent those samples to German physicist Otto Lehmann for further studies under the temperature-controlled microscope. Lehmann found this exciting phenomenon of double melting and termed them "soft crystals" and later called them "Liquid crystals"<sup>13</sup>. This historic discovery in 1888 paved the path for the origin of the field liquid crystals<sup>14,15</sup>. Lehmann started studying the liquid crystalline property of many natural products and several synthetic organic molecules. He also observed the spontaneous alignment of these molecules when in contact with a solid substrate that eventually led to their application in display devices.



Figure 1.2. Chemical structure of cholesteryl benzoate.

Daniel Vorlander, a German chemist, and his coworkers have synthesized many new liquid crystalline molecules. He extensively studied the structure-property relationship of molecules with linear structure (calamitic) and observed more than one mesophase type in a single substance<sup>16</sup>. Later, stable room temperature liquid crystal derivatives such as 4-alkyl- and 4-alkoxy-4<sup>'</sup>- cyanobiphenyls were synthesized by Gray et al., which contributed significantly to their applications in optoelectronic devices<sup>17</sup>.

In 1924, Vorlander suggested the possibility of a new type of mesophase formed by "leaf" shaped molecules, but his attempts to achieve this phase were unsuccessful, probably due to the

absence of flexible hydrocarbon chains. However, in 1977, Chandrasekhar and his coworkers from Raman Research Institute reported for the first time that not only the rod-shaped molecules but also the flat disc-shaped molecules do form liquid crystalline phases. They synthesized a series of benzene hexaesters and characterized a new class of LCs through optical, thermodynamic, and X-ray diffraction techniques<sup>18</sup>. This discovery drew attention to chemists worldwide and established a whole new field of fascinating discotic liquid crystal research. Till now, mesophases such as nematic, smectic, and cholesteric (chiral nematic) in rod-like liquid crystals and columnar as well as nematic phases in disc-like liquid crystals have been extensively explored<sup>19,20</sup>. Due to the number of factors that contribute to mesophase formation, it becomes challenging to predict how a molecule self-assemble into an LC phase. In general, the molecular shape is a reliable indicator of the liquid crystalline nature, which has brought forth the classification of mesogens as calamitic and discotic<sup>21–24</sup>. Presumably, rod-shaped molecules tend to form smectic and nematic phases, whereas disc-like molecules tend to self-organize into columnar and nematic liquid crystals.

#### **1.2 Classification of liquid crystals**

Among the various ways of classifying liquid crystalline materials, according to the molecular weight of individual molecules, they can be classified into low molar mass or high molar mass liquid crystals<sup>8,25,26</sup>. The low molecular LCs generally include monomers, dimers, and oligomers, whereas the high molecular mass ones are mainly polymeric LCs. Based on the ways to obtain liquid crystals, they can be either thermotropic or lyotropic LCs. In general, thermotropic mesophases are obtained by heating a solid or cooling an isotropic liquid. These thermotropic LCs are further divided into a thermodynamically stable enantiotropic phase (mesophase observed in both heating and cooling cycle) and a metastable monotropic phase (usually observed in cooling the isotropic liquid). The lyotropic LCs are solvent-dependent and can arrange into lamellar, columnar, or cubic geometrical lattices depending on the solvent concentration that affects the aggregation and liquid crystal properties. The general classification of LCs is shown in **Figure 1.3**. We will restrict our interest to thermotropic LC phases and further consider the LCs formed by disc-like molecules.



Figure 1.3. Classifications of liquid crystals<sup>8</sup>.

The thermotropic LCs can further be classified into calamitic (rod-like), discotic (disclike), and bent-core (banana-shaped) based on their geometry. Rod-like calamitics are the most common class of thermotropic mesophases whose constituent molecules possess an elongated shape whose length (l) is much longer than the breath (b) and freely rotate along the long axis. The general template of molecules that form calamitic liquid crystals is shown in **Figure 1.4**. Most of the calamitic liquid crystals contain two or more aromatic rings connected directly with the alkyl chain or via a linking group. Due to the resultant cylindrical shape, these molecules tend to form layer-like smectic (Sm) or nematic (N) structures.



Crystal – 24 °C – Nematic – 35 °C - Isotropic

### Figure 1.4. General molecular template of calamitic mesogens.

Calamitic mesogenic molecules possess strong intermolecular interactions that are anisotropic due to their rod-like structure. In such molecules, the loss of one, two, or three-dimensional long-range translational order precedes the collapse of long-range orientational order on heating. Consequently, these crystals do not show just one transition on heating but instead enter into mesophase (melting point) before clearing to isotropic liquid (clearing point). The smectic phase arises when the lateral intermolecular forces of attraction are stronger than the terminal forces. On heating the crystal, the terminal forces break down first, resulting in loss of inplane translational order and formation of lamellar arrangement of molecules<sup>27,28</sup>. There are many smectic phases possible as a result of the difference in correlation within and between the layers. The loss of both in-plane and out-of-plane translational order gives rise to nematic mesophase in which the molecules have no positional order but are orientated along an average direction, defined as director *n* (Figure 1.5).



**Figure 1.5**. Schematic representation of molecular arrangements in Nematic, Smectic mesophases<sup>29</sup>.

On the other hand, discotic liquid crystals (DLCs) are formed by disc-like molecular structures. These discs generally comprise a central planar core of aromatic rings, with flexible aliphatic chains protruding radially outside the core<sup>24,30,31</sup>. In addition to calamitics and discotics, there also exists another unique liquid crystalline phase formed by banana or boomerang-shaped molecules, called bent-core LCs. **Figure 1.6** shows an example of a bent-core and discotic liquid crystal. Due to the sterically induced packing of bent-core molecules, structural features of these mesophases lead to unusual physical properties. This special molecular packing gives rise to ferri, ferro- and antiferroelectric properties<sup>32</sup>.



Figure 1.6. Schematic representation of bent-core and discotic liquid crystals.

#### 2. Discotic liquid crystals

Since the discovery of the first discotic mesogen by Sivaramakrishna Chandrasekhar et al. in 1977, which was probably the first observation of thermotropic mesomorphism in a pure singlecomponent system of disk-shaped molecules, enormous efforts have been directed towards the understanding of the molecular parameters that favor such mesophase formation and control their thermal properties. Chandrashekar et al. have designed and synthesized several benzene hexaalkanoates and reported that these disk-like molecules self-assemble into a new class of LCs in which the molecules are stacked on top of each other, forming a column that constitutes a 2D hexagonal arrangement (**Figure 1.7**).



**Figure 1.7**. The molecular structure, self-organization into the hexagonal columnar structure of benzene hexa-alkanoate, and general molecular template of DLCs.

A typical discotic mesogen generally includes a central aromatic core functionalized with flexible aliphatic chains through a linking group such as ester, ether, or amide (**Figure 1.7**). These molecules form the four main classes of DLCs known as nematic, smectic, columnar, and cubic phases. Columnar mesophases are primarily observed in DLCs followed by nematic, whereas other phases are rarely observed (**Figure 1.8**). Although the majority of discotic mesogens form columnar mesophase, several other molecular structures also are known to form columnar mesomorphism. Self-aggregated surfactant molecules forming lyotropic columnar phases, rod-like molecules, dendrimers, and even some bent-core molecules are reported to exhibit columnar mesophase<sup>33,34</sup>.



**Figure 1.8**. Schematic representation of a) discotic nematic ( $N_D$ ) and b) columnar discotic ( $Col_h$  – hexagonal columnar) mesophase<sup>35</sup>.

The design and recent progress in the development of DLCs as promising candidates in electronic devices have been addressed in many recent articles<sup>22–24,30,35–37</sup>. Shape anisotropy, nano-segregation between the core and flexible alkyl chains, strong core-core interactions are the primary driving forces for the formation of columnar mesophases. The efficient  $\pi$ - $\pi$  columnar stacks produce high charge carrier mobility along the direction of columns, the magnitude of which is primarily due to the degree of order, efficient  $\pi$ - $\pi$  molecular overlap, and relative positioning of neighboring molecules. The core-core distance in columnar DLCs is usually in the order of 3.5 Å, and the intercolumnar distance is dictated by the size of the mesogens and typically in the order of 20-40 Å. The molten alkyl chains around the central core separate the cores of neighboring columns; hence conductivity in the columnar axis is significantly higher and acts as one dimensional nanowires<sup>36</sup>.

#### **2.1. Classification of discotic liquid crystals**

The liquid crystalline phases formed by disc-shaped molecules are divided primarily into four types: nematic, columnar, lamellar, and cubic.

### 2.1.1. Nematic mesophases of discotic Mesogens

The nematic mesophases of disc-like molecules can be further classified into four types that are i) discotic nematic ( $N_D$ ), ii) chiral nematic ( $N_D^*$ ), iii) columnar nematic ( $N_{Col}$ ) and iv) nematic lateral ( $N_L$ ) (**Figure 1.9**).



**Figure 1.9**. Structures of some discotic nematic mesophases a) discotic nematic  $(N_D)$ , b) chiral nematic  $(N^*_D)$ , c) columnar nematic  $(N_{Col})$  and d) nematic lateral  $(N_L)$ .

The discotic nematic is the least ordered and least viscous mesophase among all nematic phases. In discotic nematic mesophase, the molecules have rotational and translational freedom along the short molecular axis<sup>38</sup>. However, the short axis, on average, is orientated along a particular direction, called director n. Chiral discotic molecules and chiral dopants in discotic nematic mesophase resulted in the formation of chiral nematic mesophase, which has a helical structure similar to the cholesteric phase<sup>39,40</sup>. The columnar nematic phase is identified from the columnar arrangement of the discotic molecules where the columns do not arrange in any 2D crystal lattice. These columns behave like supramolecular rods that orient along a particular direction but do not display any positional order<sup>41–44</sup>. In some cases, the disc-shaped molecules aggregate to form large superstructures that exhibit nematic arrangement. This is known as the nematic lateral phase due to the presence of strong lateral interactions<sup>45</sup>.

The nematic mesophase of discotic molecules exhibits schlieren texture under polarized optical microscopy (POM) similar to calamitic nematics (**Figure 1.10a**). Columnar nematic phase obtained from donor and acceptor mixtures shows the same schlieren textures with deep colors due to the charge transfer process<sup>42</sup>. X-ray diffractogram of N<sub>D</sub> phase resembles that on an isotropic liquid. The wide-angle peak is related to the lateral distance between the cores, while the small-angle reflection corresponds to the molecular diameter (**Figure 1.10b**). The diffraction profile of N<sub>Col</sub> phase has relatively sharp reflections in the wide-angle region that correspond to the regular stacking of disks inside the column. The molecular structures of some of the nematic phase forming discotic mesogens are shown in **Figure 1.11**, along with their mesophase type and phase transition temperatures.



**Figure 1.10**. a) Schlieren texture under crossed polarizer and b) X-ray diffraction pattern of nematic discotics<sup>24</sup>.



**Figure 1.11**. The molecular structures of a few DLCs and their phase transition temperatures<sup>39,46–48</sup>. (Cr-Crystal, N<sub>D</sub>- Discotic nematic,  $N^*_D$ - Chiral discotic nematic,  $N_{Col}$ - Columnar nematic).

#### 2.1.2. Columnar mesophases of discotic Mesogens

The stacking of disc-like molecules on top of each other into 1D columns form the most characteristic class of DLCs, the family of columnar mesophases. Depending on the exact nature of stacking and intracolumnar order, there can be "disordered columns" with irregular stacking of discs and "ordered columns" where the molecules are regularly arranged equidistantly. Molecules can also be tilted to a particular angle to their columnar axis, resulting in "tilted columns." These columns further occupy various 2D lattices in which the columns are arranged parallel to each

other. Columnar discotic liquid crystals hence can be classified based on their difference in symmetry of 2D crystalline structures<sup>49</sup>.

In the hexagonal columnar mesophase (Col<sub>h</sub>), the columns are arranged in hexagonal lattice whose planar space group is *p6/mmm*. Schematic representation of molecular arrangement in Col<sub>h</sub> is shown in **Figure 1.12(a)**. X-ray diffraction (XRD) and polarized optical microscopy are widely used to characterize diverse columnar mesophases. A typical 2D X-ray diffraction pattern of Col<sub>h</sub> phase is shown in **Figure 1.12(b)**, which contains many sharp reflections in the small-angle region and two broad diffused peaks in the wide-angle regime. The reflections of the small-angle region whose d-spacings are in the characteristic ratio of  $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}...$  according to the following equation where *a* is lattice parameter.

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + k^2 + hk}{a^2}$$

The broad diffuse peak in the wide-angle region corresponds to the liquid-like order of molten alkyl chains. A second relatively narrow peak arises due to the regular packing of cores in the columns. Due to the shape anisotropy, the liquid-crystalline phases are in general birefringent in nature under crossed polarizer<sup>50</sup>. Each mesophase type shows a characteristic "texture" in POM that resulted from a combination of symmetry-dependent elasticity, defect formation, and the surface conditions of the sample. Typical textures of the Col<sub>h</sub> phase are shown in **Figure 1.12(c-f)** that including predominantly observed focal conic and pseudo focal conic textures. Dendritic and mosaic textures are less common, and rectilinear defects are associated with ordered columnar structures<sup>51,52</sup>.



**Figure 1.12**. POM micrigraphes of  $Col_h$  mesophases. a) focal conic b) pseudo focal conic c) dendritic d) mosaic textures with rectilinear defects (Ordered Columnar)<sup>8</sup>

In the rectangular columnar mesophase (Col<sub>r</sub>), the molecules are tilted with respect to the columnar axis resulting in an elliptic cross-section of molecules. These columns further occupy rectangular lattices<sup>53,54</sup>. There are three types of Col<sub>r</sub> phases based on the symmetry of three different planar space groups  $P2_1/a$ , P2/a, C2/m. The 2D X-ray diffractogram of a typical Col<sub>r</sub> phase is shown in **Figure 1.13**, and it can be observed that the (10) plane of the Col<sub>h</sub> phase is split
into two different reflections in the small-angle region. In rectangular lattice, the lattice parameters *a* and *b* are related to the d-spacing of different planes according to the following equation,

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2}$$

The wide-angle peaks resemble those of  $Col_h$  mesophase, with a diffuse halo corresponding to the fluidity of the alkyl chain and a relatively narrow core-core peak. Stronger core-core interaction is necessary to form  $Col_r$  than  $Col_h$  mesophase, consequently making them higher-order mesophases. Subsequently, cross-over from  $Col_r$  to  $Col_h$  mesophase is observed with increasing flexible aliphatic chain length. Since there is only a minor difference between the structures, the POM textures of  $Col_r$  resemble more often the textures observed for  $Col_h$  mesophase (**Figure 1.12**). However, broken fan textures and mosaic textures are most commonly observed for columnar rectangular mesophases.



**Figure. 1.13 a**) The molecular arrangement b) X-ray profile and c) different types of rectangular columnar mesophase.

Columnar oblique mesophase (Col<sub>ob</sub>) is characterized by the arrangement of columns in an oblique lattice whose space group is  $P_1$ . The X-ray diffraction pattern shows many sharp reflections in the small-angle regime corresponding to all allowed peaks (*hk*) due to the primitive planar space group. Since strong core-core interactions are required, these mesophase type is scarcely observed<sup>55</sup>. Along with fan-shaped textures, spiral textures are also observed for columnar oblique mesophase under POM<sup>56</sup>. Columnar tetragonal (square) phase (Col<sub>tet</sub>) is formed by the tetrangular arrangement of the columns of specific disc-shaped molecules. Spontaneous homeotropic alignment is observed for Col<sub>tet</sub> phase, similar to that of Col<sub>h</sub> phase. The small-angle XRD pattern displays the d-spacing values that are in the ratio of 1:  $\sqrt{2}$  for (10) and (11) planes. In addition, the columns are self-assembled in layered structures in some discotic compounds to form columnar lamellar mesophase (Col<sub>L</sub>) (**Figure 1.14c**).



**Figure 1.14**. Schematic representation of molecular arrangement in a) hexagonal columnar plastic  $(Col_p)$ , b) hexagonal columnar helical (H), and c) columnar lamellar mesophases. d) XRD pattern and e) POM textures of  $Col_p$  mesophase of hexabutoxytriphenylene (HAT4)<sup>8,57</sup>.

Recently, a highly ordered columnar hexagonal mesophase has been observed in which the molecules inside the columns are regularly arranged like crystals. This phase is identified as the columnar plastic phase denoted as Col<sub>p</sub>, where the rotational freedom about the column axis is still preserved, as in the case of plastic crystals (**Figure 1.14a**). The small-angle diffraction pattern of columns is indexed to hexagonal lattice while the core-core peak in the wide-angle region is split into two peaks as opposed to the diffused core-core reflection of Col<sub>h</sub> mesophase<sup>58</sup> (**Figure 1.14d**). Dendritic textures are more often observed for the Col<sub>p</sub> phase in POM than commonly observed phases for the hexagonal columnar phase (**Figure 1.14e**). In addition to these, an exceptional mesophase with helical ordering of molecules within the columns is observed in a few triphenylene derivatives (**Figure 1.14b**). The X-ray diffraction pattern of this helical columnar mesophase (H) indicates the crystals like helical intracolumnar ordering<sup>59</sup>.

#### 2.2. Classes of compounds used for discotic liquid crystals

#### 2.2.1 Polycyclic aromatic hydrocarbons (PAH) based DLCs

A large number of discotic cores based on polycyclic aromatic hydrocarbons (PAHs) (all carbon and hydrogen) have been reported to form columnar liquid crystals. Disc-shaped molecules containing the derivatives of benzene, naphthalene, phenanthrene, triphenylene, pyrene, dibenzochrysene, dibenzonaphthacene, anthraquinone, truxene, perylene, coronene (**Figure 1.15**) with suitable hydrocarbon chains are found to show diverse mesomorphism. The nature of such mesomorphic phases as a function of the molecular structure has been studied extensively. Since the pioneering discovery of columnar liquid crystals by Chandrasekhar et al. on benzene hexaesters, many hexa and 1,3,5-trisubstituted benzene derivatives have been used for DLCs.

Among all the polycyclic aromatic hydrocarbons used as a core for discotic liquid crystals, triphenylene has been the widely explored core system. Triphenylene was recognized for the design of DLCs by a French group in 1978 and emerged as one of the largest classes of discotic mesogens<sup>60,61</sup>. Several groups have proposed diverse synthetic strategies to synthesize and study the structure-property relationship of triphenylene-based DLCs. Symmetrical triphenylenes were commonly synthesized by oxidative trimerization of dialkoxybenzene or by "biphenyl route," that is, the cocyclization of tetraalkoxybiphenyl and dialkoxybenzene with FeCl<sub>3</sub> in dichloromethane (**Figure 1.16**).







**Figure 1.16**. Synthetic scheme of symmetrically substituted triphenylene (HAT). i) RBr, K<sub>2</sub>CO<sub>3</sub>, Ethanol, reflux, 12h. ii) FeCl<sub>3</sub>, Dichloromethane(DCM), rt, 15 mins.

The fairly accessible chemistry, high thermal stability, and one-dimensional chargetransporting properties of triphenylene derivatives stimulated the synthesis of various triphenylene DLCs. Symmetrically substituted triphenylenes and well-defined unsymmetrical derivatives of triphenylene were synthesized by various reaction pathways, and their mesomorphic properties were explored by many research groups<sup>62</sup>. Electrophilic aromatic substitution in triphenylene resulted in mono, di, and tri-functionalized triphenylenes (**Figure 1.17**). Functionalization of triphenylene-based DLCs by nitration produced mono, di, and trinitro triphenylene derivatives. The mono nitro triphenylenes showed a broad mesophase range with highly ordered columnar structures confirmed by POM and X-ray diffraction studies. Functionalization of triphenylenes modifies the electronic structure of the molecules and acts as an important intermediate step to access various processable monomeric, oligomeric, and polymeric derivatives<sup>63</sup>.



**Figure 1.17**. Synthesis of various functionalized triphenylene derivatives. a) HNO<sub>3</sub>, DCM/CH<sub>3</sub>NO<sub>2</sub>. b) Raney Ni, H<sub>2</sub>, THF. c) Pyridine, Ac<sub>2</sub>O. d) DCM, AcOH, NaNO<sub>2</sub>.

Significantly larger PAH cores, known as nanographenes, are also reported to form columnar mesomorphism that found applications in organic electronic devices as hole-transporting materials. It is expected that the increase in the size of the central aromatic ring will lead to enhancement in columnar stability by the increase in  $\pi$ -overlap. However, only very few reports on large discotics showed liquid crystalline property over a broad temperature range. For example, triangle-shaped discotic graphenes containing the same number of carbons as C60 fullerene with swallow-tailed alkyl substituents have been synthesized and reported to exhibit stable columnar mesophase over an extremely broad temperature range<sup>64</sup>. Superphenalene discotics have been subjected to crosslinking at high temperatures to give thin transparent graphene films and used as window electrodes in organic photovoltaics<sup>65</sup>.

#### 2.2.2 Heterocyclic DLCs.

The majority of the discotic liquid crystals reported are synthesized from electron-rich PAHs that exhibit high hole-transporting behavior. However, the fabrication of organic electronics requires both p-type and n-type materials to design bipolar transistors, p-n junction diodes. For this purpose, the demand for electron-deficient molecules increased significantly in developing electron-transporting columnar liquid crystals. Most of the columnar electron-transporting materials are achieved by replacing the aromatic –CH with nitrogen atoms. Nitrogen-containing triazine, phenazine, azatriphenylene, tristriazolotriazine, triindole, tricycloquinazoline, phenazine, porphyrin, coronene diimide (**Figure 1.18**) were some of the widely explored heterocyclic cores for DLCs. The nature of the discotic core and flexible hydrocarbon chains in the periphery affects the self-assembly of these mesogens.

Among all triphenylene derivatives, hexaazatriphenylene is widely studied as potential electron carriers in view of the presence of six nitrogen atoms and strongly electron-deficient nature. Hexaazatriphenylene forms columnar mesophase with the suitable side chains with amide linkage forcing the neighboring molecules to stack in columns through hydrogen bonding<sup>66</sup>. The alkyl and thioalkyl derivatives are non-liquid crystalline in nature, possibly because of large negative charges on the nitrogen atoms that lead to the repulsion of adjacent cores<sup>67</sup>. However, hexaazatrinaphthylene derivatives which have extended  $\pi$ -delocalization were found to exhibit polymorphism with suitable thioalkyl chains.



#### Figure 1.18. Structures of some heterocyclic cores used as DLCs.

The peripheral substitution of phthalocyanine (Pc) induced liquid crystallinity in these twodimensional heterocyclic core and a tetradentate ligand. Phthalocyanines are known to selfassemble into columnar structures and form thermotropic liquid crystals and highly ordered thin films<sup>68,69</sup>. Tricycloquinazoline (TCQ) was introduced as a novel electron-deficient core fragment for discotic mesogens by Kumar et al. Many derivatives of TCQ with alkoxy and thioether with varying alkyl chains were found to form hexagonal columnar mesophase with broad temperature range<sup>70,71</sup>. **Figure 1.19** shows molecular structures and self-assembling behavior of a few heterocyclic DLCs.



Figure 1.19. Nitrogen-based heterocyclic DLCs and their phase transition temperatures (°C).

#### 2.3. Characterization of discotic liquid crystals

The bulk properties of the thermotropic liquid crystalline materials are usually studied by the combination of polarized optical microscopy (POM), differential scanning calorimetry (DSC), and powder X-ray diffraction (XRD). These techniques allow us to understand the nature of self-assembly, stability, phase transition temperatures, and enthalpy associated with the transition of the discotic mesogens.

#### Polarized optical microscopy (POM)

POM is one of the most widely used techniques to give an early insight into the existence and, to some extent, the nature of mesophase in discotic compounds. The sample is placed between two glass slides in the POM experiment and loaded onto a microscope stage equipped with a variable temperature controller. Liquid crystalline phases are anisotropic fluids exhibiting optical birefringent and showing a typical pattern (textures) under crossed polarizers. The nature of textures in the mesophase range is characteristic of a specific LC phase. The textures originate from the symmetry-dependent elasticity of the LC phase in combination with defects and surface conditions. However, the birefringent is not observed in homeotropically aligned samples, and instead, a dark field is observed. Crystals also are optically anisotropic and birefringent under POM, but can be easily distinguished from LCs due to the fluid nature of the mesophase. Liquid crystals with low viscosity start to flow upon melting from the crystalline phase. On cooling from isotropic phase, they form textures which, on pressing the glass changes its structure. On the other hand, crystals do not show any change in textures or cracks with defined edges form on pressing the glass slide. Schlieren and thread-like textures are often associated with nematic liquid crystals, while fan-shaped structures, mosaic and dendritic textures are commonly observed in columnar mesophase. Textures of the ordered columnar mesophase typically exhibit straight linear defects. (Figure 1.12).

#### Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is an important thermo-analytical technique used to evaluate the phase transition temperatures of mesophase and the enthalpy associated with the transition. Although DSC does not provide any concrete evidence of the liquid crystallinity of the material, it acts as a complementary technique to POM. The magnitude of the enthalpy change during a phase transition provides certain information regarding the change in the degree of ordering at the transition. In general, an enantiotropic discotic mesogen on heating shows two endothermic (heat absorbed) peaks in DSC corresponding to the crystal to mesophase and mesophase to isotropic transitions. Similar behavior is observed in the cooling cycle, where two exothermic peaks are observed on cooling from isotropic phase to crystalline state. Monotropic LCs show mesophase character in only one cycle and most often form mesophase on cooling from isotropic liquid. Many phase transition peaks are observed for compounds exhibiting more than one type of mesophase. The typical DSC thermogram is usually plotted as heat flow (mW) as a function of temperature (°C). The peaks correspond to the phase transition temperatures and area under the curve to the associated enthalpy change. Usually, a large enthalpy change (20-100 kJ/mol) is observed for the transition from crystal to LC phase transition as it goes from highly ordered crystalline state to less ordered (or short-range order) LC phase. However, the LC phase to isotropic phase transition involves relatively lesser enthalpy values (below 10 kJ/mol). DSC thermogram provides information regarding the number of mesophase transitions and the structural ordering of the LC materials.

#### X-ray diffraction technique (XRD)

Powder X-ray diffraction is a powerful technique used to understand the structure and symmetry of liquid crystalline materials. X-ray diffraction of LC phases is used to determine the liquid crystalline ordering and cell parameters. The XRD technique works on the principle of Bragg's law, where  $\lambda$  is the X-ray wavelength, d is the interplanar spacing generating the diffraction, and  $\theta$  is the diffraction angle.

#### $n\lambda$ =2d sin $\theta$

A typical one-dimensional intensity-diffraction angle XRD profile of some of the columnar liquid crystalline phases is shown in **Figure 1.12**, which is usually split into two angle regions. The small-angle region consists of sharp reflections that describe the lateral packing of the columns (2D arrangement of columns). In contrast, the wide-angle region provides information about the packing of fluid-like hydrocarbon chains and core-core ordering within the column. The small-angle region usually shows few sharp peaks that are indexed to a specific mesophase structure such as  $Col_h$ ,  $Col_r$ ,  $Col_{ob}$ . The wide-angle region contains two broad peaks corresponding to the side-chain packing and  $\pi$ -  $\pi$  core stacking (core-core distance), differentiating the mesophase from "true" crystals. The core-core separation is usually in the order of 3-4 Å. The XRD profile provides information on the structural symmetry along with the data on i) ordering of the peripheral

hydrocarbon chains and the central core, ii) the core-core correlation length along the columnar axis, and iii) the intercolumnar distance and lattice parameters.

#### 2.4. Applications of discotic liquid crystals

#### DLCs in liquid crystal displays (LCD)

Since the invention of liquid crystal displays, twisted nematic (TN) and super twisted nematic (STN) have dominated commercial devices. The active layer in these devices primarily is rod-like calamitic liquid crystals<sup>72</sup>. However, there is a major disadvantage such as the narrow and non-uniform viewing angle of these LCDs required many alternative approaches including multidomain techniques<sup>73</sup>, the introduction of an optical compensator<sup>74</sup>, application of electric field parallel to the substrate<sup>75</sup>, etc. These methods have been shown to increase the viewing angle of display devices in combination with high contrast ratio. Fuji photo films utilized the nematic phase discotic liquid crystals as optical compensation films to increase the viewing angle and contrast ratio<sup>76</sup>. The optical compensation film is a hybrid alignment of discotic nematic LCs film that widens the viewing angle of LCD by compensating the positive optical anisotropy of calamitic nematic by the negative optical anisotropy of DLCs. These films are made of triphenylene esters with epoxide or acrylate groups homeotropically aligned in the nematic phase, followed by photopolymerization. The optical compensation films are the most commercially successful application of DLCs. Chandrasekhar and coworkers designed a display device employing discotic nematic liquid crystalline materials instead of conventional calamitic nematic LCs<sup>77,78</sup>. The LCD made using hexaalkynylbenzene derivative was simple to fabricate, showed excellent viewing angle characteristics, having less difference in pixel capacitance between ON and OFF states. However, the response time of the device was slower than conventional calamitic nematic-based devices due to the high viscosity of the discotic nematic mesophase. Decreasing the viscosity by doping a small concentration of long-chain alkanes to the parent room-temperature discotic nematic material has improved response time.

Page | 25

#### Charge transport properties

Organic electronics is a growing multidisciplinary research field comprising organic synthesis, materials science, and solid-state physics develop organic to new semiconductors. Organic molecules are of particular interest owing to their low-cost solution processability and readily available synthetic modifications for various applications such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells. Charge mobility plays an indispensable role in optoelectronic applications since it specifies the frequency of charge transport, an essential criterion of semiconductors that heavily depends on molecular aggregation, which, in turn, relies on the molecular structure. It becomes evident with an argument that the specific design of a molecular structure which induces these highly ordered supramolecular assemblies favors charge transport.





Organic compounds often form crystals upon solution processing which have domain boundaries that severely restrict the charge mobility. Thermotropic discotic liquid crystalline materials overcome this restriction through columnar organization, that is, the disc-shaped molecules stack on top of each other to form a one-dimensional column which further occupies various two-dimensional lattices. These mesogenic materials, known as one of the delicate phases of matter, exhibit both order and mobility. The homogeneous domains can sometimes be achieved to a larger length scale, which is essentially required for semiconducting devices<sup>23</sup>. These supramolecular structures contain immense potential in organic electronic devices as a result of their advantageous properties, including the long-range self-assembling, self-healing, high charge carrier mobility, and ease of processing<sup>35</sup>.

As a result of the self-assembly of aromatic cores with an approximate distance of about 3.5 Å, there is a considerable overlap of  $\pi^*$ -  $\pi^*$  LUMO orbitals leading to the formation of conduction band for the charge transport along the columnar axis. The columns act as molecular wires which is surrounded by insulating alkyl chains, thus acting as one-dimensional charge transporting materials (**Figure 1.20**). In general, the bigger the core size, the better the mobility due to the stronger  $\pi$ - overlap resulting in increased columnar stability<sup>80</sup>. Along with core size, the nature of the substitution plays a vital role in charge transport as they significantly alter the intracolumnar order. For example, the alkoxy substituted triphenylene derivatives have shown lesser mobility values compared to the thioether counterparts.

Adam and coworkers studied electron and hole transport properties of a homeotropically aligned sample of HAT5 and found the hole mobility is higher than that of electrons<sup>81,82</sup>. Much higher hole mobility of 0.001 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> was measured for HHTP using TOF technique in the mesophase range independent of temperature. They also reported increased mobility in the helical mesophase compared to the hexagonal columnar phase and very low mobility in the isotropic phase. This stepwise change in the charge transport is associated with the increase in order of the system from isotropic to helical phase<sup>83,84</sup>. The self-organization and charge transport properties made these materials prime candidates for developing organic electronic devices. Electron-rich columnar liquid crystalline hexa-peri-hexabenzocoronene combined with non-mesomorphic perylene bisimide as electron acceptor produces vertically segregated thin films, which showed up efficiency<sup>85</sup>. 2% photovoltaic Mesomorphic 3.4.9.10fluorescent to tetra(alkoxycarbonyl)perylenes as the luminescent electron-transport layer in combination with triphenylene mesogens as the hole-transporting layer have been successfully used in OLED devices<sup>86,87</sup>. However, the design of organic electronics needs both p-type and n-type materials,

but most discotic molecules are electron-rich p-type materials. Thus, novel n-type columnar liquid crystals are required for applications in device fabrication.

#### DLCs in organic photovoltaic cells (PV)

Recently, photovoltaic devices based on discotic liquid crystals attracted significant attention due to their low cost, easy processability, and large area applications<sup>22,88,89</sup>. The photovoltaic cell requires the absorption of solar radiation and the generation of electrons and holes, charge separation, and the transport of electrons and holes for collection at their respective electrodes. These processes should be highly efficient, and charge recombination should be minimum for a high-efficiency solar cell output. Self-organization of columnar DLCs and crystalline  $\pi$ -conjugated materials have been used to create thin films directly from solution with structures optimized for the applications in photovoltaics<sup>85</sup>. Thin films made by self-organization of columnar mesomorphic hole-accepting hexa-*peri*-hexabenzocoronene (HBC) combined with electron-accepting perylene bisimide (**Figure 1.21**). They have been shown to exhibit photovoltaic response with external quantum efficiencies of greater than 34 % at 490 nm and power efficiencies up to 2 %. This high efficiency resulted from the efficient charge transfer between the donor-acceptor and effective charge transport through the layered structure. Several other p-type DLCs like porphyrin<sup>90</sup>, phthalocyanine<sup>91</sup>, and triphenylene<sup>92</sup> have been explored to construct solar cells. Perylene derivatives were used as an n-type semiconductor in most discotic devices<sup>93</sup>.

#### DLCs as organic light-emitting diodes (OLED)

In an organic LED device, the active component is layered between two electrodes, one of which is a transparent anode (ITO), and another is a metal cathode. Under an external electric field, the electrons are injected into the LUMO of the acceptor and holes into the HOMO of the donor. In a typical bilayer OLED device, the electron drifts through the n-type material and combines with the hole which drifts through the p-type material. The recombination of electrons and holes results in luminescence. High charge carrier mobility is essential for OLED in order to obtain high current densities that would result in increased light intensities. The charge carrier mobility in columnar liquid crystal is high (in the order of  $10^{-1}$  cm V<sup>-1</sup>s<sup>-1</sup>) and thus exploited in OLEDs. A typical OLED cell consisting of both p-type and n-type material is shown in the **Figure 1.22**. Triphenylene has been the most widely used molecule in LED devices due to its high charge carrier

mobility and the relatively matching work function of TP with ITO electrodes<sup>94</sup>. The columnar hexabutoxytriphenylene as hole transporting material and fluorescent columnar perylene as electron transporting medium in between ITO and Al electrodes exhibited red fluorescence above 10 V. Orange-red electroluminescence was obtained in a single layer OLED device containing perylene 3,4,9,10-tetracarboxylic acid ethyl ester as active component<sup>86</sup>. The ability to self-heal by expelling the defects is an important advantage of these mesomorphic materials, leading to an increased lifetime of devices.



**Figure 1.21**. The chemical structure of HBC-PhC<sub>12</sub> (A), perylene bisimide (B). C) schematic representation of the  $\pi$ -stacking configuration of columnar mesophase of HBC. D) the electron diffraction image of perylene molecule taken from a spin-coated xylene film (intermolecular spacing of approximately 3.5 Å). E) Energy level diagrams of HBC-PhC<sub>12</sub> and perylene<sup>85</sup>.



Figure 1.22. Schematic arrangement of donor and acceptor columnar mesophases forming a double layer in the  $LED^{23}$ .

#### 3. References.

- From Molecular to Supramolecular Chemistry. in *Supramolecular Chemistry* 1–9 (Wiley-VCH Verlag GmbH & Co. KGaA, 2006). doi:10.1002/3527607439.ch1.
- Lehn, J.-M. Toward Self-Organization and Complex Matter. Science (80-.). 295, 2400– 2403 (2002).
- M., W. G., P., M. J. & T., S. C. Molecular Self-Assembly and Nanochemistry: a Chemical Strategy for the Synthesis of Nanostructures. *Science* (80-. ). 254, 1312–1319 (1991).
- Lehn, J.-M. Supramolecular Chemistry—Scope and Perspectives Molecules, Supermolecules, and Molecular Devices(Nobel Lecture). *Angew. Chemie Int. Ed. English* 27, 89–112 (1988).
- Suárez, M., Lehn, J.-M., Zimmerman, S. C., Skoulios, A. & Heinrich, B. Supramolecular Liquid Crystals. Self-Assembly of a Trimeric Supramolecular Disk and Its Self-Organization into a Columnar Discotic Mesophase. *J. Am. Chem. Soc.* 120, 9526–9532 (1998).

- Peter J. Collings. *Liquid Crystals: Nature's Delicate Phase Of Matter*. (Princeton Univ. Press, Princeton, NJ, 1990).
- Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., and Vill, V. *Handbook of Liquid Crystals*. (Wiley VCH, Weinheim, Germany, 1998).
- 8. Kumar, S. Chemistry of discotic liquid crystals: From monomers to polymers. (CRC press, 2011).
- 9. Peter J. Collings, Patel, J. S. *Handbook Of Liquid Crystal Research*. (Oxford University Press, Oxford, 1997).
- De Gennes, P.-G. & Prost, J. *The physics of liquid crystals*. (Oxford university press, 1993).
- Chandrasekhar, S. *Liquid Crystals*. (Cambridge University Press, 1992). doi:DOI: 10.1017/CBO9780511622496.
- Goodby, J. W., Davis, E. J., Mandle, R. J. & Cowling, S. J. Chemical Structure and Mesogenic Properties. *Handbook of Liquid Crystals* 1–30 (2014) doi:https://doi.org/10.1002/9783527671403.hlc011.
- 13. Lehmann, O. Über fliessende krystalle. Zeitschrift für Phys. Chemie 4, 462–472 (1889).
- 14. Reinitzer, F. Contributions to the knowledge of cholesterol. *Liq. Cryst.* 5, 7–18 (1989).
- 15. Crystals That Flow. (CRC Press, 2004). doi:10.1201/9780203022658.
- 16. Vorlander, D. Kristallinisch-Flussige Substanzen. (1908).
- Harrison, K., Gray, G. & Nash, J. new family of nematic liquid crystals for displays. in 543–548 (2004). doi:10.1201/9780203022658.ch7d.
- Chandrasekhar, S., Sadashiva, B. K. & Suresh, K. A. Liquid crystals of disc-like molecules. *Pramana* 9, 471–480 (1977).
- Unconventional Liquid Crystals and Their Applications. (De Gruyter, 2021). doi:doi:10.1515/9783110584370.

- 20. Kumar, S. Chemistry of Discotic Liquid Crystals. Chemistry of Discotic Liquid Crystals (CRC Press, 2016). doi:10.1201/b10457.
- 21. Goodby, J. W. Phase Structures of Calamitic Liquid Crystals. *Handbook of Liquid Crystals* 3–21 (1998) doi:https://doi.org/10.1002/9783527620555.ch1.
- 22. Laschat, S. *et al.* Discotic Liquid Crystals: From Tailor-Made Synthesis to Plastic Electronics. *Angew. Chemie Int. Ed.* **46**, 4832–4887 (2007).
- 23. Sergeyev, S., Pisula, W. & Geerts, Y. H. Discotic liquid crystals: a new generation of organic semiconductors. *Chem. Soc. Rev.* **36**, 1902 (2007).
- Kumar, S. Self-organization of disc-like molecules: chemical aspects. *Chem. Soc. Rev.* 35, 83–109 (2006).
- 25. Demus, D. Types and Classification of Liquid Crystals. in *Liquid Crystals Applications and Uses* 1–36 (WORLD SCIENTIFIC, 1990). doi:10.1142/9789814368278\_0001.
- Tschierske, C., Pelzl, G. & Diele, S. Definitionen von Grundbegriffen mit Bezug zu niedermolekularen und polymeren Flüssigkristallen. *Angew. Chemie* 116, 6340–6368 (2004).
- Peter J. Collings, M. H. Introduction to Liquid Crystals Chemistry and Physics. (CRC Press, 1997). doi:https://doi.org/10.1201/9781315272801.
- Peter J. Collings, J. W. G. Introduction to Liquid Crystals Chemistry and Physics. (CRC Press, 2019).
- Ian Robert Nemitz. Liquid Crystals : Surfaces, Nanostructures, and Chirality. (Université Pierre et Marie Curie, 2016).
- Bushby, R. J. & Lozman, O. R. Discotic liquid crystals 25 years on. Curr. Opin. Colloid Interface Sci. 7, 343–354 (2002).
- Chandrasekhar, S. & Ranganath, G. S. Discotic liquid crystals. *Reports Prog. Phys.* (1990) doi:10.1088/0034-4885/53/1/002.
- 32. Pelzl, G., Diele, S. & Weissflog, W. Banana-Shaped Compounds—A New Field of Liquid

Page | 32

Crystals. Adv. Mater. 11, 707–724 (1999).

- Malthête, J., Levelut, A. M. & Tinh, N. H. Phasmids : a new class of liquid crystals. J. Phys. Lett. 46, 875–880 (1985).
- Ekwall, P. Composition, Properties and Structures of Liquid Crystalline Phases in Systems of Amphiphilic Compounds. in (ed. Brown, G. H. B. T.-A. in L. C.) vol. 1 1–142 (Elsevier, 1975).
- Kaafarani, B. R. Discotic Liquid Crystals for Opto-Electronic Applications † ‡. *Chem. Mater.* 23, 378–396 (2011).
- 36. Kumar, S. Recent developments in the chemistry of triphenylene-based discotic liquid crystals. *Liquid Crystals* (2004) doi:10.1080/02678290410001724746.
- Boden, N., Bushby, R. J. & Lozman, O. R. DESIGNING BETTER COLUMNAR MESOPHASES. *Mol. Cryst. Liq. Cryst.* 400, 105–113 (2003).
- Bisoyi, H. K. & Kumar, S. Discotic nematic liquid crystals: Science and technology. *Chem. Soc. Rev.* (2010) doi:10.1039/b901792p.
- Langner, M., Praefcke, K., Krüerke, D. & Heppke, G. Chiral radial pentaynes exhibiting cholesteric discotic phases. *J. Mater. Chem.* 5, 693–699 (1995).
- 40. Booth, C. J., Krüerke, D. & Heppke, G. Highly twisting enantiomeric radial multiyne dopants for discotic liquid-crystalline systems. *J. Mater. Chem.* **6**, 927–934 (1996).
- Kouwer, P. H. J., van den Berg, O., Jager, W. F., Mijs, W. J. & Picken, S. J. Induced Liquid Crystalline Diversity in Molecular and Polymeric Charge-Transfer Complexes of Discotic Mesogens. *Macromolecules* 35, 2576–2582 (2002).
- Kouwer, P. H. J., Jager, W. F., Mijs, W. J. & Picken, S. J. Charge Transfer Complexes of Discotic Liquid Crystals: A Flexible Route to a Wide Variety of Mesophases. *Macromolecules* 35, 4322–4329 (2002).
- 43. Kohmoto, S., Mori, E. & Kishikawa, K. Room-Temperature Discotic Nematic Liquid Crystals over a Wide Temperature Range: Alkali-Metal-Ion-Induced Phase Transition

from Discotic Nematic to Columnar Phases. J. Am. Chem. Soc. 129, 13364–13365 (2007).

- Bala, I., Gupta, S. P., De, J. & Pal, S. K. Room-Temperature Columnar Nematic and Soft Crystalline Columnar Assemblies of a New Series of Perylene-Centred Disc Tetramers. *Chem. – A Eur. J.* 23, 12767–12778 (2017).
- Kouwer, P. H. J., Jager, W. F., Mijs, W. J. & Picken, S. J. The Nematic Lateral Phase: A Novel Phase in Discotic Supramolecular Assemblies. *Macromolecules* 34, 7582–7584 (2001).
- Kumar, S. & Varshney, S. K. Design and Synthesis of Discotic Nematic Liquid Crystals. Org. Lett. 4, 157–159 (2002).
- Yang, Y. *et al.* Molecular Engineering of Mesomorphic Fluorene-Bridged Triphenylene Triads: Thermotropic Nematic/Columnar Mesophases, and p-Type Semiconducting Behavior. *Cryst. Growth Des.* 18, 4296–4305 (2018).
- 48. De, J. *et al.* Molecular Engineering for the Development of a Discotic Nematic Mesophase and Solid-State Emitter in Deep-Blue OLEDs. *J. Org. Chem.* **86**, 7256–7262 (2021).
- Oswald, P. & Pieranski, P. Smectic and Columnar Liquid Crystals. (CRC Press, 2005). doi:10.1201/9781420036343.
- 50. Dr. Ingo Dierking. *Textures of Liquid Crystals*. (Wiley VCH, Weinheim, Germany, 2003). doi:10.1002/3527602054.
- 51. Ribeiro, A. C. *et al.* Rectangular to hexagonal columnar phase transition exhibited by a biforked mesogen. *Eur. Phys. J. E* **10**, 143–151 (2003).
- Zheng, H., Lai, C. K. & Swager, T. M. Controlling Intermolecular Interactions between Metallomesogens: Side-Chain Effects in Discotic Copper, Palladium, and Vanadyl Bis(.beta.-Diketonates). *Chem. Mater.* 7, 2067–2077 (1995).
- 53. Frank, F. C. & Chandrasekhar, S. Evidence of a tilted columnar structure for mesomorphic phases of benzene-hexa-n-alkanoates. *J. Phys.* **41**, 1285–1288 (1980).
- 54. Destrade, C. et al. Disc-Like Mesogen Polymorphism. Mol. Cryst. Liq. Cryst. 106, 121-

146 (1984).

- Destwde, C., Tinh, N. H., Mamlok, L. & Malthete, J. Trioxatruxenes: A New Family of Disc-Like Mesogens with a Complex Polymorphism. *Mol. Cryst. Liq. Cryst.* 114, 139– 150 (1984).
- Morale, F. *et al.* Columnar Mesomorphism from Hemi-Disklike Metallomesogens Derived from 2,6-Bis[3',4',5'-tri(alkoxy)phenyliminomethyl]pyridines (L): Crystal and Molecular Structures of [M(L)Cl2] (M=Mn, Ni, Zn). *Chem. – A Eur. J.* 9, 2484–2501 (2003).
- Mahesh, P. *et al.* Carbon dot-dispersed hexabutyloxytriphenylene discotic mesogens: structural, morphological and charge transport behavior. *J. Mater. Chem. C* 8, 9252–9261 (2020).
- Prasad, S. K., Rao, D. S. S., Chandrasekhar, S. & Kumar, S. X-RAY Studies on the Columnar Structures of Discotic Liquid Crystals. *Mol. Cryst. Liq. Cryst.* 396, 121–139 (2003).
- Fontes, E., Heiney, P. A. & de Jeu, W. H. Liquid-Crystalline and Helical Order in a Discotic Mesophase. *Phys. Rev. Lett.* 61, 1202–1205 (1988).
- DESTRADE, C., MONDON, M. C. & MALTHETE, J. HEXASUBSTITUTED TRIPHENYLENES : A NEW MESOMORPHIC ORDER. *Le J. Phys. Colloq.* (1979) doi:10.1051/jphyscol:1979305.
- Billard, J.; Dubois, J. C.; Nguyen Huu Tinh; Zann, A. A disk-like mesophase. *Nouv. J. Chim.* 2, 535–40 (1978).
- 62. Pal, S. K., Setia, S., Avinash, B. S. & Kumar, S. Triphenylene-based discotic liquid crystals: recent advances. *Liquid Crystals* (2013) doi:10.1080/02678292.2013.854418.
- Kumar, S., Manickam, M., Balagurusamy, V. S. K. & Schonherr, H. Electrophilic aromatic substitution in triphenylene discotics: Synthesis of alkoxynitrotriphenylenes. *Liq. Cryst.* 26, 1455–1466 (1999).

- Feng, X. *et al.* Supramolecular Organization and Photovoltaics of Triangle-shaped Discotic Graphenes with Swallow-tailed Alkyl Substituents. *Adv. Mater.* 20, 2684–2689 (2008).
- 65. Wang, X. *et al.* Transparent Carbon Films as Electrodes in Organic Solar Cells. *Angew. Chemie Int. Ed.* **47**, 2990–2992 (2008).
- 66. Gearba, R. I. *et al.* Tailoring Discotic Mesophases: Columnar Order Enforced with Hydrogen Bonds. *Adv. Mater.* **15**, 1614–1618 (2003).
- Roussel, O. *et al.* Discotic Liquid Crystals as Electron Carrier Materials. *Mol. Cryst. Liq. Cryst.* 396, 35–39 (2003).
- 68. Van Der Pol, J. F. *et al.* Homologous series of liquid-crystalline metal free and copper octa-n-alkoxyphthalocyanines. *Liq. Cryst.* **6**, 577–592 (1989).
- Nolte, R. J. M. *et al.* Liquid-crystalline phthalocyanines revisited. *Liq. Cryst.* 33, 1373–1387 (2006).
- Kumar, S., Wachtel, E. J. & Keinan, E. Hexaalkoxytricycloquinazolines: New Discotic Liquid Crystals. J. Org. Chem. (1993) doi:10.1021/jo00067a013.
- 71. Keinan, E., Kumar, S., Singh, S. P., Ghirlando, R. & Wachtel, E. J. New discotic liquid crystals having a tricycloquinazoline core. *Liq. Cryst.* **11**, 157–173 (1992).
- 72. Schadt, M. & Helfrich, W. VOLTAGE-DEPENDENT OPTICAL ACTIVITY OF A TWISTED NEMATIC LIQUID CRYSTAL. *Appl. Phys. Lett.* **18**, 127–128 (1971).
- 73. N. Koma, Y. Yaba, and K. M. No-rub multi-domain TFT-LCD using surroundingelectrode method. *SID Symp. Dig. Tech. Pap* **26**, 869–872 (1995).
- Kawata, K. Orientation Control and Fixation of Discotic Liquid Crystal. *Chem. Rec.* 2, 59–80 (2002).
- Lee, S. H., Lee, S. L. & Kim, H. Y. Electro-optic characteristics and switching principle of a nematic liquid crystal cell controlled by fringe-field switching. *Appl. Phys. Lett.* 73, 2881–2883 (1998).

- Mori, H., Itoh, Y., Nishiura, Y., Nakamura, T. & Shinagawa, Y. Performance of a Novel Optical Compensation Film Based on Negative Birefringence of Discotic Compound for Wide-Viewing-Angle Twisted-Nematic Liquid-Crystal Displays. *Jpn. J. Appl. Phys.* 36, 143–147 (1997).
- 77. Chandrasekhar, S. et al. EuroDisplay'99. in *The 19th International Display Research Conference Late-News Papers* vol. 9 (1999).
- Nair, G. G., Rao, D. S. S., Prasad, S. K., Chandrasekhar, S. & Kumar, S. Electrooptic and Viewing Angle Characteristics of a Display Device Employing a Discotic Nematic Liquid Crystal. *Mol. Cryst. Liq. Cryst.* **397**, 245–252 (2003).
- Kumar, M., Varshney, S. & Kumar, S. Emerging nanoscience with discotic liquid crystals. *Polym. J.* 53, 283–297 (2021).
- Van De Craats, A. M. & Warman, J. M. Core-size effect on the mobility of charge in discotic liquid crystalline materials. *Adv. Mater.* (2001) doi:10.1002/1521-4095(200101)13:2<130::AID-ADMA130>3.0.CO;2-L.
- Adam, D. *et al.* Transient photoconductivity in a discotic liquid crystal. *Phys. Rev. Lett.* (1993) doi:10.1103/PhysRevLett.70.457.
- Haarer, D. *et al.* Photoconductivity in Discotic Liquid Crystals: A New Class of High-Mobility Materials. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A. Mol. Cryst. Liq. Cryst.* 252, 155–164 (1994).
- Adam, D. *et al.* Fast photoconduction in the highly ordered columnar phase of a discotic liquid crystal. *Nature* 371, 141–143 (1994).
- Van De Craats, A. M. *et al.* The mobility of carriers in all four phases of the columnar discotic material hexakis(hexylthio)triphenylene: Combined tof and PR-TRMC results. *Adv. Mater.* (1996) doi:10.1002/adma.19960081012.
- Schmidt-Mende, L. Self-Organized Discotic Liquid Crystals for High-Efficiency Organic Photovoltaics. *Science* (80-. ). 293, 1119–1122 (2001).

- Hassheider, T., Benning, S. A., Kitzerow, H.-S., Achard, M.-F. & Bock, H. Color-Tuned Electroluminescence from Columnar Liquid Crystalline Alkyl Arenecarboxylates. *Angew. Chemie Int. Ed.* 40, 2060–2063 (2001).
- 87. Benning, S., Kitzerow, H.-S., Bock, H. & Achard, M.-F. Fluorescent columnar liquid crystalline 3,4,9,10-tetra-(n-alkoxycarbonyl)-perylenes. *Liq. Cryst.* **27**, 901–906 (2000).
- Bisoyi, H. K. & Li, Q. Discotic Liquid Crystals for Self-organizing Photovoltaics BT -Nanomaterials for Sustainable Energy. in (ed. Li, Q.) 215–252 (Springer International Publishing, 2016). doi:10.1007/978-3-319-32023-6\_6.
- Kumar, M. & Kumar, S. Liquid crystals in photovoltaics: a new generation of organic photovoltaics. *Polym. J.* 49, 85–111 (2017).
- 90. Gregg, B. A., Fox, M. A. & Bard, A. J. Photovoltaic effect in symmetrical cells of a liquid crystal porphyrin. *J. Phys. Chem.* **94**, 1586–1598 (1990).
- 91. Petritsch, K. *et al.* Liquid crystalline phthalocyanines in organic solar cells. *Synth. Met.*102, 1776–1777 (1999).
- Oukachmih, M. *et al.* New organic discotic materials for photovoltaic conversion. *Sol. Energy Mater. Sol. Cells* 85, 535–543 (2005).
- 93. Kim, J. Y. & Bard, A. J. Organic donor/acceptor heterojunction photovoltaic devices based on zinc phthalocyanine and a liquid crystalline perylene diimide. *Chem. Phys. Lett.* 383, 11–15 (2004).
- 94. Seguy, I., Destruel, P. & Bock, H. An all-columnar bilayer light-emitting diode. *Synth. Met.* 111–112, 15–18 (2000).

## **Chapter 2**

# Synthesis and Characterization of Novel Naphthophenanthridine DLCs

#### Introduction

Although the earlier studies on discotic liquid crystals mainly revolved around small aromatic rings like benzenes, the need for the larger cores became evident as the larger aromatic cores effectively increase the  $\pi$ - $\pi$  overlap hence increasing the core stacking. Therefore, it is not surprising to see that enormous research was done in studying the core size effect on mesomorphism, and molecules like triphenylene (**Figure 2.1**) have been explored extensively<sup>1-3</sup>.



Figure 2.1. The structure of C<sub>3</sub> symmetrical Triphenylene.

Triphenylenes have been the "workhorses" among the discotic cores reported till now<sup>4–13</sup>. Liquid crystalline triphenylenes are attractive due to their low-cost preparation in a short time and their richness in mesomorphic behavior. The variations reported in triphenylene mainly revolve around substitution in the ring as well as the peripheral tail positions and linking to form dimers, polymers, etc. These modifications have often helped researchers in exploring novel mesogens. Generally, in discotics, the size of the  $\pi$ -conjugated core plays a vital role in the stability of mesophases. The extension of the  $\pi$  core can improve the compound to be more useful in device applications<sup>14</sup>, possibly because the larger discs form columns with a significantly stronger overlap of aromatic region than that of smaller ones<sup>15</sup>. The introduction of hetero atoms in these  $\pi$ -conjugated systems can influence the electronic behavior of the system, their mesomorphic and other properties. Many research groups worldwide have extensively used this strategy by extending the core with available chemical methods<sup>16</sup>. Heteroatom doping of polycyclic aromatic

hydrocarbons is of high importance in molecular electronics. It fine-tunes the band gaps of the small molecule materials for n-type semiconductors and opens new possibilities for device applications<sup>16–18</sup>. This new class of molecules is termed polycyclic heteroaromatic molecules (PHA), and many families of PHA are found to be excellent objects of photophysical investigations and have been used as NIR-active dyes, two-photon absorbers, and fluorescence sensors<sup>19–21</sup>. Due to their molecular anisotropy, intrinsic dipole moment, and extended conjugation, PHAs exhibit a great variety of self-assembling behavior and are excellent candidates for liquid crystalline materials<sup>22–24</sup>.



Figure 2.2. Structure of phenanthrophenazine mesogens.

Nitrogen has been the primary choice of dopant in PHA due to its readily available synthetic methods and the stability of nitrogen-containing heterocyclic molecules. Nitrogen incorporation in the polycyclic aromatic hydrocarbons through ring fusion, N-annulation, and substitution tailored the electronic properties and found applications in the field of organic field-effect transistors, organic light-emitting diodes, organic photovoltaics, etc. Kumar and coworkers have hybridized phenazine and triphenylene molecules and synthesized phenanthrophenazine derivatives (**Figure 2.2**) via the condensation of different o-quinone triphenylene moieties and 1,2-phenylenediamine. These unsymmetrical, polar, and colored molecules showed columnar mesophase for a wide temperature range, while derivative **2** showed monotropic columnar mesophase<sup>25,26</sup>.



Figure 2.3. Structures of some azatriphenylene molecules.

Ohta et al. have reported the hexagonal columnar mesophase for diazatriphenylene derivatives **4** (**Figure 2.3**), which was intermediate to synthesize porphyrin complexes. These nitrile substituted molecules were synthesized from acid-catalyzed condensation of benzil derivative with diaminomalanonitrile, followed by ring cyclization, which showed stable mesophase over a wide temperature range<sup>27</sup>. Williams et al. have reported the mesomorphic properties of several disc-shaped azatriphenylene molecules (**3** & **5**) and the effect of various substituent groups on the structure-property relationship. The core-size impact and the increase in stability of columnar mesophase upon the introduction of electron-withdrawing groups were discussed<sup>28,29</sup>. Surprisingly, it is observed that not only the introduction of the nitrogen atom but also the position of the nitrogen atom in these cores play an essential role in the formation of columns. Williams et al. have also investigated the effect of the functional groups with respect to their position significantly alters the liquid crystalline property of dibenzophenazine derivatives  $6^{30-32}$ .



Figure 2.4 Phenanthrophenazine with various terminal substituents.

Our group recently used this strategy by synthesizing ring extended, and nitrogen incorporated discotic liquid crystal (**Figure 2.4**) and investigated their mesomorphic properties<sup>33–36</sup>. Phenanthrophenazine derivatives were obtained from the condensation of triphenylene-1,2-diquinone and substituted 1,2-diamino benzenes, and the effect of substituted groups on the mesophase behavior was studied. The bromo derivative **7** exclusively formed enantiotropic hexagonal columnar mesophase for a wide temperature range. The thiol substituted molecules **8** showed similar behavior with reduced phase transition temperature due to more flexible alkyl chains. The hole mobility of one of the compounds in its Col<sub>h</sub> phase was measured using the time-of-flight (TOF) technique and found to be in the order of  $10^{-4}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>.



Figure 2.5 Heterocyclic ring incorporated triphenylene discotics.

Imidazole, a five-membered heterocyclic ring, has been utilized as a building block in the supramolecular self-assembly of triphenylene derivatives. Covalently linked achiral imidazole unit with pentaalkoxytriphenylene **11** (**Figure 2.5**) forms long twisted self-assembled columns and shows thermotropic liquid crystalline property with benzene-1,3,5-tricarboxylic acid through hydrogen bonding<sup>37</sup>. On the other hand, imidazole fused triphenylene molecules **12** were synthesized by the coupling of diketotriphenylene with ammonia and aldehyde in the presence of acetic acid to obtain  $\pi$  extended unsymmetrical triphenylenes. These derivatives showed columnar hexagonal mesophase, and the inclusion of the imidazole unit improved the DC electrical and photoconductivity<sup>38</sup>. Ring annulation has been the widely used method in fine-tuning the electronic and mesomorphic property of PAHs. Nitrogen annulation in the bay region of perylene tetraesters enhanced the Col<sub>h</sub> mesophase range and induced homeotropically aligned columns through intermolecular hydrogen bonding<sup>39</sup>. Photocyclization of perylene diamines with aldehydes yielded bisazacoronenes, a nitrogen annulated ring system that self-assembles into nanobelts and have reasonably good electron carrying property<sup>40</sup>.

Donnio et al. have reported the complexes of quarternised azatriphenylene motif with inorganic anions through ionic self-assembly strategy (**Figure 2.6**). The highly stable complexes show two exotic hexagonal (p3m1) & rectangular (p2mg) columnar phases, depending on the nature of the counterion. Moreover, the complexes show yellow luminescence with a 75% quantum yield, and the quantum yield was found to be sensitive towards the nature of counter ion.



Figure 2.6. Azatriphenylene ionic discotic liquid crystals.

Phenanthridine is an isostere of phenanthrene and an aza counterpart, an essential constituent in secondary metabolites obtained from various plants and realized as excellent dyes (**Figure 2.7**). They have been identified as pharmacophores in the development of anticancer, antiprotozoal, antibacterial drugs. One of the remarkable properties of phenanthridines is that they are identified as champion DNA intercalators<sup>41,42</sup>. Polycyclic phenanthridines have been part of the chemical structure of many alkaloids. By analyzing the structure of different alkaloids, four different isomers of benzophenanthridine-based alkaloids have been identified from plant extracts. Four different isomers of fused phenanthridines enabled chemists to explore for synthetic feasibility to achieve new materials.

There are few reports of extension of discotic cores in which the modifications of triphenylenes were explored for designing new systems<sup>25,34,38</sup>. Cross-coupling reactions have carried in the extension of the triphenylene core, and these extended cores have been found to display excellent mesomorphism<sup>43–47</sup>. These molecules were found to be acting as an electron acceptor moiety and could be used to design donor-acceptor dyads. The incorporation of heteroatoms like sulfur was found to have a significant influence on photo physical properties<sup>44</sup>. Extending triphenylene to coronene modified the electronic properties and reflected in the device applications. Triazacoronenes have been synthesized using Pictet-Spengler reaction from triphenylenes in high yield<sup>48–50</sup>.



Figure 2.7. Some notable phenanthridines moieties.

Naphtho[1,2,3,4-lmn]phenanthridine is one such polycyclic heteroatomic molecule with a pyridine fused triphenylene-like structure having one nitrogen atom as a dopant in benzo[e]pyrene. There are not many reports on these systems in literature, but the chemical analogues are isolated from coal tar and synthesized from photochemical transformations<sup>51,52</sup>. The planarity and the structural similarity of this core to triphenylene prompted us to investigate the mesomorphic properties of this heterocyclic system. The bay region of hexaalkoxytriphenylene is targeted for the N-annulation reaction with various aldehydes. Pictet-Spengler reaction condition is used for this ring annulation of triphenylene-1-amines to get alkoxy substituted phenanthridine derivatives. In this chapter, the strategy of expanding the triphenylene ring by annulating with nitrogen using aromatic, aliphatic, and some chromophoric aldehyde units are discussed. These annulated triphenylenes have been analyzed for mesomorphism, and photophysical properties.

## 2.1. Synthesis and Characterization of Novel 5-

### Phenylnaphthophenanthridine DLCs



Triphenylenes have been the frontrunner in discotic liquid crystalline materials since their discovery. They possess a great richness of mesomorphism within them. Chemists have been exploring this potential quite often by some substitutions in the core or periphery of the triphenylene molecule. In this chapter, we extended the triphenylene ring system by fusing with nitrogen and studied their mesomorphic and optical properties. Four new compounds are prepared using Pictet-Spengler cyclization of hexabutoxytriphenylen-1amine with substituted benzaldehydes. All the new compounds are well characterized using spectral and elemental analysis. Their mesomorphic properties are evaluated using polarizing optical microscopy, differential scanning calorimetry, and X-ray diffractometry. These derivatives showed columnar hexagonal phase with great promise for further studies.

#### 2.1.1. Results and discussion

#### 2.1.1.1. Synthesis

The general procedure for the preparation of all the compounds is given in **scheme 1**. Compounds **1-5** were synthesized following the literature procedures<sup>49,53</sup>.



Scheme. 2.1 Synthesis of annulated triphenylene derivatives.

Hexabutoxytriphenylene **3** (HAT4) was prepared using Scholl reaction following the literature procedure. The purified HAT4 was mononitrated by using HNO<sub>3</sub>. Then the nitro group was reduced to amine using  $H_2$  in presence of Raney Nickel. The isolated amine was used as such for the next step. The Pictet-Spengler reaction was carried out with appropriate aldehyde and amine

with triflic acid as catalyst in DMF to obtain the final products (**Scheme 2.1**). The target molecules were purified using column chromatography and analyzed for their chemical purity before further characterization. The purity and structure of the isolated products were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS, and elemental analysis. Finally, the compounds were taken for analyzing mesomorphic, thermal, and photophysical behavior.

#### 2.1.1.2. Mesophase characterization



Figure 2.8. TGA spectra of 6a, 6b, 6c and 6d.

All the compounds were analyzed for their thermal stability using thermogravimetric analysis (TGA). TGA showed that all the compounds have excellent thermal stability (**Figure 2.8**). They were stable till 400 °C, eliminating the possibility of thermal decomposition of the material during their mesophase characterization. The samples were viewed in POM under cross-polarized conditions. Compound **6a** has a crystalline appearance at room temperature, melts into mesophase at around 78 °C on heating, and finally goes to the isotropic phase at about 150 °C. Upon cooling, the mesophase appeared at about 148 °C exhibiting pseudo focal conic textures characteristics of columnar liquid crystals that remained stable down to room temperature (**Figure 2.9a**). However, compounds **6c** and **6d** show only one transition on heating from crystal to isotropic phase at around 140 and 130 °C, respectively. Both **6c** and **6d** displayed characteristic textures of columnar mesophase on cooling without crystallization (**Figure 2.9c&d**). Compound **6b**, on the other hand, showed a fluid character at room temperature and deformed upon shearing, indicating the existence

of RT mesophase, which cleared to isotropic phase at about 145 °C (**Figure 2.9e & f**). Upon cooling, it formed mosaic-like textures at 142 °C that remained stable on further cooling to room temperature (**Figure 2.9b**). All the compounds were mesomorphic in nature; they displayed mosaic and focal conic textures, which are typical indications for columnar mesomorphism.



**Figure 2.9.** The focal conic and mosaic textures observed under POM for compound a) **6a**; b) **6b**; c) **6c** and d) **6d** upon cooling from the isotropic phase. The texture of Col<sub>hp</sub> phase of compound **6b** (e) at 52 °C; f) at 72 °C.

The mesomorphic phase transitions were further confirmed using DSC analysis. DSC thermograms of all four compounds are given in **Figure 2.10**, and corresponding enthalpy values are summarized in **Table 2.1**. Among four compounds, **6a & 6b** showed enantiotropic mesophase, whereas the compounds **6c & 6d** showed monotropic mesophase. The isotropization temperature was found to be decreasing on increasing the number of methoxy groups in the peripheral ring. The compound **6c & 6d** were found to be monotropic, possibly because of the presence of an additional methoxy group. The enthalpy values and POM studies obtained for **6c** and **6d** validate the existence of only melting transitions during the heating scan. In the DSC thermogram of

compound **6b**, a sharp peak at 145 °C with a low enthalpy value (7 kJmol<sup>-1</sup>) was observed that corresponds to the mesophase to isotropic transition. This DSC data further validates the transition observed on heating under POM. Apart from this, a relatively weak peak at 85 °C with a very low enthalpy value of  $1.17 \text{ kJmol}^{-1}$  was observed, which could not be identified under POM. This phase transition is associated with a more ordered columnar hexagonal plastic phase (Col<sub>hp</sub>) to columnar hexagonal phase (Col<sub>h</sub>) on heating. The existence of the columnar hexagonal plastic phase at lower temperatures was further confirmed from X-ray diffraction studies. In the cooling cycle, only one transition was observed in DSC, associated with the isotropic to columnar hexagonal mesophase that stayed stable till room temperature without entering into Col<sub>hp</sub>. POM textures of the Col<sub>hp</sub> phase below its transition temperature are shown in **Figure 2.9 e** and **f**.



**Figure 2.10.** DSC Thermograms of compounds **6a-6d** show phase transitions during heating and cooling cycles at a scan rate of  $10 \,^{\circ}$ C min<sup>-1</sup>.
	Compound	Heating		Cooling	
	ба	Cr 78 (26.48) Col <sub>h</sub> 149 (	(7.77) I I 147(7.37) Col <sub>h</sub>		
	6b	Col <sub>hp</sub> 85 (1.17) Col <sub>h</sub> 145(7.09) I Cr 139 (31.66) I		I 143 (6.95) Col <sub>h</sub> I 121 (3.98) Col <sub>h</sub>	
	6с				
	6d	Cr 128 (17.86) I		I 118 (5.36) Col <sub>h</sub> 87 (3.26) Cr	
Intensity (a.u)	10 <sup>5</sup> ( 1,0 ) d=16.22 Å	6a	10⁵] (n:	(1,0) d=16.63 Å <b>6b</b>	
	10 <sup>4</sup> - (1,1) d=9.38	(2,0) d=8.14 Â ★ d=4.20 Â	10 <sup>4</sup> - 10 <sup>3</sup> -	(1,1) (2,0) d=9.56 Å d=8.33 Å d=3.76 Å d=4.20 Å	
	0 10	0 20 30 2θ	0	10 20 3 2θ	<b>4</b> 30
Intensity (a.u)	10 <sup>5</sup> 10 <sup>4</sup> 10 <sup>4</sup> 10 <sup>3</sup>	6c 4 Å d=4.10 Å	Intensity (a.u) •01 •10 •01 •10	(1,0) d=16.33 Å 6d (1,1) d=9.42 Å (2,0) d=8.12 Å d=4.21 Å	
	0 10	D 20 30 20	0	10 20 2θ	30

Table.2.1 Phase transition temperatures (in °C) and enthalpy changes (kJ/mol) of 6a - 6d.

Figure 2.11. X-ray diffraction patterns of the hexagonal phase of compounds 6a-d

Variable temperature X-ray diffraction was carried out to validate the columnar hexagonal phase further. The small-angle region of the diffraction patterns showed peaks with their dspacings in the ratio of  $1:1/\sqrt{3:1/2}$ , which is typical for a hexagonal lattice and a broad halo corresponding to alkyl chains in the wide-angle region (Figure 2.11). On further analysis, the number of molecules occupying a single slice of a column was found to be 1. Apart from the enantiotropic columnar hexagonal phase, compound **6b** was found to exhibit a phase transition associated with a very low enthalpy value around 85 °C. While cooling, the phase mentioned above was found to appear slowly (after a few hours). This was confirmed by analyzing the second heating scan where this small phase transition was absent. The POM and X-ray diffraction studies have been carried out at different temperatures to characterize the phase involved. The X-ray diffractogram was recorded for the sample at RT and 50 °C (Figure 2.12). The peaks observed at 100 °C (Figure 2.11b) are also seen at 50 °C and room temperature. However, in addition, some additional reflections were also seen at lower temperatures. Therefore, we have indexed diffraction patterns at lower temperatures assuming that the hexagonal packing of columns remains as in the high-temperature phase (**Table 2.3**). The additional peaks observed at a lower temperature are consequences of the presence of an additional periodicity along the column axis, with a periodicity of around 31.56 Å. This also paves the way for explaining the lower enthalpy associated with this phase transition. A similar kind of phase behavior has been reported in the literature<sup>54,55</sup> where this kind of mesophase was termed as columnar plastic phase and was found to be highly ordered compared to the hexagonal phase.

Compound	Phase	d observed	d calculated	Miller	Parameters
				indices(h, k)	
6a	Colh	16.22	16.21	10	<b>a</b> = 18.72 Å
	(120°C)	9.38	9.36	11	$S_h = 303.488 \text{ Å}^2$
		8.14	8.10	20	$V_h = 1274.651 \text{ Å}^3$
		4.20(h <sub>a</sub> )			Z = 1.00

## Table 2.2. Layer spacing obtained from XRD for 6a, 6b, 6c and 6d.

6b	Colh	16.63	16.62	10	<b>a</b> = 19.20 Å
	(100°C)	9.56	9.6	11	$S_h = 319.251 \text{\AA}^2$
		8.33	8.31	20	$V_h = 1200.386 \text{\AA}^3$
		4.20(h <sub>a</sub> )			Z = 0.91
		3.76(h <sub>c</sub> )			
6с	Colh	16.33	16.32	10	<b>a</b> =18.85 Å
	(120°C)	9.42	9.42	11	$S_h = 307.718 \text{ Å}^2$
		8.12	8.16	20	$V_h = 1295.494 \text{ Å}^3$
		4.21(h <sub>a</sub> )			<b>Z</b> =0.94
6d	Colh	16.39	16.38	10	<b>a</b> = 18.92 Å
	(120°C)	9.44	9.46	11	$S_h = 310.007 \text{ Å}^2$
		4.01 (h <sub>a</sub> )			$V_h = 1243.132 \text{ Å}^3$
					<b>Z</b> =0.87

(**a** = lattice parameter =  $\sqrt{(4/3) \times d_{10}}$ ; lattice area  $S_h$ = a<sup>2</sup>sin60°; lattice volume  $V_h$ = a<sup>2</sup>sin60° × h<sub>c</sub> (h<sub>a</sub> if h<sub>c</sub> is not observed); No of molecules per slice of column (**Z**) = ( $\sqrt{3} \times N_a \times \rho \times a^2 \times h$ )/2M; N<sub>a</sub>=Avogadro number;  $\rho$  =Density in Kg/m<sup>3</sup>; **a**=lattice parameter; hc=core core peak (h<sub>a</sub> if core core is not observed); M=molecular weight in Kg/m<sup>3</sup>).

Among all the samples, only **6b** showed a broader core-core peak around 3.7Å indicating that the core-core interactions are not very strong. The molecules may be arranged with some staggered conformation which was evident in optimized structures obtained from Gaussian showed in (**Figure 2.14**). The optimized structures show peripheral benzene ring is not precisely in plane with the triphenylene ring. The introduction of an additional methoxy group in the periphery ring further weakens the core-core interactions leading to an absence of wide-angle peaks. The X-ray data of all compounds are summarized in (**Table 2.2**).



Figure 2.12. X-ray diffraction pattern of compound 6b at various temperatures

Table 2.3. Indexation of  $\operatorname{Col}_{hp}$  XRD pattern of compound 6b

d observed	d calculated	hkl	
16.58	16.58	100	
14.42	14.69	101	
9.54	9.57	110	
8.26	8.29	200	a = 19.15 Å

7.89	7.89	004	c = 31.56 Å
7.56	7.36	202	
6.24	6.27	210	
4.28	4.50	007	
3.76	3.94	008	
3.52	3.50	009	
3.36	3.15	001	

## 2.1.1.3. Photo physical properties & DFT studies

The samples were analyzed for their optical properties using UV visible absorption spectroscopy and fluorescence spectroscopy in the micromolar concentration of chloroform solutions (**Figure 2.13**). The absorption spectra show four absorption peaks at 254 to 260 nm, 316 nm, 340 nm and 388nm ( $\varepsilon_{370nm} = 1.33 \times 10^4 M^{-1} cm^{-1}$  (**6a**), 1.53  $\times 10^4 M^{-1} cm^{-1}$  (**6b**), 1.35  $\times 10^4 M^{-1} cm^{-1}$  (**6c**), 1.11  $\times 10^4 M^{-1} cm^{-1}$  (**6d**). The emission spectra were recorded in chloroform, and all the compounds were excited at 370 nm. The emission spectra of all the compounds looked similar, with three intense peaks at wavelengths of 410 nm, 436 nm, and 465 nm for **6a-d**, and maxima at around 436 nm for all four compounds. Though multiple peaks in the emission spectra are less common, they have been observed in similar systems.<sup>46,56–58</sup> The Stokes shifts between the absorption excitation maxima and emission maxima of around 66 nm were observed for **6a-d**.



Figure 2.13. a) Absorption spectra and b) emission spectra of compounds 6a, 6b, 6c and 6d



Figure 2.14. a) Energy-minimized structure of 6a, 6b, 6c, and 6d by using B3LYP employing the 6-311G (d p) basis set.

Density functional theory (DFT) studies were done with the help of the GAUSSIAN-09 program with a Becke's three-parameter functional and Lee, Yang and Parr correlation functional (DFTB3LYP) by using the 6-311G (d, p) basis set. **Figure 2.14** shows the energy minimized structures of **6a** - **6d**. The obtained energy gap after analysis was around 3.5 eV. The optical energy gap ( $E_g$ ) was calculated to be 2.7eV (according to the equation  $E_g = 1240/\lambda_{onset}$ , where  $\lambda_{onset}$  was obtained by the intersection of the extrapolated tangent of the longest wavelength absorption peak and the x-axis). The optimized structures and HOMO, LUMO Molecular orbitals are given in (**Figure 2.15**).



**Figure 2.15.** HOMO and LUMO (Energy gap) energy level diagrams of **6a**, **6b**, **6c** and **6d** calculated by using **B3LYP** employing the **6-311G** (**d**,**p**) basis set.

#### 2.1.2. Conclusion

A series of annulated triphenylene derivatives has been synthesized from well-established hexaalkoxytriphenylenes using Pictet-Spengler reaction. These compounds were found to be mesomorphic. They exhibit columnar hexagonal phase, which was confirmed by XRD (X-ray diffraction), POM, and DSC. In addition to the columnar hexagonal, one compound was found to show a more ordered columnar plastic phase at a lower temperature. The optical studies reveal that these compounds can be potent semiconducting material with an appropriate bandgap that can be utilized in devices.

#### 2.1.3. Experimental section

#### 2.1.3.1. Reagents and Instruments

All the chemicals and reagents were purchased from Sigma Aldrich and used directly. The ARgrade solvents were distilled and dried using corresponding protocols before usage. The crude products were subjected to column chromatography using silica gel (100-200 mesh) and recrystallized using suitable solvents. NMR, Mass, Elemental analysis confirmed all the intermediates and final product structure. <sup>1</sup>H NMR and <sup>13</sup>C NMR (Nuclear magnetic resonance spectroscopy) were recorded on Bruker 500 MHz instrument using CDCl<sub>3</sub> as the solvent and trimethyl silane as internal standard. Chemical shift values are given in ppm, and the solvent CDCl<sub>3</sub> peaks appear at <sup>1</sup>H NMR:  $\delta = 7.23$  ppm and <sup>13</sup>C NMR  $\delta = 77.0$  ppm. Peak multiplicity is given as s = singlet, d = doublet, t = triplet, m = multiplet, b = broad peak. Mass spectra were recorded on a Micro Mass ESI-TOF spectrometer. Elemental analysis was done by using Elementar Vario MICRO Select instrument. Samples were placed between the glass slides and kept inside Mettler FP82HT hot stage, which Mettler FP90 central processor controls, and the liquid crystal textures were recorded using Olympus BX51 polarising optical microscope (Olympus, Tokyo, Japan). Mettler Toledo DSC instrument was used to record the phase transition temperatures of all the compounds. The peak temperatures are given in °C, and corresponding enthalpy values are given in kJ/mol. Panalytical (Empyrean) X-ray diffractometer was used to confirm the mesophase structure of all compounds further. Absorption studies were carried out by Perkin Elmer UV-Vislambda 35 double-beam spectrophotometer. Emission spectra obtained from fluoromax-4

spectrofluorometer. The thermal stability of all the compounds was studied using TGA 4000 thermo gravimetric analysis instrument.

## 2.1.3.2. Synthetic procedures and spectral data

**Synthesis of 2:** To the mixture of catechol (10 g, 90.8 mmol, 1 eq) potassium carbonate (50.20 g, 363.2 mmol, 4 eq) in acetone (100 ml), was added 1-bromobutane (27.37 g, 199.7 mmol, 2.2 eq). The mixture was refluxed for 48 hours and filtered upon cooling. The filtrate was extracted with dichloromethane, and the organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated using vacuum to give a crude product. The crude was then purified by column chromatography using petroleum ether: dichloromethane (90:10) as eluent to get desired product as a colorless liquid (80%). <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 6.92 (s,4 H), 4.03 (t, *J* = 6.5 Hz, 4H), 1.83 (m, 4H), 1.54 (m, 4H), 1.01 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 149.3, 121.05, 114.3, 69.0, 31.4, 19.3, 13.9. Elemental analysis: C, 75.63; H, 9.97; (calcd.); C, 74.40; H, 10.11; (expt.).

Synthesis of 3: Compound 2 (10 g, 44.9 mmol, 1 eq) was added dropwise to a solution of ferric chloride (21.84 g, 134.7 mmol, 3 eq) in dichloromethane (150 ml) and a catalytic amount of conc.H<sub>2</sub>SO<sub>4</sub>. The mixture was stirred at room temperature for an hour and poured onto cold methanol (500 ml). The mixture was then kept inside the fridge for few hours, and the crude solid product was filtered and washed with ethanol. The crude was purified by column chromatography using petroleum ether: dichloromethane (90:10) as eluent and recrystallized using ethanol to get while solid (72%). <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 7.76 (s, 6H), 4.16 (s, 12H), 1.85 (m, 12H), 1.53 (m, 12H), 0.98 (m, *J* = 7.0 Hz, 18H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 149.0, 123.6, 107.4, 69.4, 31.5, 19.4, 14.0. Elemental analysis: C, 76.33; H, 9.15; (calcd.); C, 76.15; H,9.45; (expt.).

Synthesis of  $4^{53}$ : 70% HNO<sub>3</sub> (0.6809 g, 7.564 mmol, 1 eq) was added slowly to a solution of compound **3** (5 g, 7.564 mmol, 1 eq) in dichloromethane/nitromethane (50 ml /10 ml) and stirred for 15 minutes at room temperature. Solution of sodium bicarbonate was added after 15 min and the mixture was extracted using dichlomethane. The organic layer was washed with brine, dried

in Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The crude was purified using column chromatography using petroleum ether: dichlomethane (1:1) as eluent. Recrystallization using methanol to give yellow solid (76%). <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 7.93 ( s, 1H), 7.82 (s, 1H), 7.79 (s, 2H), 7.51 (s, 1H), 4.25 (m, 12H), 1.8-2 (m, 12H), 1.5-1.7 (m, 12H), 1.0-1.1 (m, 18H). 13C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 150.5, 150.3, 149.1, 149.0, 143.9, 140.6, 126.7, 124.8, 124.4, 122.0, 119.4, 114.4, 108.0, 107.5, 107.4, 107.1, 106.6, 75.0, 69.7, 69.4, 69.1, 69.0, 68.5, 32.1, 31.5, 31.4, 31.3, 31.1, 19.4, 19.35, 19.33, 19.31, 19.0, 13.94, 13.90, 13.86. Elemental analysis: C, 71.46; H, 8.42; N, 2.07 (calcd.); C, 71.44; H, 8.71; N, 1.89 (expt.).

**Synthesis of 5**<sup>49</sup>: Raney Ni (4. 98 g, 84.99 mmol, 20 eq) was added to the solution of compound **4** (3 g, 4.249 mmol, 1eq) in THF: Ethanol (1:1). The reaction mixture was stirred at room temperature and hydrogen atmosphere. The conversion from nitro to amine was monitored using TLC. After completion of the reaction, the catalyst was removed by filtration. The solvent was evaporated under reduced pressure and purified by column chromatography using dichloromethane as eluent. Recrystallization using methanol to give greyish white solid (90%). 1H NMR (500 MHz, CDCl3),  $\delta$  (ppm) = 8.74 (s,1H), 7.76 (s, 1H), 7.72 (s, 1H), 7.70 (s, 1H), 7.30 (s, 1H), 4.53 (broad peak, 2H), 4.1 (m, 12H), 1.80 (m, 12H), 1.52 (m, 12H), 0.96 (m, 18H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 150.8, 149.4, 148.8, 147.9, 147.4, 138.2, 135.5, 126.9, 124.6, 124.4, 123.9, 123.8, 113.9, 110.2, 108.4, 108.1, 107.0, 97.3, 72.8, 69.6, 69.3, 69.0, 68.3, 32.6, 31.6, 31.5, 31.49, 31.46, 31.44, 19.5, 19.42, 19.39, 19.35, 14.00, 13.95, 13.93. M. P = 102°C. Elemental analysis: C, 74.63; H, 9.10; N, 2.07 (calcd.); C, 74.58; H, 9.08; N, 1.86 (expt.)

## General procedure for the synthesis of compound 6

Compound **6** was prepared using the literature procedure<sup>49</sup>. A mixture of compound **5** (1 eq) and aldehyde (2 eq) in dry DMF (10 ml) and 1% triflic acid were heated to 100 °C. The reaction was monitored using TLC. Water (20 ml) was added to the reaction mixture after the completion of the reaction. The mixture was alkalized with 15% NaOH solution and extracted using dichloromethane, and washed with brine. The organic layer was dried using anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude was purified by column chromatography using petroleum ether: ethyl acetate (90:10) as eluent to give yellow solid (60%).

**Compound 6a: 5** (0.500 g, 0.739 mmol, 1eq), benzaldehyde (0.156 g, 1.479 mmol, 2 eq), DMF 10 ml, 1% triflic acid, yield: 56%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.35 (s, 1H), 8.16 (s, 1H), 7.94 (s,2H), 7.68 (m, 2H), 7.36 (m, 3H), 4.41 (t, *J* = 6.0 Hz, 2H), 4.2-4.3 (m, 8H), 3.48 (t, *J* = 6 Hz, 2H), 1.8-1.9 (m, 10H), 1.56 (m, 12H), 0.87-1.05 (m, 18H), 0.70 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 158.5, 151.5, 150.9, 150.0, 149.5, 145.2, 144.4, 144.0, 136.3, 129.4, 127.4, 126.9, 124.5, 124.1, 123.3, 123.2, 122.6, 117.9, 113.7, 110.5, 108.7, 107.7, 107.0, 75.1, 74.4, 70.9, 69.5, 69.2, 32.5, 31.8, 31.6, 31.5, 31.4, 31.2, 19.4, 19.3, 19.3, 18.9, 13.9, 13.9, 13.8. ESI-MS: m/z calcd: 762.47, found: 762.47. Elemental analysis: C, 77.23; H, 8.33; N, 1.84 (calcd.); C, 76.82; H, 8.52; N, 1.74 (expt.).

**Compound 6b: 5** (0.500 g, 0.739mmol, 1 eq), 4-methoxy benzaldehyde (0.201 g, 1.479 mmol, 2 eq), DMF 10 ml, 1% triflic acid, yield: 61%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.43 (s, 1H), 8.23 (s, 1H), 8.04 (s, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.52 (t, *J* = 6.2 Hz, 2H), 4.33 - 4.42 (m, 8H), 3.93 (s, 3H), 3.59 (m, 2H), 1.91-1.99 (m, 10H), 1.68 (m, 11H), 1-1.17 (m, 19H), 0.81 (t, *J* = 6.5 Hz, 3H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 159.5, 158.0, 151.5, 150.9, 150.0, 149.6, 145.3, 144.3, 136.6, 139.4, 131.0, 124.6, 124.2, 123.3, 123.2, 122.8, 117.8, 113.7, 112.5, 110.5, 108.6,107.7, 107.1, 75.1, 74.6, 71.0, 69.6, 69.6, 69.2, 55.4, 32.6, 31.9, 31.6, 31.5, 31.4, 31.4, 19.4, 19.0, 14.0, 13.9, 13.8. ESI-MS: m/z calcd: 792.48, found: 792.48. Elemental analysis: C, 75.82; H, 8.27; N, 1.77 (calcd.); C, 75.43; H, 8.22; N, 1.85 (expt.).

**Compound 6c: 5** (0.500 g, 0.739mmol, 1 eq), 3, 4-dimethoxy benzaldehyde (0.245 g, 1.479 mmol, 2 eq), DMF 10 ml, 1% triflic acid, yield: 59%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.33 (s, 1H), 8.14 (s, 1H), 7.94 (s, 2H), 7.39 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.42 (t, *J* = 6.0 Hz, 2H), 4.22 - 4.32 (m, 8H), 3.89 (d, *J* = 4.5 Hz, 6H), 3.53 (s, 2H), 1.8 - 1.9 (m, 10H), 1.52 - 1.59 (m, 11H), 1.0 (m, 4H), 0.95 - 1.01 (m, 12H), 0.88 - 0.91 (t, 3H), 0.71 (t, 3H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 158.0, 151.5, 151.0, 150.1, 149.6, 149.1, 147.9, 145.5, 144.4, 136.8, 136.3, 124.5, 124.1, 123.3, 123.2, 122.9, 122.8, 117.8, 113.7, 113.3, 110.9, 110.1, 108.6, 107.7, 107.1, 75.0, 74.6, 71.0, 69.8, 69.6, 69.2, 56.1, 56.0, 32.7, 31.9, 31.7, 31.5, 31.4, 31.45, 19.4, 19.3, 19.0, 14.0, 13.9, 13.92, 13.8. ESI-MS: m/z calcd: 822.49, found: 822.49. Elemental analysis: C, 74.51; H, 8.22; N, 1.70 calculated (%): C, 74.21; H, 8.44; N, 1.56(expt. %).

**Compound 6d: 5** (0.500 g, 0.739 mmol, 1 eq), 3, 4, 5-trimethoxy benzaldehyde (0.29 g, 1.479 mmol, 2 eq), DMF 10 ml, 1% triflic acid, yield: 56%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.34 (s, 1H), 8.16 (s, 1H), 7.94 (s, 2H), 6.93 (s, 2H), 4.41 (t, *J* = 6.2 Hz, 2H), 4.23 - 4.32 (m, 8H), 3.87 (s, 3H), 3.83 (s, 6H), 3.61 (s, 2H), 1.80 - 1.89 (m, 10H), 1.52 - 1.58 (m, 12H), 1.18 - 1.21 (m, 2H), 1.12 (m, 4H), 0.96 - 1.01 (m, 12H), 0.88 (m, 3H), 0.75 - 0.80 (m, 3H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 158.1, 152.2, 151.6, 151.0,150.1, 149.6, 145.5, 144.3, 139.8, 138.1, 136.2, 124.4, 124.1, 123.3, 122.8, 117.8, 113.8, 111.4, 108.8, 107.7, 107.2, 107.0, 75.0, 74.4, 71.0, 70.0, 69.6, 69.2, 61.0, 56.3, 32.6, 31.9, 31.7, 31.5, 31.4, 29.7, 19.43, 19.4, 19.0, 14.0, 13.9. ESI-MS: m/z calcd: 852.12, found: 852.61. Elemental analysis: C, 73.30; H, 8.16; N, 1.64 calculated (%): C, 73.21; H, 8.13; N, 1.44 (expt. %).

## 2.1.4. Spectral data



Figure 2.16. HR-MS Mass spectra of a) 6a & b) 6b



Figure 2.17. HR-MS Mass spectra of c) 6c and d) 6d



Figure 2.18. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2



Figure 2.19. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3





Figure 2.21. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 5





Figure 2.23. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6b** 



Figure 2.24. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 6c



# 2.2. Synthesis and Characterization of Novel 5-

# alkylnaphthophenanthridine DLCs



A series of novel naphthophenanthridine derivatives is synthesized via N-annulation of hexabutoxytriphenylene-1-amine with various aliphatic aldehydes through Pictet-Spengler reaction. The synthesized derivatives have been found to self-assemble into columnar hexagonal mesophase over a wide temperature range as validated through polarizing optical microscopy (POM), differential scanning calorimetry (DSC) & X-ray diffraction (XRD) experiments. The photophysical properties of these compounds were studied using UV-Visible and emission spectra. The synthesized compounds exhibit ambipolar charge transport showing the temperature-independent electron and hole mobility of the order of  $3 \times 10^{-4}$  cm<sup>2</sup>/Vs, as evaluated by the time-of-flight (TOF) technique. These novel N-annulated derivatives can be of immense potential towards semiconducting applications of self-assembling supramolecular systems.

## 2.2.1. Results and discussion

## 2.2.1.1. Synthesis



Scheme 2.2. Synthetic scheme of compounds 6a-d

The synthetic pathway of the compounds is shown in **Scheme 2.2**, following the literature procedure<sup>56,59–61</sup>. The 1,2 -dibutyloxybenzene was synthesized from catechol and n-butyl bromide in presence of potassium carbonate. The purified dibutyloxy benzene was oxidatively trimerized using ferric chloride through the Scholl reaction to form hexabutoxytriphenyene (HAT4), which was nitrated using 70% nitric acid (1 eq) to get mononitro-hexabutyloxy-triphenylene. The nitro compound was reduced catalytically using Raney nickel as a catalyst under H<sub>2</sub> atmosphere to yield 1-amino-2,3,6,7,10,11-hexabutoxytriphenylene in quantitative yield. The recrystallized amine was

reacted with aliphatic aldehydes through the Pictet-Spengler reaction to form the N-annulated triphenylene. All the compounds were characterized using <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis and found to be pure for further characterization.

#### 2.2.1.2 Mesophase characterization



Figure 2.26 TGA thermogram of compounds 6a-d

All the compounds were analyzed for their thermal stability using thermogravimetric analysis (TGA). The TGA thermogram (**Figure 2.27**) shows all the compounds exhibit high thermal stability with decomposition temperatures higher than 350 °C with less than 5% weight loss. This temperature is much higher than the isotropic transition temperature, eliminating the possibility of the thermal decomposition of material during their mesophase characterization.

The liquid crystalline properties of all the compounds were studied using a combination of differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction techniques. All these compounds were found to be mesomorphic at elevated temperatures. The polarized optical microscopic images of all these compounds are given in **Figure 2.28**.



**Figure 2.27** Polarizing optical microscopic images of compounds **6a** (120°C), **6b** (135°C), **6c** (140°C) and **6d** (142°C) taken during phase transition from the isotropic phase to columnar hexagonal mesophase on cooling.

Compound **6a** on cooling from the isotropic phase to mesophase exhibits dendritic structure with homeotropically aligned domains which is consistent with hexagonal columnar mesophase. Similarly, compounds **6b**, **6c**, and **6d** show mosaic-like textures having rectilinear defects in the homeotropic dark-field background, suggesting hexagonal columnar mesophase, further confirmed by DSC and X-ray diffraction studies. This spontaneous alignment could lead to high performance in optoelectronic applications<sup>62,63</sup>.



Figure 2.28 DSC thermograms of compounds 6a-d.

**Table.2.4** Phase transition temperature (°C) and corresponding enthalpies (kJ/mol)

Compound	Heating	Cooling	
6a	Cr 81 (35.87) Col <sub>h</sub> 138 (6.05) I	I 136 (5.83) Col <sub>h</sub>	
6b	Cr 73 (23.76) Col <sub>h</sub> 145 (4.50) I	I 142 (4.25) Col <sub>h</sub>	
6с	Cr 103 (16.14) Col <sub>h</sub> 146 (6.52) I	I 148 (5.16) Col <sub>h</sub>	
6d	$Cr_1$ 75 (2.74) $Cr_2$ 97 (10.58) $Col_h$ 150 (5.78) I	I 148 (5.76) Col <sub>h</sub>	

The DSC thermograms of all the compounds, taken on the scan rate of 10°C/min, are given in **Figure 2.29**. The phase transition temperatures and corresponding enthalpy values of all the compounds are given **in Table 2.4**. All the compounds are enantiotropic, i.e., they show mesophase transition over both heating and cooling cycles, but the crystallization peak was not observed in DSC while cooling since it took a long time to crystallize. Compounds **6a**, **6b**, and **6c** showed two endothermic peaks on heating corresponding to crystal to mesophase and mesophase to the isotropic phase transitions. One exothermic peak corresponding to the isotropic phase to mesophase transition is found while cooling. Compound **6d** showed three endothermic peaks at 75 °C, 97 °C, and 150 °C and one exothermic peak at 148 °C. But there was no phase transition observed in POM at 75 °C, and this correlates the transition must be a crystalline polymorphic transition. The isotropic transition temperature was found to be increasing with increasing the length of the alkyl chain. The results are consistent with the phase transition observed in POM. All the compounds show a stable columnar hexagonal mesophase over a wide range of temperatures.



**Figure 2.29** X-ray diffractograms of compounds **6a-d** (**6a** at 95°C, **6b** at 115°C, **6c at** 105°C, **6d** at 90°C)

The self-assembly behavior of these compounds was further investigated using X-ray diffraction techniques. The samples were filled in Lindemann capillary by melting and the diffraction pattern was observed for both the heating and cooling cycle. The X-ray diffractograms of all the compounds are shown in Figure 2.30. Compound 6a showed four reflections in the small-angle region with the strongest one at 15.79 Å and other peaks at 9.13 Å, 7.92 Å, and 5.99 Å at 95 °C. These reflections are in the ratio of 1:  $1/\sqrt{3}$ : 1/2:  $1/\sqrt{7}$  which corresponds to (10), (11), (20), (21) indices of the hexagonal lattice. The lattice parameter was calculated from the observed spacing and is found to be 18.29 Å. Compounds **6b** and **6c** showed similar reflections whereas compound **6d** showed only three peaks of (10), (11), and (20) planes. In the wide-angle region, a broad halo peak was observed for compound **6a** with a d-spacing value of 4.38 Å that corresponds to the fluid-like order of molten alkyl chains. All the other compounds showed two wide-angle broad halo peaks due to alkyl chain packing and core-core packing. The core-core separation for compounds **6b**, **6c**, and **6d** were found to be 3.63 Å, 3.65 Å, and 3.73 Å, respectively. This indicates that the  $\pi$ - $\pi$  overlap is better in smaller alky chain compounds which weakens with the increasing length of the peripheral alkyl chains. The X-ray diffraction data of the compounds are summarized in **Table 2.5**. We have calculated the number of molecules per slice of a column from the diffraction data, which was found to be 1. The proposed model of the molecular organization in the hexagonal columnar phase is given in Figure 2.31.



Figure 2.30 Molecular arrangement of compounds 6a-d in the columnar phase.

Compound	Phase	<b>d</b> observed	<b>d</b> calculated	Miller indices	Parameters
		(Å)	(Å)	( <b>h</b> , <b>k</b> )	
6a	$\operatorname{Col}_h$	15.79	15.83	10	a = 18.29 Å
	95°C	9.13	9.14	11	$S_h=289.71~\AA^2$
		7.92	7.91	20	$V_h = 1268.91 \text{ Å}^3$
		5.99	5.99	21	Z = 1.05
		4.38 (h <sub>a</sub> )			
6b	Col <sub>h</sub>	16.33	16.30	10	a = 18.82 Å
	115°C	9.42	9.41	11	$S_h=306.74~\AA^2$
		8.17	8.15	20	$V_{h} = 1113.46 \ {\AA}^{3}$
		6.16	6.16	21	Z = 0.90
		4.33 (h <sub>a</sub> )			
		3.63 (h <sub>c</sub> )			
6с	Col <sub>h</sub>	16.41	16.43	10	a = 18.97 Å
	105°C	9.48	9.48	11	$S_h=311.65~\text{\AA}^2$
		8.21	8.21	20	$V_{h} = 1137.52 \ \text{\AA}^{3}$
		6.21	6.21	21	Z = 0.91
		4.39 (h <sub>a</sub> )			
		3.65 (h <sub>c</sub> )			
6d	Colh	16.73	16.75	10	a = 19.35 Å
	90°C	9.72	9.68	11	$S_h=324.25\ \text{\AA}^2$
		8.38	8.38	20	$V_h = 1209.49 \text{ Å}^3$
		4.23 (h <sub>a</sub> )			Z = 0.95
		3.73 (h <sub>c</sub> )			

## Table 2.5 The observed and calculated d spacings of compounds 6a-d.

Layer spacing obtained from XRD for **6a**, **6b**, **6c** and **6d**. (**a** = lattice parameter =  $\sqrt{(4/3) \times d_{10}}$ ; lattice area S<sub>h</sub>= a<sup>2</sup>sin60°; lattice volume V<sub>h</sub>= a<sup>2</sup> sin60° × h<sub>c</sub> (h<sub>a</sub> if h<sub>c</sub> is not observed); No of molecules per slice of column (**Z**) = ( $\sqrt{3} \times N_a \times \rho \times a^2 \times h$ )/2M; N<sub>a</sub>=Avogadro number;  $\rho$  =Density in Kg/m<sup>3</sup>; **a**=lattice parameter; hc=core core peak (h<sub>a</sub> if core core is not observed); M=molecular weight in Kg/m<sup>3</sup>).

#### 2.2.1.3 Photophysical properties & DFT studies

UV-visible and photoluminescence spectra of compounds **6a** and **6b** were measured in chloroform solution ( $10^{-6}$  M) to evaluate the absorption and emission properties. The alkyl chain length usually has no significant effect on the photophysical properties; hence, only **6a** and **6b** were used as representative molecules. Both the compounds show identical absorption peaks as expected, with the strongest one at 270 nm and other peaks at 337, 373, 473 nm ( $\varepsilon_{370} = 1.5 \times 10^4$  (**6a**),  $1.4 \times 10^4$  (**6b**). The emission spectra of both compounds in their micromolar chloroform solution show a broad peak with emission maxima at 453nm. The Stokes shifts between the absorption and emission maxima were found to be 83 nm (**Figure 2.32**). The optical energy gap (Eg) in eV was calculated to be 2.76 (according to the equation Eg =  $1240/\lambda_{onset}$  where  $\lambda_{onset}$  was resolved as the intersection of the extrapolated tangent of the longest wavelength absorption peak and the x-axis).



Figure 2.31 UV-Visible and emission spectrum of compounds 6a and 6b.

Density functional theory (DFT) studies of all the compounds were carried out using the GAUSSIAN-09 program at Becke's three-parameter functional and Lee, Yang, and Parr correlation functional (DFTB3LYP) by using the 6-31G(d) basis set 38. The energy minimized structures of all the compounds are given in **Figure 2.33**. The HOMO-LUMO energy levels of all the compounds are given in **Figure 2.34**, and the theoretical energy gap was found to be 3.59 eV.



Figure 2.32 Energy minimized structures of compounds 6a-d



Figure 2.33 HOMO- LUMO levels of compounds 6a-d.

#### 2.2.1.4. Charge transport properties

Charge mobility plays an indispensable role in optoelectronic applications since it specifies the frequency of charge transport, an essential criterion of semiconductors heavily depends on the molecular aggregations which in turn rely on the molecular structure<sup>64,65</sup>. It becomes evident with an argument that the specific design of a molecular structure which induces these highly ordered supramolecular assemblies favors charge transport. Organic compounds often form crystals upon solution processing which have domain boundaries that severely restrict the charge mobility<sup>66</sup>. Thermotropic discotic liquid crystalline materials overcome this restriction through the columnar organization, i.e., the disc-shaped molecules stack on top of each other to form one dimensional column which further occupies various 2D lattices. These mesogenic materials, known as one of the delicate phases of matter, exhibit both order and mobility, and the homogeneous domains can sometimes be achieved to a larger length scale, which is essentially required for semiconducting devices<sup>3,67,68</sup>. The charge transporting properties of many different discotic derivatives and their nanocomposites have been reported in the literature<sup>34,69–72</sup>.

The ambipolar charge transporting molecules are of particular interest for organic semiconductors as it enables the fabrication of complementary circuits, organic field-effect transistors (OFET), and organic light-emitting diodes(OLED)<sup>73–75</sup>. Generally, this type of bipolar transport has been achieved through bulk heterojunctions of donor and acceptor materials as active components<sup>76–78</sup> or by introducing different source and drain electrodes to facilitate the charge transport<sup>79</sup>. However, in principle, a single organic molecule could allow both electron and hole injection, and the most effective ambipolar transistors could be realized from a solution-processed single active layer of low bandgap materials combined with one type of electrode. The ambipolar character in discotic liquid crystals has been reported first in porphyrins and phthalocyanines<sup>80,81</sup>. The ambipolar nature of triphenylene discogens has been investigated and mobility in the hexahexylthio triphenylene (HHTT) molecule in order of 0.1  $\text{cm}^2/\text{Vs}$  is reported<sup>82,83</sup>. The literature on ambipolar mobility in discotic mesogens is quite a handful<sup>84–88</sup>. There are few reports on the ambipolar charge transport properties of discogens containing tristhiophenyltriazines<sup>89</sup>, truxene<sup>91</sup>. phthalocyanines<sup>92</sup>, benzothiophene<sup>44,93</sup>, triphenylboranes<sup>90</sup>, pyrene<sup>94</sup>. and heterocorenenes<sup>95</sup> as a central core. Herein, we discuss the temperature-independent ambipolar charge transport properties of naphthophenanthridine derivative that are investigated using the time-of-flight (TOF) technique<sup>96</sup>.

The charge transport properties of compound **6a** were measured using time of flight (TOF) measurements. The schematic of the liquid crystal cell used is shown in **Figure 2.34**. The ambipolar charge transport mechanism in compound **6a** was investigated by determining the electron and hole mobilities using the time-of-flight (TOF) technique. Compound **6a** could not absorb sufficient incident laser radiation of 355 nm; therefore, custom-made LC cells were prepared by depositing a thin layer of poly-N-vinyl carbazole (PVK) underneath the top electrode (schematically shown in **Figure 2.34**). The thickness of these cells was maintained to be 20  $\mu$ m by placing spacers between the top and bottom ITO/glass plates.





The presence of PVK does not produce any additional effect on the physical properties of the DLC and is only used for absorbing the laser radiation to generate sufficient charge carriers. For ToF measurement, compound **6a** was filled in the aforementioned LC cell and excited by a Nd:YAG pulsed laser having 5 ns pulse width. The measurements were performed in the cooling cycle with a rate of 2 °C/min using custom-made heating stage Eurotherm 3204. The hole and

electron mobilities were examined by applying the Voltage of  $\pm$  60 to  $\pm$  80V using a KEITHLEY 6487 Picoammeter/Voltage source. The induced charge displacement was observed via dispersive transient photocurrent curves recorded using a digital oscilloscope (KEYSIGHT, DSOX3022T) connected to the voltage amplifier (Stanford Research SR560). The transit time was determined by the output transient photocurrent curves that have been used to calculate the hole and electron mobilities by using the formula

$$\mu = d^2 / T_r V$$

where  $T_r$  is the transit time obtained by photocurrent curves, V is the applied voltage and d is the thickness of LC cells. **Figure 2.35** renders the transient photocurrent curves for the **6a** compound at 130 and 90 °C under the application of an optimized applied voltage of  $\pm$  50V. The dispersive transient photocurrent curves have been obtained for both electrons and holes that might be due to the formation of traps at the PVK/DLC interface. The hole and electron mobilities of the **6a** compound as a function of temperature are plotted in **Figure 2.36**. The hole and electron mobilities of discotic molecule **6a** are of the order of  $10^{-4}$  cm<sup>2</sup>/Vs and found to be invariant with the temperature change. The temperature-independent hole and electron mobilities are found to be in the order of  $2.7 \times 10^{-4}$  and  $2.1 \times 10^{-4}$  cm<sup>2</sup>/Vs, respectively. The hole mobility is slightly higher than that of electron mobility.



**Figure 2.35** Transient photocurrent curves for the hole and electron transports at (a) 130 and (b) 90 °C under the application of  $\pm$  50V.



Figure 2.36 Temperature-dependent hole and electron mobility of compound 6a

## **2.2.2. Conclusions**

We have reported the synthesis of four novel naphthophenanthridine discotic liquid crystals through the Pictet-Spengler reaction. All the synthesized compounds were explored for their liquid crystalline behavior and were found to be mesomorphic. They form a columnar hexagonal phase, as evident from POM, DSC & XRD studies. The compounds were found to show an optical bandgap of around 2.76 eV. Compound **6a** exhibited ambipolar charge transport showing almost temperature-independent hole and electron mobilities of the order of  $2.7 \times 10^{-4}$  and  $2.1 \times 10^{-4}$  cm<sup>2</sup>/Vs, respectively, revealing the potential as ambipolar charge transporting material in organic semiconductor applications.

## 2.2.3. Experimental section

## 2.2.3.1. Reagents and Instruments.

All the reagents and instruments are used as in section 2.1.3.1
#### 2.2.3.2. Synthetic procedures and spectral data

Compounds 2-5 were synthesized following the procedure given in section 2.1.3.2, and the spectral data are summarized in section 2.1.4.

#### General procedure for the synthesis of compound 6:

Compound **6** was prepared following the procedure given in literature<sup>49,61</sup>. A mixture of compound **5** (1 eq) and aldehyde (2 eq) in dry DMF (10 ml) and 1% triflic acid was heated to 40°C for overnight. The reaction was monitored using TLC, and water (20 ml) was added to the reaction mixture after the completion of the reaction. The mixture was alkalized with a 15% NaOH solution, extracted using dichloromethane, and washed with brine. The organic layer was dried using anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude was purified by column chromatography using silica gel and petroleum ether: ethyl acetate (90:10) as eluent to give yellow solid (60%).

**Compound 6a: 5** (0.500 g, 0.739mmol, 1 eq), butyraldehyde (0.106 g, 1.479 mmol, 2 eq), DMF 10 ml, 1% triflic acid, yield: 61%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 8.35 (s, 1H), 8.16 (s, 1H), 7.98 (s,2H), 4.48 (s, 2H), 4.29-4.36 (m, 8H), 4.19 (s, 2H), 3.68 (s, 2H), 1.95-2.05 (m, 14H), 1.62-1.67 (m, 12H), 1.01-1.11 (m, 21H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) =161.1, 151.4, 150.8, 149.9, 149.4, 145.4, 143.6, 136.26, 124.4, 124.0, 123.4, 123,3, 122.1, 118.8, 113.7, 109.9, 107.6, 106.9, 74.9, 74.3, 70.7, 69.5, 69.4, 69.1, 42.7, 32.7, 32.4, 31.9, 31.7, 31.8, 31.5, 31.4, 22.1, 19.5, 19.4, 14.5, 14.1, 14. Elemental analysis: C, 75.89; H, 9.00; N, 1.92 (calculated); C, 75.67; H, 8.96; N, 1.81 (Found).

**Compound 6b: 5** (0.500 g, 0.739 mmol, 1 eq), pentanal (0.127 g, 1.479 mmol, 2 eq), DMF 10 ml, 1% triflic acid, and yield: 63%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.36 (s, 1H), 8.16 (s, 1H),7.99 (s, 2H), 4.48 (s, 2H), 4.36 (d, *J* = 6.5 Hz, 4H), 4.29 (s, 4H), 4.19 (s, 2H), 3.72 (s, 2H), 1.96-2.02 (m, 14H), 1.54-1.68 (m, 14H), 1.00-1.08 (m, 21H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$ (ppm) =161.3, 151.4, 150.8, 149.9, 149.4, 145.5, 143.6, 136.3, 124.9, 124.1, 123.4, 123.3, 122.1, 118.8, 113.7, 109.9, 107.7, 107.7, 106.9, 74.9, 74.4, 70.8, 69.5, 69.4, 69.1, 40.4, 32.7, 32.4, 31.9, 3.7, 31.5, 31.4, 31.0, 23.0, 19.4, 14.0. Elemental analysis: C, 76.07; H, 9.10; N, 1.89 (calculated); C, 75.83; H, 9.02; N, 1.83 (Found).

**Compound 6c: 5** (0.500 g, 0.739mmol, 1 eq), hexanal (0.148 g, 1.479 mmol, 2 eq), DMF 10 ml, 1% triflic acid, and yield: 57%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.36 (s, 1H), 8.24 (s, 1H), 8.00 (s, 1H), 7.97 (s, 1H), 4.44 (t, *J* = 6.5 Hz, 2H), 4.33-4.38 (m, 4H), 4.29-4.31 (m, 4H), 4.18 (t, *J* = 6.5 Hz, 2H), 3.15 (t, *J* = 8Hz, 2H), 1.83-2.02 (m, 15H), 1.57-1.68 (m, 22H), 0.98-1.09 (m, 23H). <sup>13</sup>C NMR (500 MHz, CDCl3),  $\delta$  (ppm) =158.4, 151.7, 150.1, 149.7, 144.4, 135.74, 124.5, 124.1, 123.5, 123.1, 121.5, 116.2, 113.7, 110.5, 108.8, 107.5, 107.2, 73.5, 70.7, 69.5, 69.4, 69.3, 41.4, 32.57, 31.9, 31.8, 31.7, 31.5, 31.4, 25.5, 22.5, 19.5, 19.4, 19.3, 19.1, 19.9. Elemental analysis: C, 76.25; H, 9.20; N, 1.85 (calculated): C, 76.58; H, 9.29; N, 1.75(Found)

**Compound 6d: 5** (0.500 g, 0.739 mmol, 1 eq), heptanal (0.168 g, 1.479 mmol, 2 eq), DMF 10 ml, 1% triflic acid, and yield: 56%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 8.36 (s, 1H), 8.24 (s, 1H), 8.00 (s, 1H), 7.97 (s, 1H), 4.44 (s, 2H), 4.30 - 4.37 (m, 8H), 4.18 (s, 2H), 3.15 (t, *J* = 6.5 Hz, 2H), 1.87-1.97 (m, 14H), 1.59 - 1.65 (m, 12H), 1.53 - 1.55 (m, 2H), 1.40 – 1.46 (m, 4H), 0.99 - 1.07 (m, 18H), 0.94 – 0.95 (m, 3H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 158.4, 151.7, 150.1, 150.0, 149.6, 144.3, 143.3, 135.7, 124.4, 124.1, 123.5, 121.4, 116.2, 113.9, 110.5, 108.7, 107.4, 107.1, 75.1, 73.5, 70.6, 69.5, 69.3, 69.2, 41.8, 31.9, 31.8, 31.7, 31.6, 31.5, 31.4, 22.9, 22.6, 19.5, 19.4, 19.3, 19.1, 14.1, 14.0, 13.98, 13.95. Elemental analysis: C, 76.42; H, 9.29; N, 1.82 (calculated): C, 76.37; H, 9.13; N, 1.91 (Found).



# Figure 2.37 <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 6a



Figure 2.38 <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 6b



Figure 2.39 <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 6c



Figure 2.40 <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 6d

# 2.3. Synthesis and Characterization of Novel Chromophore-coupled

# Naphthophenanthridine DLCs

Abstract



In this section, the synthesis of a series of four compounds, each bears a chromophore moiety covalently attached to the naphthophenanthridine is discussed. Pyrene, anthracene, phenothiazine, and triphenylamine moieties were used as chromophores. The effect of these chromophores in the thermal and structural arrangement of these discotic cores has been explained. All the molecules show columnar liquid crystalline phase. Particularly the pyrene functionalized phenanthridine derivative was found to be liquid crystalline at room temperature. Photophysical properties were examined using UV-vis and emission spectroscopy. DFT studies were performed to understand the chromophore arrangement with central core and orientation of frontier orbitals in these extended  $\pi$  systems.

# 2.3.1. Results and discussion

### 2.3.1.1. Synthesis



Scheme. 2.3 Synthetic scheme of all naphthophenanthridine derivatives.

Hexadodecyloxytriphenyene (HAT12) was synthesized using the oxidative trimerization of 1, 2didodecyloxybenzene with FeCl<sub>3</sub> in dichloromethane at room temperature. The purified triphenylene (HAT12) was nitrated using 70% nitric acid (1 eq), which gave mononitro triphenylene. The nitro compound was further reduced catalytically using Raney nickel as a catalyst under H<sub>2</sub> atmosphere to yield 1-ammine-2,3,6,7,10,11-hexakis dodecyloxytriphenylene in quantitative yield. The recrystallized amine was directly used for the final step. Pictet-Spengler cyclization was carried out for triphenylene amine and various aromatic aldehydes in dimethyl formamide (DMF) as the solvent and 1% Triflic acid as a catalyst at 100 °C to give final compounds. All the compounds were characterized using <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis and found to be pure for the characterization.

### 2.1.1.2. Mesophase characterization

The thermal stability of all the compounds is analyzed using thermogravimetric analysis. TGA thermograms of the compounds are given in **Figure 2.41**, which shows compounds are stable up to 370 °C with less than 5% weight loss. The high thermal stability of these compounds eliminates the possibility of molecular decomposition during their phase transition studies.



Figure 2.41. TGA thermograms of all the derivatives.

The mesophase characterization of all the compounds was analyzed by the combination of POM, DSC, and X-ray diffraction techniques.. The POM micrographs are given in **Figure 2.43**. **NP-PY** on cooling from isotropic phase exhibited pseudo focal conic textures at 115 °C characteristics of columnar hexagonal mesophase. This texture remained unchanged upon further cooling to room temperature with no crystallization for a long time. **NP-AC** showed pseudo focal conic textures on cooling from isotropic till 65 °C. Below this temperature, there seemed to be a change in texture which looked like crystallization while maintaining the pseudo focal conic structure. However, the sample deformed when pressing the glass slide, thus proving this was not the transition related to crystallization. **NP-PT** and **NP-TP** showed mosaic-like and pseudo focal conic textures at 110 °C and 85 °C, respectively, on cooling corresponding to columnar hexagonal liquid crystals. All the compounds exhibited typical textures of columnar mesophase with bright birefringence with extensive dark regions that correspond to homeotropically aligned columnar domains.



**Figure 2.42** POM micrographs of compounds on cooling from isotropic phase. **NP-PY** at 115 °C, **NP-AC** at 83 °C, **NP-PT** at 110 °C, and **NP-TP** at 85 °C.

The DSC traces of compounds recorded at the scan rate of  $10^{\circ}$ C/min are shown in **Figure** 2.44, and their corresponding phase transition enthalpy values are given in Table 2.6. Enantiotropic mesomorphic behavior of all the compounds is evident from mesophase existence in both heating and cooling cycle. Compound **NP-PY** on heating showed only one endothermic phase transition at 121 °C with significantly less enthalpy value (10 kJmol<sup>-1</sup>), indicating the phase transition from the columnar hexagonal liquid crystalline phase isotropic liquid. Upon cooling, it revealed an exothermic peak at 119 °C corresponding to isotropic to mesophase transition. The crystal to mesophase at -11 °C on second heating and crystallization peaked at -14 °C on second cooling cycle, confirming the presence of the room temperature liquid crystallinity perceived through POM. **NP-AC** displayed two endothermic peaks on heating at 55 and 98 °C correlating to Cr to Col<sub>h</sub> and Col<sub>h</sub> to isotropic transition with one exothermic peak at 95 °C on cooling. Both **NP-PT** and **NP-TP** showed similar behavior observed in POM that remained in columnar mesophase on cooling till room temperature.



Figure 2.43 DSC thermograms of all four compounds.

Compound	Heating	Cooling	
NP-PY	Col <sub>h</sub> 121 (10.10) I	I 119 (8.12) Col <sub>h</sub>	
NP-AC	Cr 55 (4.25) Col <sub>h</sub> 98 (9.51) I	I 95 (8.69) Col <sub>h</sub>	
NP-PT	Cr 45 (80.54) Col <sub>h</sub> 119 (6.28) I	I 117 (6.18) Col <sub>h</sub>	
NP-TP	Cr 45 (70.52) Col <sub>h</sub> 90 (4.16) I	I 89 (3.33) Col <sub>h</sub>	

Table 2.6 Phase transition temperature (°C) and corresponding enthalpies (kJ/mol)

The self-assembly characteristics of all four compounds were further confirmed, and the 2D arrangement of the columns is deduced from variable temperature X-ray diffraction. Compounds were filled in capillaries by melting, and diffraction patterns were observed for heating and cooling cycles. The intensity vs  $2\theta$  profiles are shown in Figure 2.44, and the lattice parameters are calculated and summarized in Table 2.7. The diffractogram of NP-PY on cooing at room temperature shows three peaks in the small-angle region, with the strongest one at 24.57 Å and the remaining peaks are at 14.14 Å and 12.24 Å that are indexed to (10), (11) and, (20) planes of the hexagonal lattice. Apart from this, there are two relatively broad peaks in the wideangle region at 4.30 Å and 3.70 Å, which are assigned to alkyl halo and core-core stacking. The lattice parameter was calculated from observed d-spacing values and found to be 28.26 Å. Compound NP-AC has three reflections in the small-angle region corresponding to (10), (11), and (21) planes of hexagonal lattice, and one broad peak in the wide-angle region correlates to disordered alkyl chains. The core-core peak was not observed, possibly due to the non-planar nature of anthracene moiety restricting the core-core ordering. In the small-angle region, compound **NP-PT** shows three reflections whose spacings are in the ratio of  $1:1/\sqrt{3}:1/2$ , and compound **NP-TP** shows four peaks whose spacings are in the ratio of  $1:1/\sqrt{3}:1/2:1/\sqrt{7}$ characteristic of the hexagonal lattice. These compounds have two broad peaks arising from fluidlike alkyl chain ordering and core-core ordering in the wide-angle region. The intercolumnar distance **a** shows minimal variation among all the compounds since all of them possess alkoxy

chain of the same length. The number of molecules per slice of the column was found to be 1 for all the compounds. The POM, DSC, and X-ray diffraction studies revealed the presence of enantiotropic columnar hexagonal mesophase in all the compounds over a wide temperature range. Interestingly, pyrene coupled naphthophenanthridine derivative is liquid crystalline at room temperature, and the mesophase is stable up to 120°C.



**Figure 2.44** X-ray diffractograms of compounds **NP-PY** at 25 °C, **NP-AC** at 85 °C, **NP-PT** at 95 °C, and **NP-TP** at 25 °C.

Compound	Phase	<b>d</b> observed	<b>d</b> calculated	Miller indices	Parameters	
		(Å)	(Å)	(h,k)		
NP-PY	Col <sub>h</sub>	24.57	24.47	10	a = 28.26  Å	
	25°C	14.14	14.13	11	$S_h=691.63~\AA^2$	
	(cooling)	12.24	12.24	20	$V_{h} = 2559.03 \ \text{\AA}^{3}$	
		4.37 (h <sub>a</sub> )			Z = 0.95	
		3.70 (h <sub>c</sub> )				
NP-AC	Colh	23.19	23.01	10	a = 26.57 Å	
	85°C	13.39	13.28	11	$S_h=611.79~\text{\AA}^2$	
	(heating)	8.70	8.70	21	$V_{h} = 2691.89 \ {\AA}^{3}$	
		4.40 (ha)			Z = 1.05	
NP-PT	Col <sub>h</sub>	24.70	24.68	10	a = 28.49 Å	
	95°C	14.23	14.24	11	$S_h=702.93~\AA^2$	
	(cooling)	12.34	12.34	20	$V_{h}{=}2565.71~{\AA}^{3}$	
		4.47 (h <sub>a</sub> )			Z = 0.96	
		3.65 (h <sub>c</sub> )				
NP-TP	Col <sub>h</sub>	25.54	25.54	10	a = 29.49 Å	
	25°C	14.69	14.74	11	$S_h=753.19~\AA^2$	
	(cooling)	12.75	12.77	20	$V_{h}{=}2726.58\;{\text{\AA}}^{3}$	
		9.60	9.60	21	Z = 1.00	
		4.45 (ha)				
		3.62 (h <sub>c</sub> )				

**Table 2.7** The observed and calculated d spacings and lattice parameters of all the compounds.

(**a** = lattice parameter =  $\sqrt{(4/3) \times d_{10}}$ ; lattice area  $S_h$ =  $a^2 \sin 60^\circ$ ; lattice volume  $V_h$ =  $a^2 \sin 60^\circ \times h_c$ ( $h_a$  if  $h_c$  is not observed); No of molecules per slice of column (**Z**) = ( $\sqrt{3} \times N_a \times \rho \times a^2 \times h$ )/2M;  $N_a$ =Avogadro number;  $\rho$  =Density in Kg/m<sup>3</sup>; **a**=lattice parameter;  $h_c$ =core-core peak, ( $h_a$  = alkyl-alkyl peak, if  $h_c$  is not observed); M=molecular weight in Kg/m<sup>3</sup>).

#### 2.3.1.3. Photo physical properties & DFT studies

The photophysical properties of these chromophore coupled naphthophenanthridine molecules were studied using UV absorption and florescence spectroscopy in their micromolar chloroform solution. The normalized absorption and emission spectra of all the donor-acceptor type molecules are shown in Figure 2.46, and corresponding values are summarized in Table 2.8. The absorption maxima of all the compounds ranging between 260 and 280 nm are assigned to the  $\pi$ - $\pi$ \* transition of the naphthophenanthridine (NP) molecule. Compound NP-PY shows two intense absorption peaks in the high energy region at 268 nm and 279 nm, characteristics of naphthophenanthridine core and the extended delocalization of NP core with pyrene moiety, respectively. A comparatively weak absorption at 342 nm with two shoulder peaks on the higher energy side is also observed. The absorption maxima of NP-AC is present at 260nm with relatively less intense peaks at 342, 371, and 390 nm. NP-PT and NP-TP showed similar absorption behavior with maxima at 260 and 267 nm, with a less intense peak in the lower energy region and a slightly broader peak with no feature at around 396 nm and 404 nm, respectively, which could be due to intramolecular charge transfer (ICT) in these donor-acceptor couples. This phenomenon can be understood from their highest molecular orbitals (HOMO) and lowest unoccupied orbitals (LUMO) orbitals derived from density functional calculations (Figure 2.47).



**Figure 2.45** Absorption and emission spectra of all the compounds in 7 X  $10^{-6}$  M chloroform solution.

In both **NP-PT** and **NP-TP** molecules, the Phenothiazine and triphenylamine unit mainly contributes to the HOMO orbitals, and LUMO is primarily localized on the NP central core, leading to intramolecular charge transfer<sup>97</sup>. None of the compounds show characteristics absorption peaks of their chromophore units, possibly due to the approximate superposition of the absorption feature of both NP and chromophore moieties.

The photoluminescence spectra of all the compounds with pyrene, anthracene, and triphenylamine chromophores show emission peaks between 460-490 nm except **NP-PT**, which has an emission maximum at 554 nm. All the compounds exhibit redshifted emission compared to NP ( $\lambda_{em}$  = 453 nm), and stokes shifts are 208 nm (**NP-PY** and **NP-AC**), 294 nm (**NP-PT**), and 216 nm (**NP-TP**). The large Stokes shift indicates that there could be significant structural changes that occur after electronic excitation<sup>98</sup> and can be used as fluorescent probes for biological applications, UV photo stabilizers, laser dyes, and photovoltaic materials<sup>99,100</sup>. In addition, these compounds can be potential candidates as organic light-emitting diodes since they exhibit strong emission in the blue to green region.

Compound	$\lambda_{abs}$ (nm)	E	$\lambda_{em}(nm)$	Stokes shift	$E_g^{optical}$	$E_g^{\ DFT}$
NP-PY	268, 279, 342	8.00	412 <sup>sh</sup> , 476	197	2.73	3.39
NP-AC	260	15.6	411 <sup>sh</sup> , 467	207	2.79	3.42
NP-PT	260	8.58	554	294	2.74	3.27
NP-TP	267	6.49	412 <sup>sh</sup> , 483	216	2.74	3.26

 Table 2.8
 Summary of UV-absorption and emission spectra of chromophore coupled naphthophenanthridine derivatives.

 $\lambda_{abs}$  - Absorption maxima,  $\epsilon$ - Molar absorption coefficient (x 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>),  $\lambda_{em}$  – Emission maxima (sh- shoulder peak), Stokes shift (nm),  $E_g^{optical}$  – Optical band gap according to the equation  $E_g = 1240/\lambda_{onset}$  where  $\lambda_{onset}$  was resolved as the intersection of the extrapolate tangent of the longest wavelength absorption peak and the x-axis.  $E_g^{DFT}$  – Theoretical band gap obtained using density functional model of HOMO and LUMO frontier orbitals.

Density functional theory (DFT) studies of all the compounds were carried out using the GAUSSIAN-09 program at Becke's three-parameter functional and Lee, Yang, and Parr correlation functional (DFTB3LYP) by using the 6-31G(d) basis set. The energy minimized structures and the HOMO-LUMO energy levels of all the compounds are shown in **Figure 2.47**. The energy minimized structure of all the compounds reveals a slightly out of plane conformation of chromophore moiety with respect to the naphthophenanthridine central core, which prohibits the crystallization process on the cooling of compounds **NP-PY**, **NP-PT**, and **NP-TP**, although compound **NP-AC** crystallized at 10 °C higher than the melting transition on heating possibly due to the unstable columnar organization due to completely vertical conformation of anthracene unit to the central core.

Highest occupied (HOMO) and Lowest unoccupied (LUMO) frontier orbitals of **NP-PY** are evenly delocalized throughout the  $\pi$  extension of the core consisting NP and pyrene units suggesting an extended  $\pi$  conjugation of the system. In **NP-AC**, the HOMO orbitals are mainly spread over the central NP core and slightly extended towards the anthracene unit, while the LUMO orbitals are localized mainly on the anthracene with less extension towards NP unit. Since the anthracene unit is not in the same plane of the central core and may not have adequate overlap with the neighboring anthracene in columnar assembly, this compound could exclusively be biased towards hole-transporting property.<sup>98</sup> However, in both **NP-PT** and **NP-TP** molecules, the phenothiazine and triphenylamine unit mainly contributes to the HOMO orbitals and LUMO is localized on the NP central core, possibly leading to electron transport behavior. The theoretical energy levels are given in **Figure 2.47**, and a band gap of about 3.5 ev was observed for all the molecules.

### 2.3.2. Conclusion

In summary, a series of four naphthophenanthridine derivatives covalently attached with various chromophore units is synthesized using the Pictet-Spengler strategy. These derivatives exhibited hexagonal columnar mesomorphism at elevated temperatures. The pyrene derivative was found to be room temperature liquid crystalline and show stable mesophase over a wide range, as evident from POM, DSC, and XRD techniques. Furthermore, all the compounds emit light in the blue to green region, suggesting the potential application in organic electronic devices.



**Figure 2.46** Energy minimized structures and electron density of HOMO and LUMO frontier orbitals of all the compounds.

### 2.3.3. Experimental section

### 2.3.3.1. Reagents and Instruments

Reagents and instruments used are as same as in section 2.1.3.1

#### 2.1.3.2. Synthetic procedures and spectral data

Compounds 2-5 are synthesized following the literature procedures given in section 2.1.3.2.

**Compound 2:** <sup>1</sup>H NMR (500 MHz, CDCl3):  $\delta$  (ppm) = 6.88 (s, 4H), 3.98 (t, J = 6.75 Hz, 4H), 1.78 – 1.83 (m, 4H), 1.43 – 1.48 (m, 4H), 1.26 – 1.36(m, 33H), 0.88 (t, J = 7.0 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl3):  $\delta$  ppm = 149.25, 121.00, 114.12, 69.29, 31.94, 29.71, 29.67, 29.65, 29.46, 29.38, 29.36, 26.07, 22.70, 14.13.

**Compound 3:** <sup>1</sup>H NMR (500 MHz, CDCl3):  $\delta$  (ppm) =7.83 (s, 6H), 4.22 (t, J = 6.75 Hz, 12H), 1.92 – 1.96 (m, 12H), 1.53 – 1.57 (m, 19H), 1.31 – 1.43(m, 105H), 0.88 (t, J = 7.0 Hz, 6H).<sup>13</sup>C NMR (125 MHz, CDCl3):  $\delta$  ppm = 148.98, 123.62, 107.39, 69.74, 31.94, 29.75, 29.72, 29.69, 29.56, 29.50, 29.39, 26.22, 22.70, 14.12.

**Compound 4:** <sup>1</sup>H NMR (500 MHz, CDCl3): δ (ppm) =7.89 (s, 1H), 7.78 (s, 1H), 7.75 (s, 2H), 7.47 (s, 1H), 4.23 (t, 10H), 4.07 (s, 2H), 1.78 – 1.93 (m, 12H), 1.56 (m, 12H), 1.27(m, 96H), 0.88 (t, 18H). <sup>13</sup>C NMR (125 MHz, CDCl3): δ ppm = 150.47, 150.17, 148.97, 148.94, 148.9, 143.81, 140.53, 126.61, 124.64, 124.38, 121.91, 119.3, 114.28, 107.82, 107.35, 107.29, 106.92, 106.5, 75.38, 69.9, 69.67, 69.37, 69.26, 68.78, 31.97, 30.11, 29.77, 29.75, 29.72, 29.67, 29.58, 29.52, 29.42, 29.13, 26.31, 26.24, 26.19, 26.15, 25.87, 22.72, 14.12.

**Compound 5:** <sup>1</sup>H NMR (500 MHz, CDCl3): δ (ppm) =8.81 (s, 1H), 7.82 (s, 1H), 7.79 (s, 1H), 7.76 (s, 1H), 7.36 (s, 1H), 4.56 (s, broad, 2H), 4.11-4.22 (m, 12H), 1.86 – 1.91 (m, 12H), 1.54-1.55 (m, 12H), 1.27(m, 96H), 0.88 (t, *J* = 6.5 Hz, 18H). <sup>13</sup>C NMR (125 MHz, CDCl3): δ ppm = 150.82, 149.38, 148.78, 147.84, 147.38, 138.37, 135.39, 126.86, 124.63, 124.42, 123.91, 123.84, 113.83, 110.11, 108.37, 108.06, 106.93, 97.14, 73.1, 69.89, 69.56, 69.26, 68.61, 31.95, 29.75, 29.73, 29.7, 29.4, 26.22, 22.71, 14.13.

#### General procedure for the synthesis of targeted final compounds

All the final compounds are prepared following the literature procedure. A mixture of compound **5** (1 eq) and aromatic aldehyde (2 eq) in dry DMF (10 ml) and 1% triflic acid were heated to 100 °C. The reaction was monitored using TLC, and Water (20 ml) was added to the reaction mixture after the reaction. The mixture was alkalized with 15% NaOH solution and extracted using dichloromethane and washed with brine. The organic layer was dried using anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude was purified by column chromatography using petroleum ether: ethyl acetate (90:10) as eluent to give yellow solid (60%).

**Compound NP-PY:** Hexadodecyloxytriphenylen-1-amine (0.500 g, 0.370 mmol, 1 eq), Pyrene-1-carbaldehyde (0.170 g, 0.741 mmol, 2 eq), DMF 10 ml, 1% triflic acid, yield: 61%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.43 (s, 1H), 8.30 (s, 1H), 8.26-8.27 (d, 1H), 8.14-8.19 (m, 3H), 8.04-8.11 (m, 4H), 7.92-7.98 (m, 2H), 7.84-7.85 (d, 1H), 4.19-4.45 (m, 10H), 3.40-3.44 (q, 1H), 3.08-3.12 (q, 1H), 1.94-2.02 (m, 6H), 1.83-1.84 (m, 2H), 1.70-1.75 (m, 2H), 1.60-1.64 (m, 6H), 1.17-1.46 (m, 86H), 0.90-1.04 (m, 12H), 0.79-0.88 (m, 12H), 0.18-0.50 (m, 6H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) =158.05, 151.59, 150.96, 150.08, 149.59, 145.27, 144.52, 140.23, 136.41, 131.53, 131.06, 130.57, 129.16, 127.59, 127.01, 126.94, 126.91, 125.89, 125.6, 125.09, 124.82, 124.72, 124.58, 124.46, 124.17, 124.09, 123.36, 123.33, 122.31, 119.8, 113.93, 110.93, 108.9, 107.66, 107.02, 74.1, 71.26, 69.88, 69.81, 69.53, 32.00, 31.95, 31.9, 30.36, 29.87, 29.77, 29.74, 29.71, 29.67, 29.62, 29.57, 29.53, 29.46, 29.42, 29.41, 29.38, 29.34, 29.09, 29.05, 28.78, 26.25, 26.05, 25.11, 22.76, 22.71, 22.69, 22.67, 14.18, 14.13, 14.11, 14.1. Elemental analysis: C, 82.41; H, 10.54; N, 0.90 (calculated); C, 82.24; H, 10.59; N, 0.87 (Found).

**Compound NP-AC:** Hexadodecyloxytriphenylen-1-amine (0.500 g, 0.370 mmol, 1 eq), Anthracene-9-carbaldehyde (0.152 g, 0.741 mmol, 2 eq), DMF 10 ml, 1% triflic acid, yield: 63%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.51 (s, 1H), 8.40 (s, 1H), 8.32 (s, 1H), 8.03-8.08 (m, 4H), 7.50-7.52 (d, 2H), 7.36-7.39 (t, 2H), 7.13-7.16 (t, 2H), 4.37-4.40 (t, 2H), 4.29-4.35 (m, 6H), 4.16-4.19 (t, 2H), 1.93-2.04 (m, 6H), 1.76-1.82 (m, 2H), 1.59-1.62 (m, 10H), 1.38-1.46 (m, 12H), 1.16-1.29 (m, 76H), 0.95-1.08 (s, 8H), 0.84-0.92 (m, 18H), 0.77-0.80 (m, 2H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) =157.19, 151.6, 150.82, 150.1, 149.62, 145.23, 144.44, 139.65, 136.66, 131.66, 130.0, 128.27, 126.87, 125.69, 124.82, 124.3, 124.2, 123.42, 123.38, 121.96, 120.75, 113.98, 110.87, 108.85, 107.72, 107.09, 75.81, 73.42, 71.22, 69.93, 69.66, 69.57, 31.97, 31.94, 31.92, 30.11, 29.88, 29.77, 29.75, 29.72, 29.68, 29.62, 29.6, 29.57, 29.54, 29.49, 29.47, 29.42, 29.39, 29.36, 29.29, 28.53, 26.26, 25.88, 25.16, 22.76, 22.73, 14.13. Elemental analysis: C, 82.14; H, 10.70 N, 0.91 (calculated); C, 82.10; H, 11.18; N, 1.02 (Found).

**Compound NP-PT:** Hexadodecyloxytriphenylen-1-amine (0.500 g, 0.370 mmol, 1eq), N-methylphenothiazine-3-carbaldehyde (0.178 g, 0.741 mmol, 2 eq), DMF 10 ml, 1% triflic acid, yield: 57%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.38 (s, 1H), 8.20 (s, 1H), 8.00 (s, 2H), 7.61-7.62 (d, J = 2 Hz, 1H), 7.54-7.56 (m, 1H), 7.15-7.19 (m, 2H), 6.91-6.94 (t, J = 7.5 Hz, 1H), 6.87-6.89 (d, J = 8 Hz, 1H), 6.84-6.85 (d, J = 8 Hz, 1H), 4.45-4.48 (t, J = 6.5 Hz, 2H), 4.28-4.37 (m, 8H), 3.56-3.58 (t, J = 6.5 Hz, 2H), 3.45 (s, 1H), 1.89-1.98 (m, 12H), 1.59 (m, 12H), 1.25-1.27 (m, 98H), 0.86-0.88 (m, 18H). <sup>13</sup>C NMR (500 MHz, CDCl3),  $\delta$  (ppm) =157.28, 151.51, 150.92, 150.03, 149.52, 145.83, 145.39, 145.17, 144.29, 138.45, 136.29, 129.17, 128.13, 127.23, 127.1, 124.52, 124.13, 123.77, 123.29, 123.2, 122.7, 122.3, 121.77, 117.77, 113.89, 113.74, 112.64, 110.54, 108.64, 107.68, 107.0, 75.48, 74.85, 71.28, 69.93, 69.88, 69.5, 35.47, 31.97, 31.95, 30.61, 26.33, 26.3, 26.25 25.9, 22.71, 14.13. Elemental analysis: C, 79.54; H, 10.53; N, 1.78; S, 2.04 (calculated): C, 79.36; H, 10.19; N, 2.08; S, 1.84 (Found).

**Compound NP-TP:** Hexadodecyloxytriphenylen-1-amine (0.500 g, 0.370 mmol, 1 eq), 4-(diphenylamino)benzaldehyde (0.202 g, 0.741 mmol, 2 eq), DMF 10 ml, 1% triflic acid, yield: 56%.<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.46 (s, 1H), 8.23 (s, 1H), 8.01-8.02 (d, *J* = 5.5 Hz, 2H), 7.73-7.74 (d, *J* = 8.5 Hz, 2H), 7.30-7.33 (t, *J* = 8 Hz, 4H), 7.23-7.24 (d, *J* = 7.5 Hz, 4H), 7.17-7.19 (d, *J* = 8.5 Hz, 2H), 7.06-7.09 (t, *J* = 7.5 Hz, 2H), 4.54 (t, 2H), 4.36-4.41 (m, 4H), 4.31-4.33 (t, *J* = 6.5 Hz, 4H), 3.65-3.68 (t, *J* = 6.5 Hz, 2H), 1.94-2.01 (m, 12H), 1.59-1.64 (m, 12H), 1.45-1.47 (m, 12H), 1.25-1.44 (m, 84H), 0.91 (m, 18H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 157.95, 151.52, 150.95, 150.06, 149.54, 147.94, 147.49, 145.18, 144.37, 137.93, 136.36, 130.86, 129.19, 124.66, 124.53, 124.18, 123.31, 123.21, 122.82, 122.73, 122.3, 117.66, 113.76, 110.46, 108.91, 107.73, 107.01, 75.55, 75.05, 71.47, 69.98, 69.89, 69.5, 31.95, 30.6, 29.91, 29.8, 29.76, 29.71, 29.62, 29.58, 29.53, 29.45, 29.4, 26.34, 26.31, 26.25, 26.08, 22.71, 14.13. Elemental analysis: C, 81.69; H, 10.57; N, 1.75 (calculated): C, 81.41; H, 11.19; N, 1.55 (Found).

# 2.1.5. Spectral data



Figure 2.47 <sup>1</sup>H and <sup>13</sup>C NMR of compound 2.



Figure 2.48 <sup>1</sup>H and <sup>13</sup>C NMR of compound 3.



Figure 2.49 <sup>1</sup>H and <sup>13</sup>C NMR of compound 4.



Figure 2.50 <sup>1</sup>H and <sup>13</sup>C NMR of compound 5.



Figure 2.51 <sup>1</sup>H and <sup>13</sup>C NMR of NP-PY



Figure 2.52  $^{1}$ H and  $^{13}$ C NMR of NP-AC



Figure 2.53 <sup>1</sup>H and <sup>13</sup>C NMR of NP-PT



Figure 2.54 <sup>1</sup>H and <sup>13</sup>C NMR of NP-TP

#### 2.4. References

- 1. Chandrasekhar, S., Sadashiva, B. K. & Suresh, K. A. Liquid crystals of disc-like molecules. *Pramana* **9**, 471–480 (1977).
- Kumar, S. Design Concepts and Synthesis of Discotic Liquid Crystals. in Handbook of Liquid Crystals (2014). doi:10.1002/9783527671403.hlc068.
- 3. Sergeyev, S., Pisula, W. & Geerts, Y. H. Discotic liquid crystals: a new generation of organic semiconductors. *Chem. Soc. Rev.* **36**, 1902 (2007).
- 4. Kumar, S. Recent developments in the chemistry of triphenylene-based discotic liquid crystals. *Liquid Crystals* (2004) doi:10.1080/02678290410001724746.
- Kumar, S. Triphenylene-based discotic liquid crystal dimers, oligomers and polymers. Liquid Crystals (2005) doi:10.1080/02678290500117415.
- 6. Pal, S. K., Setia, S., Avinash, B. S. & Kumar, S. Triphenylene-based discotic liquid crystals: recent advances. *Liquid Crystals* (2013) doi:10.1080/02678292.2013.854418.
- Boden, N., Borner, R. C., Bushby, R. J., Cammidge, A. N. & Jesudason, M. V. The synthesis of triphenylene-based discotic mesogens New and improved routes. *Liq. Cryst.* 15, 851–858 (1993).
- Boden, N., Bushby, R. J. & Cammidge, A. N. Triphenylene-Based Discotic-Liquid-Crystalline Polymers: A Universal, Rational Synthesis. *J. Am. Chem. Soc.* 117, 924–927 (1995).
- Rego, J. A., Kumar, S. & Ringsdorf, H. Synthesis and Characterization of Fluorescent, Low-Symmetry Triphenylene Discotic Liquid Crystals: Tailoring of Mesomorphic and Optical Properties. *Chem. Mater.* 8, 1402–1409 (1996).
- van de Craats, A. M. *et al.* The mobility of charge carriers in all four phases of the columnar discotic material hexakis(hexylthio)triphenylene: Combined TOF and PR-TRMC results. *Adv. Mater.* 8, 823–826 (1996).
- 11. Motoyanagi, J., Fukushima, T. & Aida, T. Discotic liquid crystals stabilized by interionic interactions: imidazolium ion-anchored paraffinic triphenylene. *Chem. Commun.* 101–103

(2005) doi:10.1039/B414649B.

- Paraschiv, I. *et al.* H-Bond-Stabilized Triphenylene-Based Columnar Discotic Liquid Crystals. *Chem. Mater.* 18, 968–974 (2006).
- Zelcer, A., Donnio, B., Bourgogne, C., Cukiernik, F. D. & Guillon, D. Mesomorphism of Hybrid Siloxane-Triphenylene Star-Shaped Oligomers. *Chem. Mater.* 19, 1992–2006 (2007).
- Liu, C., Fechtenkötter, A., Watson, M. D., Müllen, K. & Bard, A. J. Room Temperature Discotic Liquid Crystalline Thin Films of Hexa- p eri -hexabenzocoronene: Synthesis and Optoelectronic Properties. *Chem. Mater.* 15, 124–130 (2003).
- Laschat, S. *et al.* Discotic Liquid Crystals: From Tailor-Made Synthesis to Plastic Electronics. *Angew. Chemie Int. Ed.* 46, 4832–4887 (2007).
- Stępień, M., Gońka, E., Żyła, M. & Sprutta, N. Heterocyclic Nanographenes and Other Polycyclic Heteroaromatic Compounds: Synthetic Routes, Properties, and Applications. *Chem. Rev.* 117, 3479–3716 (2017).
- Ambrosi, A., Chua, C. K., Bonanni, A. & Pumera, M. Electrochemistry of Graphene and Related Materials. *Chem. Rev.* **114**, 7150–7188 (2014).
- Miao, Q. Ten years of N-heteropentacenes as semiconductors for organic thin-film transistors. *Advanced Materials* (2014) doi:10.1002/adma.201305497.
- Qian, G. & Wang, Z. Y. Near-infrared organic compounds and emerging applications. *Chemistry - An Asian Journal* (2010) doi:10.1002/asia.200900596.
- 20. Sun, Z. & Wu, J. Higher Order Acenes and Fused Acenes with Near-infrared Absorption and Emission. *Aust. J. Chem.* **64**, 519 (2011).
- 21. Pawlicki, M., Collins, H. A., Denning, R. G. & Anderson, H. L. Two-Photon Absorption and the Design of Two-Photon Dyes. *Angew. Chemie Int. Ed.* **48**, 3244–3266 (2009).
- 22. Rieger, R. & Müllen, K. Forever young: polycyclic aromatic hydrocarbons as model cases for structural and optical studies. *J. Phys. Org. Chem.* **23**, 315–325 (2010).
- 23. Wu, J., Pisula, W. & Müllen, K. Graphenes as Potential Material for Electronics. Chem.

*Rev.* **107**, 718–747 (2007).

- Grimsdale, A. C. & Müllen, K. The Chemistry of Organic Nanomaterials. *Angew. Chemie Int. Ed.* 44, 5592–5629 (2005).
- Kumar, S. & Manickam, M. Synthesis of phenanthro[b] phenazine, a novel heterocyclic ring structure for discotic liquid crystals. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A. Mol. Cryst. Liq. Cryst.* 338, 175–179 (2000).
- 26. KUMAR, S. & MANICKAM, M. Synthesis of phenanthro[a] phenazine derivatives: a novel ring structure forming discotic liquid crystals. *Liq. Cryst.* **26**, 1097–1099 (1999).
- Mohr, B., Wegner, G. & Ohta, K. Synthesis of triphenylene-based porphyrazinato metal(II) complexes which display discotic columnar mesomorphism. *J. Chem. Soc. Chem. Commun.* (1995) doi:10.1039/C39950000995.
- Foster, E. J., Jones, R. B., Lavigueur, C. & Williams, V. E. Structural Factors Controlling the Self-Assembly of Columnar Liquid Crystals. *J. Am. Chem. Soc.* 128, 8569–8574 (2006).
- Lavigueur, C., Foster, J. E. & Williams, V. E. Modular assembly of elliptical mesogens. Liq. Cryst. (2007) doi:10.1080/02678290701407243.
- Lavigueur, C., Foster, E. J. & Williams, V. E. Self-assembly of discotic mesogens in solution and in liquid crystalline phases: Effects of substituent position and hydrogen bonding. *J. Am. Chem. Soc.* (2008) doi:10.1021/ja803406k.
- 31. Roy, B., De, N. & Majumdar, K. C. Advances in metal-free heterocycle-based columnar liquid crystals. *Chemistry A European Journal* (2012) doi:10.1002/chem.201200483.
- 32. Foster, E. J., Babuin, J., Nguyen, N. & Williams, V. E. Synthesis of unsymmetrical dibenzoquinoxaline discotic mesogens. *Chem. Commun.* (2004) doi:10.1039/b400998c.
- 33. Kumar, S. Investigations on discotic liquid crystals. *Liq. Cryst.* 47, 1195–1203 (2020).
- Gowda, A., Jacob, L., Singh, D. P., Douali, R. & Kumar, S. Charge Transport in Novel Phenazine Fused Triphenylene Supramolecular Systems. *ChemistrySelect* 3, 6551–6560 (2018).

- Gowda, A., Jacob, L., Joy, N., Philip, R. & Kumar, S. Novel phenazine fused triphenylene discotic liquid crystals: synthesis, characterisation, thermal, optical and nonlinear optical properties. *New J. Chem.* 42, 19034–19042 (2018).
- Patra, A., Swamynathan, K. & Kumar, S. Synthesis of novel regioisomeric phenanthro[ a ]phenazine derivatives through the S N Ar strategy and their self-assembly into columnar phases. *New J. Chem.* 45, 4185–4194 (2021).
- 37. Kimura, M. *et al.* Self-assembled helical nanofibers made of achiral molecular disks having molecular adapter. *Chem. Mater.* (2010) doi:10.1021/cm102276a.
- Kumar, S. & Gupta, S. K. Novel triphenylenoimidazole discotic liquid crystals. *Tetrahedron Lett.* 52, 5363–5367 (2011).
- Gupta, R. K. *et al.* Self-assembly of luminescent N-annulated perylene tetraesters into fluid columnar phases. *Soft Matter* 11, 3629–3636 (2015).
- 40. Zhang, Y. *et al.* N-type organic semiconductor bisazacoronene diimides efficiently synthesized by a new type of photocyclization involving a Schiff base. *RSC Adv.* (2012) doi:10.1039/c2ra22488g.
- Bisai, V., Saina Shaheeda, M. K., Gupta, A. & Bisai, A. Biosynthetic Relationships and Total Syntheses of Naturally Occurring Benzo[ c ]Phenanthridine Alkaloids. *Asian J. Org. Chem.* 8, 946–969 (2019).
- Tumir, L.-M., Radić Stojković, M. & Piantanida, I. Come-back of phenanthridine and phenanthridinium derivatives in the 21st century. *Beilstein J. Org. Chem.* 10, 2930–2954 (2014).
- Zhao, K. Q. *et al.* Star-shaped triphenylene discotic liquid crystalline oligomers and their hydrogen-bonded supramolecular complexes with simple acids. *J. Mater. Chem. C* 3, 11735–11746 (2015).
- Liu, C. X. *et al.* Molecular design of benzothienobenzothiophene-cored columnar mesogens: Facile synthesis, mesomorphism, and charge carrier mobility. *J. Mater. Chem.* C 6, 4471–4478 (2018).

- Zhao, K. Q. *et al.* Discogens Possessing Aryl Side Groups Synthesized by Suzuki Coupling of Triphenylene Triflates and Their Self-Organization Behavior. *European J. Org. Chem.* 2016, 2802–2814 (2016).
- Zhao, K. Q. *et al.* Facile transformation of 1-aryltriphenylenes into dibenzo[fg,op]tetracenes by intramolecular Scholl cyclodehydrogenation: synthesis, self-assembly, and charge carrier mobility of large π-extended discogens. *J. Mater. Chem. C* 5, 669–682 (2017).
- Zhao, K. Q. *et al.* Design of Janus triphenylene mesogens: Facile synthesis, mesomorphism, photoluminescence, and semiconductivity. *Dye. Pigment.* 143, 252–260 (2017).
- Tan, Q., Chen, H., Xia, H., Liu, B. & Xu, B. Parent and trisubstituted triazacoronenes: Synthesis, crystal structure and physicochemical properties. *Chem. Commun.* (2016) doi:10.1039/c5cc08853d.
- 49. Wei, J. *et al.* 1,5,9-triazacoronenes: A family of polycyclic heteroarenes synthesized by a threefold pictet-spengler reaction. *Angew. Chemie Int. Ed.* **49**, 8209–8213 (2010).
- 50. Liu, B. *et al.* Triazacoronene Derivatives with Three peri-Benzopyrano Extensions: Synthesis, Structure, and Properties. *European J. Org. Chem.* **2018**, 869–873 (2018).
- 51. Kosuge, T. *et al.* Isolation and structural determination of mutagenic substances in coal tar. *Chem. Pharm. Bull.* (1982) doi:10.1248/cpb.30.1535.
- Mallory, F. B. & Mallory, C. W. Photocyclization of Stilbenes and Related Molecules. in Organic Reactions 1–456 (John Wiley & Sons, Inc., 1984). doi:10.1002/0471264180.or030.01.
- 53. Bushby, R. J. *et al.* Helical geometry and liquid crystalline properties of 2,3,6,7,10,11hexaalkoxy-1-nitrotriphenylenesElectronic supplementary information (ESI) available: calculation of dipolar interactions, details of syntheses and analytical data, DSC data, and full deta. *J. Mater. Chem.* **13**, 470–474 (2003).
- Gupta, M. & Pal, S. K. Triphenylene-Based Room-Temperature Discotic Liquid Crystals: A New Class of Blue-Light-Emitting Materials with Long-Range Columnar Self-

Assembly. Langmuir 32, 1120–1126 (2016).

- Wang, Y., Zhang, C., Wu, H. & Pu, J. Synthesis and mesomorphism of triphenylenebased dimers with a highly ordered columnar plastic phase. *J. Mater. Chem. C* 2, 1667 (2014).
- Tan, Q., Chen, H., Xia, H., Liu, B. & Xu, B. Parent and trisubstituted triazacoronenes: synthesis, crystal structure and physicochemical properties. *Chem. Commun.* 52, 537–540 (2016).
- Zhao, Y. *et al.* Triphenothiazinyl triazacoronenes: donor–acceptor molecular graphene exhibiting multiple fluorescence and electrogenerated chemiluminescence emissions. *J. Mater. Chem. C* 5, 4293–4301 (2017).
- Zyła, M., Gońka, E., Chmielewski, P. J., Cybińska, J. & Stępień, M. Synthesis of a peripherally conjugated 5-6-7 nanographene. *Chem. Sci.* 7, 286–294 (2015).
- Kumar, S., Manickam, M., Balagurusamy, V. S. K. & Schonherr, H. Electrophilic aromatic substitution in triphenylene discotics: Synthesis of alkoxynitrotriphenylenes. *Liq. Cryst.* 26, 1455–1466 (1999).
- 60. Bushby, R. J. *et al.* Helical geometry and liquid crystalline properties of 2,3,6,7,10,11hexaalkoxy-1-nitrotriphenylenes. *J. Mater. Chem.* **13**, 470–474 (2003).
- Vadivel, M., Kumar, I. S., Swamynathan, K., Raghunathan, V. A. & Kumar, S. Novel Annulated Triphenylene Discotic Liquid Crystals Generated by Pictet-Spengler Cyclization. *ChemistrySelect* 3, 8763–8769 (2018).
- Mu, B. *et al.* Discotic columnar liquid-crystalline polymer semiconducting materials with high charge-carrier mobility via rational macromolecular engineering. *Polym. Chem.* 8, 3286–3293 (2017).
- Kaafarani, B. R. Discotic Liquid Crystals for Opto-Electronic Applications † ‡. *Chem. Mater.* 23, 378–396 (2011).
- 64. Termine, R. & Golemme, A. Charge Mobility in Discotic Liquid Crystals. *Int. J. Mol. Sci.*22, 877 (2021).

- Coropceanu, V. *et al.* Charge Transport in Organic Semiconductors. *Chem. Rev.* 107, 926–952 (2007).
- Vladimirov, I., Kühn, M., Geßner, T., May, F. & Weitz, R. T. Energy barriers at grain boundaries dominate charge carrier transport in an electron-conductive organic semiconductor. *Sci. Rep.* 8, 14868 (2018).
- Pisula, W., Zorn, M., Chang, J. Y., Müllen, K. & Zentel, R. Liquid Crystalline Ordering and Charge Transport in Semiconducting Materials. *Macromol. Rapid Commun.* 30, 1179–1202 (2009).
- Wöhrle, T. *et al.* Discotic Liquid Crystals. *Chemical Reviews* (2016) doi:10.1021/acs.chemrev.5b00190.
- Mahesh, P. *et al.* Carbon dot-dispersed hexabutyloxytriphenylene discotic mesogens: structural, morphological and charge transport behavior. *J. Mater. Chem. C* 8, 9252–9261 (2020).
- 70. Shah, A. *et al.* Charge transport in phenazine-fused triphenylene discotic mesogens doped with CdS nanowires. *New J. Chem.* **44**, 14872–14878 (2020).
- Ma, T. *et al.* Butterfly-like Shape Liquid Crystals Based Fused-Thiophene as Unidimensional Ambipolar Organic Semiconductors with High Mobility. *Chem. – An Asian J.* asia.202100173 (2021) doi:10.1002/asia.202100173.
- Zou, G. *et al.* Columnar Iridium(III) Metallomesogens Based on Polycatenar Pyridyltetrazolate with Ambipolar Carrier Mobility Behavior. *Inorg. Chem.* 58, 861–869 (2019).
- 73. Muccini, M. A bright future for organic field-effect transistors. *Nat. Mater.* 5, 605–613 (2006).
- 74. Rost, C. *et al.* Ambipolar light-emitting organic field-effect transistor. *Appl. Phys. Lett.*85, 1613–1615 (2004).
- 75. Chikamatsu, M. *et al.* Ambipolar organic field-effect transistors based on a low band gap semiconductor with balanced hole and electron mobilities. *Appl. Phys. Lett.* **91**, 43506
(2007).

- Dodabalapur, A., Katz, H. E., Torsi, L. & Haddon, R. C. Organic Heterostructure Field-Èffect Transistors. *Science (80-. ).* 269, 1560 LP – 1562 (1995).
- Tada, K., Harada, H. & Yoshino, K. Polymeric Bipolar Thin-Film Transistor Utilizing Conducting Polymer Containing Electron Transport Dye. *Jpn. J. Appl. Phys.* 35, L944– L946 (1996).
- Tsao, H. N. *et al.* From Ambi- to Unipolar Behavior in Discotic Dye Field-Effect Transistors. *Adv. Mater.* 20, 2715–2719 (2008).
- 79. Zaumseil, J., Friend, R. H. & Sirringhaus, H. Spatial control of the recombination zone in an ambipolar light-emitting organic transistor. *Nat. Mater.* **5**, 69–74 (2006).
- 80. Yuan, Y., Gregg, B. A. & Lawrence, M. F. Time-of-flight study of electrical charge mobilities in liquid-crystalline zinc octakis(β-octoxyethyl) porphyrin films. *J. Mater. Res.* 15, 2494–2498 (2000).
- Fujikake, H., Murashige, T., Sugibayashi, M. & Ohta, K. Time-of-flight analysis of charge mobility in a Cu-phthalocyanine-based discotic liquid crystal semiconductor. *Appl. Phys. Lett.* 85, 3474–3476 (2004).
- 82. Wegewijs, B. R. *et al.* Charge-carrier mobilities in binary mixtures of discotic triphenylene derivatives as a function of temperature. *Phys. Rev. B* **65**, 245112 (2002).
- Bino, H., Takayashiki, Y., Hanna, J., Bushby, R. J. & Haarer, D. High electron mobility of 0.1cm2V–1s–1 in the highly ordered columnar phase of hexahexylthiotriphenylene. *Appl. Phys. Lett.* 87, 192105 (2005).
- Monobe, H., Shimizu, Y., Okamoto, S. & Enomoto, H. Ambipolar Charge Carrier Transport Properties in the Homologous Series of 2,3,6,7,10,11-hexaalkoxytriphenylene. *Mol. Cryst. Liq. Cryst.* 476, 31/[277]-41/[287] (2007).
- Hayashi, H. *et al.* Segregated Donor–Acceptor Columns in Liquid Crystals That Exhibit Highly Efficient Ambipolar Charge Transport. *J. Am. Chem. Soc.* 133, 10736–10739 (2011).

- Camerel, F. *et al.* Ambipolar Discotic Liquid Crystals Built Around Platinum Diimine-Dithiolene Cores. *Chem. – A Eur. J.* 25, 5719–5732 (2019).
- Bala, I. *et al.* Room temperature perylene based columnar liquid crystals as solid-state fluorescent emitters in solution-processable organic light-emitting diodes. *J. Mater. Chem. C* 8, 12485–12494 (2020).
- Bala, I. *et al.* Room temperature discotic liquid crystalline triphenylenepentaalkynylbenzene dyads as an emitter in blue OLEDs and their charge transfer complexes with ambipolar charge transport behaviour. *J. Mater. Chem. C* 7, 5724–5738 (2019).
- Yasuda, T., Shimizu, T., Liu, F., Ungar, G. & Kato, T. Electro-Functional Octupolar π-Conjugated Columnar Liquid Crystals. *J. Am. Chem. Soc.* 133, 13437–13444 (2011).
- Kushida, T., Shuto, A., Yoshio, M., Kato, T. & Yamaguchi, S. A Planarized Triphenylborane Mesogen: Discotic Liquid Crystals with Ambipolar Charge-Carrier Transport Properties. *Angew. Chemie Int. Ed.* 54, 6922–6925 (2015).
- 91. Liu, X., Usui, T. & Hanna, J. A Windmill-Shaped Discotic Columnar Liquid Crystal with Fast Ambipolar Charge Carrier Transport. *Chem. Mater.* **26**, 5437–5440 (2014).
- Sosa-Vargas, L. *et al.* Liquid crystalline and charge transport properties of novel nonperipherally octasubstituted perfluoroalkylated phthalocyanines. *J. Mater. Chem. C* 3, 1757–1765 (2015).
- 93. Méry, S. *et al.* Bipolar carrier transport in a lamello-columnar mesophase of a sanidic liquid crystal. *J. Mater. Chem.* **12**, 37–41 (2002).
- 94. Sienkowska, M. J., Monobe, H., Kaszynski, P. & Shimizu, Y. Photoconductivity of liquid crystalline derivatives of pyrene and carbazole. *J. Mater. Chem.* **17**, 1392–1398 (2007).
- De, J., Bala, I., Gupta, S. P., Pandey, U. K. & Pal, S. K. High Hole Mobility and Efficient Ambipolar Charge Transport in Heterocoronene-Based Ordered Columnar Discotics. *J. Am. Chem. Soc.* 141, 18799–18805 (2019).
- 96. Vadivel, M., Singh, S., Singh, D. P., Raghunathan, V. A. & Kumar, S. Ambipolar Charge

Transport Properties of Naphthophenanthridine Discotic Liquid Crystals. J. Phys. Chem. B acs.jpcb.1c06009 (2021) doi:10.1021/acs.jpcb.1c06009.

- 97. Xi, Y. *et al.* Mechanical stimuli induced emission spectra blue shift of two D-A type phenothiazine derivatives. *Chem. Lett.* (2018) doi:10.1246/cl.180089.
- 98. Eichhorn, S. H. *et al.* A combined study of mesomorphism, optical, and electronic properties of donor-acceptor columnar liquid crystals. in *Liquid Crystals XV* (ed. Khoo, I. C.) 811402 (2011). doi:10.1117/12.893149.
- Paramaguru, G., Solomon, R. V., Jagadeeswari, S., Venuvanalingam, P. & Renganathan, R. Tuning the Photophysical Properties of 2-Quinolinone-Based Donor-Acceptor Molecules through N - versus O -Alkylation: Insights from Experimental and Theoretical Investigations. *European J. Org. Chem.* 2014, 753–766 (2014).
- 100. Shao, J. *et al.* Thiophene-Inserted Aryl-Dicyanovinyl Compounds: The Second Generation of Fluorescent Molecular Rotors with Significantly Redshifted Emission and Large Stokes Shift. *European J. Org. Chem.* **2011**, 6100–6109 (2011).

## **Chapter 3**

# Synthesis and Characterization of Novel Triazacoronene DLCs



This chapter discusses the synthesis of triazacoronene based discotic liquid crystals through different strategies and their structural and mesomorphic behavior. We have synthesized substituted triphenylene-1,5,9-triamine and coupled it with aliphatic aldehydes to obtain triazacoronene derivatives as a yellow solid. The compounds are characterized by spectral and elemental analysis and found to be non-liquid crystalline in nature, possibly due to the imbalance in the rigid core size and flexible units in the structure. The above prediction was validated by replacing the alkyl chains in the periphery with the alkoxy substituted phenyl rings. All the compounds are near room temperature liquid crystals with a wide temperature range. The diffraction data of the compounds suggest the hexagonal order of the mesophase.

#### **3.1. Introduction**

Graphene, one of the modern scientific wonder which won the Nobel prize has inspired the organic chemists to synthesize polycyclic aromatic systems, also termed as nano graphene<sup>1</sup>. Infinite graphene possesses a zero bandgap, but the structurally similar yet confined nanographene shows non-zero bandgaps mainly depending on their size and edge configurations. Graphene has a hexagonal arrangement of carbon atoms (**Figure 3.1**). Within graphene, subgraphs for many novel aromatic hydrocarbons such as coronene, curculene, kekulene can be found<sup>2</sup>. These polycyclic aromatic hydrocarbons (PAH), regarded as nanographenes, have been synthesized extensively by ring extension, heteroatom doping, and edge functionalization. Incorporating the heteroatom in the graphene motif reflects in the modulation of bandgaps, electrochemical activity, potential sites for metal coordination, spin and charge stabilization in the carbon skeleton<sup>3</sup>. The nature of heteroatom has been the deciding factor in their electronic behavior, such as electronrich or deficient. The nitrogen-fused nanographene cannot be ignored because of its immense potential for semiconducting applications due to its excellent photophysical and charge transport properties. The heterocyclic nanographene has often been realized through synthetic pathways such as cycloisomerization, cycloaddition, multicomponent couplings, and oxidative coupling.



Figure 3.1. Graphene subunits as a model for PAHs.

Nanographenes are observed to be one of the model systems for the study of the selforganization phenomenon<sup>4</sup>. The attention to nanographene has paved the way for discovering a range of extended  $\pi$  conjugated systems, among which most of them contain heterocyclic rings<sup>3</sup>. These  $\pi$ -extended PAHs have received immense attention in the interdisciplinary fields due to their potential play in future organic electronic applications. Hexa-*peri*-hexabenzocoronene (**Figure 3.2**), one such PAH, was synthesized through the oxidative intramolecular cyclodehydrogenation of hexaphenylbenzene<sup>5</sup>. Wei et al. synthesized substituted HBCs (**Figure 3.3**) from 1,3,5tri(bromomethyl)-benzene and benzaldehyde building blocks in a one-pot synthesis. Replacing benzaldehyde with thienaldehyde and phenanthraldehyde in the same method provided C<sub>3</sub> symmetrical  $\pi$  extended graphene nanostructures<sup>6</sup>.



Figure 3.2. Synthesis of Hexa-peri-hexabenzocoronene.

The self-assembly of some nanographenes (discotics) comprising structural contrast has often resulted in columnar liquid crystalline systems. These columnar structures of disc-shaped molecules are achieved through non-covalent interactions, primarily  $\pi$ - $\pi$  interactions<sup>7-9</sup>. Coronene, a six-fold symmetrical unique polycyclic aromatic hydrocarbon, is purely carbon and hydrogenbased and is electron-rich, hence hole-transporting compound. It has been on the highlights for several years, not just for its graphene-like planar structure but also for the continuous challenge in the preparation pathways. Coronene derivatives are synthesized from their structurally similar perylene counterpart and studied for the mesomorphic properties<sup>10,11</sup>. Many coronene-based molecules are hexabenzocoronenes, and their derivatives show columnar mesophase for a wide temperature range and are found to have high charge mobility<sup>12-14</sup>.



Figure 3.3. Coronene-based symmetrical and highly substituted nanographenes.

Mullen et al. have studied the effect of these parameters by rationally designing the shape of the discotic core and the peripheral substitutions using molecular dynamic simulations and proved the high charge carrier mobility in semi-triangle shaped polycyclic aromatic hydrocarbons<sup>15,16</sup>. They have reported high mobility of 0.2 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for hexabenzocoronene molecules with hydrophilic and hydrophobic side chains possessing three-fold symmetry with the molecular twist of 60° between neighboring molecules forming a helical structure<sup>16</sup>. The thermodynamic stability of columnar liquid crystals is improved by extending the rings into larger aromatic cores and introducing additional aromatic interactions in the periphery<sup>15,17,18</sup>. These extended aromatic systems have proven to show high charge carrying properties, a function of electron-rich PAHs, which act as good hole-transporting p-type materials such as triphenylene<sup>19–23</sup>, phthalocyanine<sup>24–27</sup>, coronene<sup>16,28</sup>, etc. Electron deficient systems are needed for the n-type electron-transporting properties, and those are obtained using rational synthetic strategies. Such

modifications are achieved by incorporating heteroatoms like nitrogen in the core of discs which reduces electron density of the core<sup>29–35</sup>. In particular, polycyclic aromatic hydrocarbons with zigzag periphery have been widely used to construct enormous heterocyclic molecules through ring annulation<sup>36–39</sup>. Heteroatom doping in these PAHs proved to influence the structure, electronic as well as charge transport properties. However, doping in these nanographene structures with precise control over the system has not been achieved. Several bottom-up synthetic methods have been established to obtain heteroatom-doped small PAH molecules with perfect control of the size, doping position and substituents to understand the structure-property relationship.

Heteroatom annulated PAHs have been explored extensively over the decades due to the well-established and efficient synthetic methods. Nitrogen incorporation in coronene through various synthetic strategies resulted in a brand new class of heterocoronene known as azacoronene (**Figure 3.4**). Diazacoronene, a coronene analogue **2** with two nitrogen, was synthesized from diazaperylenes by annulating with thiophene or benzene rings and studied for proton sensor applications<sup>40</sup>. Triphenylene has been used as a precursor, and many heteroatoms were introduced in its bay regions to provide various chalcogen and nitrogen annulated PAHs. 1,5,9-triazacoronene **4**, an analogue of coronene, was obtained from triphenylene through Pictet-Spengler cyclization conditions and their structural, photo physical properties were investigated<sup>41</sup>.

Further, triazacoronene molecule extensions have been achieved in various synthetic routes such as ring fusion and heteroatom annulation<sup>41–43</sup>. In addition, perylene core is also a precursor for heteroannulation due to its excellent properties and uncomplicated functionalization in bay regions. Few examples of these coronene analogous are sulfur-annulated benzoperylene, namely thiacoronene, nitrogen incorporated 1,2-diazacoronene, and 1,2,7,8-tetraazacoronene **3** (**Figure 3.4**)<sup>39</sup>. The triazaocoronene analogue shows red-shifted absorption and lower oxidation and reduction onsets signifying the electron-deficient nature than all carbon analogue hexamethoxycoronene.



Figure 3.4. Structures of Coronene and Azacoronene analogues

Reasonable modifications of molecular structure resulted in the n-type electrontransporting materials. The doping of heteroatoms like nitrogen in the core of discs reduces the electron density of the core and enhances the  $\pi$ - $\pi$  overlap<sup>29-32,34,35</sup>. Hexa-alkyl-substituted hexaperi-hexabenzocoronenes derivatives **5** (Figure 3.5) were found to exhibit hexagonal columnar mesomorphism for an extensive temperature range, one of the few examples of liquid crystalline compound with alkyl chain without any heteroatom<sup>12</sup>. Suitably substituted coronene bis(dicarboximide)s **6** has a combination of coronene and perylene bis(dicarboximide) like structure. These molecules exhibit highly ordered columnar superstructure and have excellent fluorescence properties<sup>10</sup>. The coronene-monoimide **7** revealed a room temperature columnar liquid crystallinity. A high one-dimensional charge carried mobility of 0.2 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> in its mesophase was measured using pulse-radiolysis time-resolved microwave conductivity technique<sup>11</sup>.



Figure 3.5. Coronene-based liquid crystalline derivatives.

Bisazacoronene bisimide derivatives 8 and 9 (Figure 3.6) were prepared through photocyclization of schiff base and are found to self-assemble into ordered nanobelts of 565 nm

width. A reasonable electron carrier mobility of  $5.65 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was measured in space charge-limited (SCLC) device<sup>44</sup>. Imidazole and triazole rings fused hetero-coronene tetracarboxylic acid diimides 10 and 11 were synthesized by Li et al. through photocyclization reactions. The electron-rich imidazole-embedded heterocoronenes form a one-dimensional nanostructure by strong  $\pi$ - $\pi$  stacking interactions, while the electron-poor triazole analogue lacked the self-assembling property<sup>45</sup>. Liu et al. have synthesized benzo and thieno fused highly functional azacoronenes 12 and 13 with various core annulation and peripheral group modifications. These azacoronenes exhibited acid-induced spectroscopic changes, a potential proton sensing property<sup>40</sup>. Wei et al reported a range of substituted 1,5,9-triazacoronenes 14 following a three fold Pictet-Spengler reaction and oxidative aromatization. The resulting azacoronenes show red-shifted absorption compared to all carbon coronene analogue, and relatively lower HOMO energy levels suggest an intrinsic n-type semiconductor behavior<sup>41</sup>. Parent unsubstituted triazacoronene derivatives 15 were achieved subsequently through three-fold Bischler–Napieralski cyclization. Single crystal X-ray studies showed the brick-wall arrangement of the molecules with strong  $\pi - \pi$ interactions along with the tunable electronic properties, making them potential candidates for electron transport<sup>46</sup>.



Figure 3.6. Substituted diazacoronene and triazacoronene derivatives.

Azacoronene fused with thiophene moieties have been synthesized from 1,5diaminoanthraquinone through multistep procedure<sup>47</sup>. The resulting thienoazacoronene (**Figure 3.7**) having suitable side chains displays columnar mesomorphism and a high degree of selforganization in thin-film, exhibiting mobility up to 0.028 cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup>, which is among the high field-effect mobilities for discotic materials.



Figure 3.7. Liquid crystalline thienoazacoronene derivatives. .

Tetraazacoronene tetraesters (**Figure 3.8**) were synthesized by a double Diels-Alder reaction of perelyne with diethyl azodicarboxylate, and the ester groups were subjected to saponification to yield tetraazacoronene **16**<sup>48</sup>. Mullen et al. extended this strategy to prepare isomeric substituted tetraazocoronenes **17** and **18** by various synthetic approaches<sup>49,50</sup>. These blue-colored compounds have absorption at 585 nm and form stable liquid crystalline phases of hexagonal columnar or smectic depending on the position and length of peripheral alkyl chains<sup>51-53</sup>. In addition, fully thiophene-annulated coronenes known as hexathienocoronenes (HTCs) have been synthesized, and Mullen et al. investigated their self-assembling behavior. The dodecyloxy substituted HTCs revealed a remarkably stable columnar mesophase over a wide temperature range<sup>54</sup>. A series of pyrrole fused azacoronenes were synthesized by stepwise replacement of pyrazole ring to dialkoxy benzene through oxidative dehydrogenation of corresponding hexaarylbenzenes. In contrast to the N-doped electron-deficient molecules, these derivatives are electron-rich due to electron-donating pyrrole moiety and show multiple oxidation processes<sup>55</sup>. It

becomes evident that the incorporation of heteroatoms in the right position plays a crucial role in deciding both electronic and optical character of the molecules.



Figure 3.8. Parent tetraazacoronene and its liquid crystal derivatives.

This chapter introduces triazacoronene as a novel discotic molecule to the columnar liquid crystalline family by attaching it with peripheral alkoxy phenyl substituents. A series of four compounds has been successfully synthesized and well-characterized for purity and physical properties. This is the first report on triazacoronene based columnar mesophase in the literature, and the observations are discussed. Two compounds having six alkoxy and two having nine alkoxy chains around the central core have been synthesized. The purity and structural confirmation were carried out using spectral and elemental analysis. All the compounds are found to be mesomorphic for a wide temperature range. Most of them are liquid crystalline at very near room temperature and stable till high temperature. Their mesomorphic properties were analyzed using POM, DSC, and X-ray diffraction techniques. Optical properties were measured using UV-Vis and fluorescence spectroscopy.

#### 3.2. Results and discussion

3.2.1. Synthesis.



Scheme. 3.1 Synthesis of triazacoronene derivatives.



Scheme. 3.2 Synthesis of triphenyltriazacoronene derivatives.

Alkoxyalkyltriazacoronene derivatives **6a** and **6b** are synthesized following the literature procedures<sup>41,56</sup>, and the synthetic route is shown in **Scheme 3.1**. Hexabutoxytriphenylene (HAT4) **3** was prepared using the Scholl reaction. The purified HAT4 was nitrated by using conc.HNO<sub>3</sub>, which was further reduced catalytically to 2,3,6,7,10,11-hexabutoxytriphenylene-1,5,9-triamine **5**. The Pictet-Spengler reaction was carried out with aliphatic aldehydes and compound **5** with triflic acid as catalyst in DMF to give substituted 1,5,9-triazacoronene derivatives **6a** and **6b**.

The synthetic scheme of compounds **4a-d** is given in **Scheme 3.2**. 2,3dichloronitrobenzene is subjected to 3-fold Ullman coupling using copper powder in DMF. The resultant 1,5,9-trinitrotriphenylene is reduced catalytically by Pd /C under H<sub>2</sub> atmosphere to give triphenylene-1,5,9-triamine. The substituted benzaldehydes were synthesized using the literature procedure<sup>57</sup>. The final compounds were prepared by reacting compound **3-i** and substituted benzaldehydes under Pictet-Spengler reaction conditions. All the compounds were analyzed for their purity using <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis. In addition, their thermal stability was found using thermogravimetric analysis. Finally, the pure compounds were taken for analyzing mesomorphic and photophysical behavior.

#### 3.2.2. Mesophase characterization

The mesomorphic property of all the compounds was studied using a combination of polarizing optical microscope (POM), differential scanning calorimetry (DSC) and X-ray diffraction techniques. Compounds **6a** and **6b** were placed on untreated glass slides and viewed under POM in crossed polarized conditions to examine the phase transition with temperature. Both the compounds 6a and 6b stayed in the crystalline phase till high temperature and melted to isotropic liquid at about 148 and 175 °C, respectively. Upon cooling, both the compounds exhibited crystallization below the isotropic temperature without any characteristic textures of mesophase suggesting the absence of mesomorphism in these derivatives. Consequently, there was no phase transition observed in DSC thermogram associated with the liquid crystalline phase. This could be due to the inadequate ratio between the core size and peripheral chain length.

In order to induce liquid crystallinity in triazacoronene, three phenyl rings with longer alkoxy chains were introduced, as shown in **Scheme 3.2**. To our expectations, all the derivatives (**4a-d**) are found to be liquid crystalline in nature. The mesophase characterization of these derivatives is discussed further. **Figure 3.9** shows the polarizing optical microscopic images of compounds **4a-d** under crossed polarizer conditions and around the phase transition from isotropic to mesophase on cooling. Upon cooling, mosaic-like textures were observed around 155°C and 125°C for compounds **4b** and **4d** respectively, that are typical characteristics of columnar hexagonal mesophase. On further cooling, these textures remain stable till room temperature for compound **4b**, and up to 40°C for **4d** before crystallizing. Interestingly, compounds **4a** and **4c** form dendric-like textures on cooling from isotropic, which shows dark domain characteristics of homeotropically aligned columns. These spontaneously aligned compounds are of great interest in discotic liquid crystals due to their charge carrying ability and can be of great potential towards organic conductor applications. Furthermore, all these compounds show mesomorphic properties for an excellent range of temperature, and mesophase is stable until near room temperature, which was validated further by differential scanning calorimetry.





The DSC thermograms are given in **Figure 3.10**, and the enthalpy values associated with these phase transitions are given in **Table 3.1**. Enantiotropic behavior of all the compounds is evident from the DSC, showing the phase transition in both heating and cooling cycles. Compound **4b** with nine dodecyloxy chains is liquid crystalline at room temperature and exhibits stable mesophase up to  $161^{\circ}$ C. All the other compounds showed two endothermic peaks in heating corresponding to Cr-Col<sub>h</sub> and Col<sub>h</sub>-Iso transitions. Two exothermic peaks on cooling correspond to Iso-Col<sub>h</sub> and Col<sub>h</sub>-Cr transitions are observed. These are crystalline at room temperature and melt at elevated temperatures. For example, **4a** with six dodecyloxy chains shows a melting transition at 31°C and remains liquid crystalline for a wide temperature range before clearing to isotropic phase at 245°C. The increase in the number of alkoxy chains around the central core decreases the melting and clearing temperature of these compounds. Similar behavior is observed for compounds **4c** with six alkoxy chains and compound **4d** with nine alkoxy chains. These phase

transitions are matching well with the polarizing optical microscopic observations and are further validated through X-ray diffraction techniques.



Figure 3.10. DSC thermograms of compounds 4a-d

**Table 3.1**. Phase transition temperatures in °C and enthalpy values in kJ/mol.

Compound	Heating	Cooling		
4a	Cr 31 (15.8) Col <sub>h</sub> 245 (8.1) Iso	Iso 241 (7.8) Col <sub>h</sub> 21 (12.7) Cr		
<b>4b</b>	Col <sub>h</sub> 161 (25.1) Iso	Iso 157 (25.1) Col <sub>h</sub>		
4c	Cr 48 (112.6) Col <sub>h</sub> 189 (5.0) Iso	Iso 188 (5.7) Col <sub>h</sub> 39 (68.4) Cr		
4d	Cr 48 (113.0) Col <sub>h</sub> 129 (14.5) Iso	Iso 122 (19.7) Col <sub>h</sub> 40 (113.3) Cr		

X-ray diffraction experiments have been carried out for all the compounds below their mesophase transition temperatures to understand the exact nature of self-assembly. The X-ray diffraction patterns of all the compounds in their mesophase state are given in **Figure 3.11**. Compound **4a** at 80°C exhibits many sharp peaks in the small-angle region that are indexed to the hexagonal lattice. Whereas in the wide-angle regime, it shows one broad peak ( $h_a = 4.58$  Å) typical of liquid-like order of aliphatic chains and another slightly sharper peak ( $h_c = 3.60$  Å) which appears due to the core-core ordering. The much sharper core-core peak suggests that the cores within the column are highly ordered. In the small-angle region, there are many peaks with a d-spacing ratio that corresponds to reflections from (10), (11), (20), (21), (30), (22), and (31) planes of the hexagonal lattice with lattice parameter *a* = 30.60 Å. Similarly, **4b** at 150°C showed many reflections in the small-angle region whose d-spacing ratio correspond to (10), (11), (20), (21), (30), (22), (31), (40) and (32) planes of the hexagonal lattice with lattice parameter *a* = 35.78 Å. The presence of these many reflections is unusual for columnar hexagonal mesophase.



**Figure 3.11**. X-ray diffractograms of compounds **4a** at 80°C, **4b** at 150°C, **4c** at 160°C and **4d** at 70°C.

They were observed due to the highly ordered nature of columns in the 2-D plane. The strong corecore peak indicates a much stronger  $\pi$ - $\pi$  overlap between the cores. Compounds **4c** and **4d** showed similar peaks in X-ray diffractogram, suggesting overall, the triazacoronene core forms highly ordered columns, which arrange themselves in a hexagonal lattice with extended periodicity. The number of molecules per slice of the column was calculated and found to be 1 for all the compounds.

Compound	Phase	<b>d</b> observed	d calculated	Miller indices	Parameters
		(Å)	(Å)	(h,k)	
<b>4</b> a	Col <sub>h</sub>	26.43	26.50	10	a = 30.60 Å
	80°C	15.29	15.29	11	$S_{h}{=}810.91~{\AA}^{2}$
		13.20	13.25	20	$V_h = 2919.28 \text{ Å}^3$
		10.04	10.01	21	Z = 1.07
		8.83	8.83	30	
		7.64	7.64	22	
		7.35	7.35	31	
		4.58 (h <sub>a</sub> )			
		3.60 (hc)			
<b>4</b> b	Col <sub>h</sub>	30.94	30.99	10	a = 35.78 Å
	150°C	17.88	17.89	11	$S_{h} = 1109.06 \ \text{\AA}^{2}$
		15.50	15.50	20	$V_h = 3970.45 \text{ Å}^3$
		11.76	11.71	21	Z = 1.09
		10.34	10.33	30	
		8.95	8.95	22	
		8.60	8.60	31	
		7.75	7.75	40	
		7.11	7.11	32	
		4.54 (h <sub>a</sub> )			
		3.58 (h <sub>c</sub> )			

Table 3.2. The layer spacings and lattice parameters calculated from X-ray diffractogram

4c	Col <sub>h</sub>	30.87	30.89	10	a = 35.67 Å
	160°C	17.81	17.83	11	$S_h = 1102.44 \text{ Å}^2$
		15.44	15.44	20	$V_h = 3957.76 \text{ Å}^3$
		11.64	11.67	21	Z = 1.20
		10.29	10.29	30	
		8.87	8.91	22	
		8.57	8.57	31	
		4.60 (h <sub>a</sub> )			
		3.59 (h <sub>c</sub> )			
4d	Col <sub>h</sub>	35.05	35.10	10	a = 40.53 Å
	70°C	20.28	20.26	11	$S_{h} = 1422.80 \ \text{\AA}^{2}$
		17.60	17.55	20	$V_{h}{=}5008.28~{\AA}^{3}$
		13.24	13.26	21	Z = 1.11
		9.74	9.73	31	
		8.80	8.77	40	
		8.08	8.05	32	
		7.66	7.66	41	
		4.52 (h <sub>a</sub> )			
		3.52 (h <sub>c</sub> )			

(**a** = lattice parameter =  $\sqrt{(4/3) \times d_{10}}$ ; lattice area  $S_h$ =  $a^2 \sin 60^\circ$ ; lattice volume  $V_h$ =  $a^2 \sin 60^\circ \times h_c$ ( $h_a$  if  $h_c$  is not observed); No of molecules per slice of column (**Z**) = ( $\sqrt{3} \times N_a \times \rho \times a^2 \times h$ )/2M;  $N_a$ =Avogadro number;  $\rho$  =Density in Kg/m<sup>3</sup>; **a**=lattice parameter;  $h_c$ =core core peak ( $h_a$  = alkyl-alkyl peak, if  $h_c$  is not observed); M=molecular weight in Kg/m<sup>3</sup>). The electron density map (EDM) was reconstructed from the diffraction data as described in previous reports<sup>58</sup>. In **Figure 3.12**, we represent the electron density of 2D Col<sub>h</sub> phase of 4b at 150 °C. The red part in the image has the highest electron density, while in the purple region, the electron density is the lowest.



Figure 3.12. Electron density map of the hexagonal phase of 4b at 150°C.

The thermal stability of all the compounds was analyzed using thermogravimetric analysis. The TGA profile of all the derivatives is shown in **Figure 3.13**. All the compounds show good thermal stability up to 400 °C before 5% weight loss was observed. This temperature is much higher than the isotropic transition temperature, which excludes any possible decomposition during the mesophase characterization.



Figure 3.13. TGA thermogram of compounds 4a-d.

#### 3.2.3. Photophysical properties and DFT studies

The photophysical properties of all the compounds were investigated in their micromolar concentration chloroform solution using UV-visible and emission spectroscopy. The absorption and emission profile of compounds are shown in **Figure 3.14**. It can be seen that compounds **4a** and **4c** show identical absorption profiles with the strongest absorption peak at 352 nm, which usually corresponds to the  $\pi$ - $\pi^*$  transition of the central aromatic core. Similarly, compounds **4b** and **4d** show the same pattern with the maximum absorption at 342 nm of  $\pi$ - $\pi^*$  transition. The difference in the number of alkoxy chains around the central core causes a difference of about 10 nm in absorption maxima. Molar extinction coefficient values of **4a-d** are  $7.2 \times 10^4$  M<sup>-1</sup>cm<sup>-1</sup>,  $7.4 \times 10^4$  M<sup>-1</sup>cm<sup>-1</sup>,  $5.9 \times 10^4$  M<sup>-1</sup>cm<sup>-1</sup> and  $7.3 \times 10^4$  M<sup>-1</sup>cm<sup>-1</sup>. Compounds **4a** and **4c** were excited at 352 nm, and the emission was recorded in chloroform solution. They showed two intense peaks at 444 and 470 nm with a weak shoulder peak at 500 nm. Compounds **4b** and **4d** were excited at 342 nm, and the emission showed a similar maximum wavelength of 468 nm. The optical band gaps were calculated from the longest absorbance wavelength by extrapolating the curve using equation 1240/ $\lambda$  and found to be 2.8 eV.



Figure 3.14. UV-vis and emission spectra of compounds 4a-d in chloroform solution ( $5 \times 10^{-6}$  M concentration).

Density functional theory (DFT) calculations were performed for the propyloxy chain analogs of all the compounds using the GAUSSIAN-09 program with a Becke's three-parameter functional and Lee, Yang, and Parr correlation functional (DFTB3LYP) by using the 6-311G (d, p) basis set. The energy minimized structures of these analogs are given in **Figure 3.15**, and it shows slightly out-of-plane peripheral phenyl rings surrounding the  $C_3$  symmetrical core. **Figure 3.16** shows the HOMO – LUMO energy level diagrams of analogue compounds obtained from computations. The HOMO orbitals are partially delocalized into the peripheral phenyl groups and LUMO orbitals are mainly focused in the core. The energy levels of both the compounds were found to be similar, with an energy gap of around 3.6 eV.



Figure 3.15. Energy minimized structures of a) analogue of 4a and 4c, b)analogue of 4b and 4d.



Figure 3.16. HOMO and LUMO energy level diagrams of analogue compounds 4a and 4c (left), compounds 4b, and 4d (right).

#### **3.3.** Conclusion

A series of novel triazacoronene derivatives were synthesized, and their mesomorphic properties were analyzed. This is the first report on columnar mesomorphism in these C<sub>3</sub>-symmetrical electron-deficient systems. All the compounds exhibited mesophase over a wide temperature range, and homeotropic alignment was achieved spontaneously in molecules with six alkoxy chains. Higher-order peaks observed in the X-ray diffraction studies suggesting the extended periodicity of these columns in a two-dimensional hexagonal lattice. Theoretical band gaps, energy minimized structures were obtained from Gaussian, and optical band gaps were calculated from absorption studies. These self-assembled spontaneously aligned materials can be potential candidates for organic electronic devices.

#### **3.4. Experimental section**

#### **3.4.1. Reagents and Instruments**

Reagents and instruments used are the same as in Section 2.1.3.1

#### 3.4.2. Synthetic procedures and spectral data of compounds 6a and 6b

All the intermediates and final compounds are synthesized following literature procedures<sup>41,42,56</sup>. The synthetic process and spectral data of compounds **2** and **3** are given in **Section 2.1.3.2**.

**Compound 4:** To a solution of hexabutoxytriphenylene **3** (4g, 1 eq) in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>NO<sub>2</sub> (50ml /10ml), 1.20 ml of fuming HNO<sub>3</sub> was added dropwise and stirred at room temperature for 15 minutes followed by addition of saturated NaHCO<sub>3</sub> solution. The reaction mixture was then extracted using CH<sub>2</sub>Cl<sub>2</sub> and the organic layer was washed with brine. The solvents were evaporated and the crude product was subjected to column chromatography using silica gel and CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (50/50) to give compound **4** as yellow solid (55 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 7.55 (s, 3H), 4.25 (t, *J* = 6.5, 6H), 4.09 (t, *J* = 6.25, 6H), 1.84-1.90 (m, 6H), 1.73-1.78 (m, 6H), 1.55-1.59 (m, 8H), 1.46-1.50 (m, 4H), 1.02 (t, *J* = 7.5 Hz, 9H), 0.97 (t, *J* = 7.5 Hz, 9H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 151.96, 143.90, 141.54, 123.15,

114.40, 108.27, 75.15, 69.05, 32.04, 30.97, 19.34, 18.96, 13.80, 13.76. Elemental analysis: C, 63.38; H, 7.22; N, 5.28 (calcd.); C, 63.43; H, 7.01; N, 5.31 (expt.)

**Compound 5:** Raney Ni (20 eq) was added to the solution of compound **4** (2g, 1eq) in 50 ml THF: ethanol mixture (1:1). The reaction mixture was stirred at room temperature under hydrogen atmosphere. The reaction was monitored using TLC and the catalyst was removed by filtration after completion of the reaction. The solvent was evaporated under reduced pressure and purified by column chromatography using dichloromethane as eluent to give compound **5** as white solid (85 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.07 (s, 3H), 4.63 (broad peak, 6H), 4.10 – 4.13 (m, 12H), 1.81 – 1.89 (m, 12H), 1.53 – 1.61 (m, 12H), 0.99 – 1.03 (m, 18H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 150.02, 138.07, 134.19, 128.00, 114.07, 99.73, 72.62, 68.18, 32.58, 31.54, 19.46, 19.41, 14.01, 13.93. Elemental analysis: C, 71.46; H, 8.99; N, 5.95 (calcd.); C, 71.59; H, 8.816; N, 5.47 (expt.)

#### General synthesis of compounds 6

A mixture of triamine **5** (1eq) and aldehyde (6eq) is dissolved in dry DMF (10 ml) and added 1% triflic acid, stirred at 40 °C. The reaction was monitored for 12 hours using TLC to check the consumption of triamine. Once the reaction is completed, water is added and the reaction mixture was alkalized using a 15% NaOH solution and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent, the crude was subjected to column chromatography on silica gel using hexane/ethyl acetate (10/1) as eluent and recrystallized using methanol to get compound **6** as yellow solid (60 %).

**Compound 6a:** (0.500g, 0.709 mmol, 1eq), butyraldehyde (0.306g, 4.255 mmol, 6eq), DMF 10 ml, 1% triflic acid, yield: 62%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 4.71 (t, *J* = 6.5 Hz, 6H), 4.59 (t, *J* = 7 Hz, 6H), 4.13 (t, *J* = 7.5 Hz, 6H), 2.22-2.28 (m, 6H), 2.08-2.14 (m, 12H), 1.66-1.80 (m, 12H), 1.21-1.25 (m, 9H), 1.08-1.11 (m, 18H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 162.48, 150.03, 146.48, 139.56, 123.31, 116.68, 112.46, 75.32, 75.20, 42.65, 32.76, 29.68, 23.27, 19.51, 19.48, 14.55, 14.14, 14.07. Elemental analysis: C, 75.22; H, 8.77; N, 4.08 (calcd.); C, 75.92; H, 8.97; N, 4.01 (found).

**Compound 6b:** (0.500g, 0.709 mmol, 1eq), pentanal (0.363g, 4.255 mmol, 6eq), DMF 10 ml, 1% triflic acid, yield: 62%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 4.71 (t, *J* = 7 Hz, 6H), 4.59 (t, *J* = 7 Hz, 6H), 4.17 (t, *J* = 8 Hz, 6H), 2.20-2.26 (m, 6H), 2.07-2.15 (m, 12H), 1.71-1.80 (m, 6H), 1.63-1.69 (m, 12H), 1.08-1.11 (m, 27H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 162.69, 150.07, 146.45, 139.56, 123.31, 116.67, 112.44, 75.31, 75.23, 40.39, 32.79, 32.60, 32.21, 23.21, 19.55, 19.48, 14.38, 14.16, 14.13. Elemental analysis: C, 75.71; H, 9.03; N, 4.65 (calcd.); C, 75.33; H, 8.98; N, 4.69 (found).

#### 3.4.3. Synthetic procedures and spectral data of compounds 4a-d

**Compound 2-i**<sup>46</sup>: To a solution of 2,3-dichloronitrobenzene (10.0 g, 52.1mmol) in DMF (60 mL), copper powder (20.0 g, 312.5mmol) was added, and the reaction mixture was stirred at reflux for 12 hours under nitrogen atmosphere. After cooling to 120 °C, the hot solution was filtered and washed with DMF to remove the excess copper powder. The filtrate was then slowly poured into a diluted ammonium solution of 400 ml (containing conc. NH<sub>3</sub>·H<sub>2</sub>O 100 mL) with vigorous stirring. The black residue was washed with dilute ammonium solution and water. The residue was then dissolved in acetone (50 mL) and refluxed for 30 min. After cooling it to room temperature, the mixture was filtered to provide a yellow solid (55%), which was directly used for the next step. M.P. 307-309 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.15$  (d, J = 8 Hz, 3H), 7.93 (d, J = 7.5 Hz, 3H), 7.67 (t, J = 8 Hz, 3H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 149.45, 129.38, 128.20, 128.11, 125.22, 122.25. Elemental analysis: C, 59.51; H, 2.50; N, 11.57 (calcd.); C, 59.89; H, 2.78; N, 11.13 (expt.)

**Compound 3-i**: To a solution of **3** (2.00g, 5.50mmol) in ethyl acetate/ethanol (100ml/10ml) was added Pd/C (0.4g, 10 % w/w) under N<sub>2</sub> atmosphere. The reaction mixture was purged with H<sub>2</sub> a few times, stirred at H<sub>2</sub> atmosphere, and monitored using TLC. After completion of the reaction, the mixture was filtered and washed with ethyl acetate and concentrated under reduced pressure to yield **4** as yellow solid in quantitative amount. <sup>1</sup>H NMR (500 MHz, DMSO-d6):  $\delta = 8.18$  (d, J = 8 Hz, 3H), 7.4 (t, J = 8 Hz, 3H), 6.85 (d, J = 7 Hz, 3H), 5.30 (s, 6H). <sup>13</sup>CNMR (500 MHz, DMSO-d6),  $\delta$  (ppm) = 146.13, 132.36, 126.58, 118.24, 114.96, 113.97. Elemental analysis: C, 79.10; H, 5.53; N, 15.37 (calcd.); C, 79.49; H, 5.64; N, 15.21 (expt.)

#### The general synthetic procedure of alkoxybenzaldehydes

3,4-dihydroxybenzaldehyde (1 eq), anhydrous. K<sub>2</sub>CO<sub>3</sub> (4 eq)and corresponding n-alkyl bromide (4 eq) were mixed in dry DMF (50 mL) and reacted at 85 °C overnight under an inert atmosphere. After cooling to room temperature, the reaction mixture was poured into water, extracted using dichloromethane, and washed with brine. The combined organic layer was evaporated and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification by column chromatography in silica gel and PE/DCM gave the desired product 3,4-dialkoxybenzaldehyde<sup>57</sup>. 3,4,5-trialkoxybenzaldehydes were synthesized following the literature procedure and the spectral data are consistent with the previous reports<sup>59</sup>.

**3,4-bis(dodecyloxy)benzaldehyde:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 9.82 (s, 1H), 7.41 (s, 1H), 7.39 (d, *J* = 1.5 Hz 3H), 6.94 (d, *J* = 8 Hz, 1H), 4.06 (m, 4H), 1.84 (m, 4H), 1.47 (m, 4H), 1.26 (m, 32H), 0.88 (t, 6H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 190.96, 154.68, 149.45, 129.88, 126.58, 111.75, 110.96, 69.13, 69.11, 31.93, 29.7, 29.67, 29.62, 29.61, 29.37, 29.08, 28.99, 26.00, 25.96, 22.69, 14.11. Elemental analysis: C, 78.43; H, 11.46; (calcd.); C, 78.85; H, 11.76; (found.).

**3,4,5-tris(dodecyloxy)benzaldehyde:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 9.85 (s, 1H), 7.10 (s, 2H), 4.06 (m, 6H), 1.84 (m, 4H), 1.77 (m, 2H), 1.49 (m, 6H), 1.28 (m, 48H), 0.90 (t, 9H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 191.27, 153.53, 143.91, 131.45, 107.9, 73.64, 69.27, 31.92, 30.35, 29.74, 29.71, 29.69, 29.65, 29.62, 29.54, 29.38, 29.36, 29.26, 26.07, 26.03, 22.69, 14.10. Elemental analysis: C, 78.36; H, 11.93; (calcd.); C, 78.67; H, 12.01; (found.).

**3,4-bis(hexadecyloxy)benzaldehyde:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 9.82 (s, 1H), 7.42 (d, *J* = 2 Hz, 1H), 7.40 (m, 1H), 6.94 (d, *J* = 8 Hz, 1H), 4.06 (m, 4H), 1.85 (m, 4H), 1.47 (m, 4H), 1.25 (m, 48H), 0.87 (t, *J* = 7 Hz, 6H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 191.01, 154.7, 149.46, 129.88, 126.58, 111.78, 111.01, 69.16, 69.13, 68.04, 31.93, 29.67, 29.63, 29.56, 29.49, 29.37, 29.23, 29.08, 28.99, 28.69, 26.00, 25.95, 25.71, 22.69, 14.11. Elemental analysis: C, 79.80; H, 12.02; (calcd.); C, 79.58; H, 11.89; (found.).

**3,4,5-tris(hexadecyloxy)benzaldehyde:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 9.85 (s, 1H), 7.10 (s, 2H), 4.06 (m, 6H), 1.84 (m, 4H), 1.77 (m, 2H), 1.49 (m, 6H), 1.28 (m, 72H), 0.90 (t, 9H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 191.23, 153.54, 143.92, 131.46, 107.9, 73.63, 69.26,

31.93, 30.35, 29.72, 29.67, 29.63, 29.55, 29.37, 29.27, 26.08, 26.04, 22.69, 14.10. Elemental analysis: C, 79.84; H, 12.43; (calcd.); C, 79.95; H, 12.62; (found.).

#### The general synthetic procedure of compounds 4a-d

A mixture of triamine **3-i** (1eq) and alkoxybenzaldehyde (6eq) is dissolved in dry DMF (10ml) and added 1% triflic acid and heated to 120 °C. The reaction was monitored for 12 hours using TLC to check the consumption of **3-i**. After completion of the reaction, water was added, and the reaction mixture was alkalized using a 15% NaOH solution and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent, the crude was subjected to column chromatography on silica gel using hexane/ethyl acetate (10/1) as eluent and recrystallized using methanol to get compound **4** as yellow solid.

**Compound 4a:** (0.100g, 0.365mmol, 1eq), 3,4-bis(dodecyloxy)benzaldehyde (1.037g, 2.195 mmol, 6eq), DMF 10 ml, 1% triflic acid, yield: 56%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 9.05-9.07 (d, J = 9.0 Hz, 3H), 8.87-8.89 (d, J = 9.0 Hz, 3H), 7.80 (s, 3H), 7.73-7.75 (d, J = 9.5 Hz, 3H), 7.26 (s, 3H), 4.22-4.26 (q, J = 7.0 Hz, 12H), 1.91-2.00 (m, 12H), 1.51-1.65 (m, 12H), 1.22-1.47 (m, 96H), 0.88-0.91 (t, J = 7.0 Hz, 9H), 0.82-0.85 (t, J = 7.0 Hz, 9H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 161.02, 150.39, 149.57, 143.21, 132.24, 128.37, 127.71, 124.90, 124.16, 119.68, 116.51, 113.63, 113.53, 69.61, 69.53, 31.98, 31.92, 29.80, 29.78, 29.75, 29.71, 29.69, 29.58, 29.51, 29.43, 29.38, 26.24, 26.20, 22.74, 22.68, 14.16, 14.10. Elemental analysis: C, 81.42; H, 10.16; N, 2.57 (calcd.); C, 81.14; H, 10.28; N, 2.43 (found.).

**Compound 4b:** (0.100g, 0.365mmol, 1eq), 3,4,5-tris(dodecyloxy)benzaldehyde (1.446g, 2.195 mmol, 6eq), DMF 10 ml, 1% triflic acid, yield: 58%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 9.29 (s, 3H), 9.14 (s, 3H), 7.36 (s, 6H), 4.15-4.19 (m, 18H), 1.86-1.92 (m, 18H), 1.49-1.57 (m, 18H), 1.23-1.42 (m, 144H), 0.87-0.90 (t, *J* = 7 Hz, 9H), 0.83-0.86 (t, *J* = 7.0 Hz, 18H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 161.96, 153.50, 143.90, 139.55, 134.51, 128.79, 128.37, 125.87, 120.51, 114.67, 109.74, 73.75, 69.52, 31.98, 31.91, 30.50, 29.86, 29.83, 29.76, 29.74, 29.72, 29.69, 29.67, 29.54, 29.49, 29.45, 29.36, 26.26, 26.21, 22.73, 22.68, 14.15, 14.10. Elemental analysis: C, 80.60; H, 10.91; N, 1.92 (calcd.); C, 80.33; H, 10.68; N, 1.89 (expt.).

**Compound 4c:** (0.100g, 0.365mmol, 1eq), 3,4-bis(hexadecyloxy)benzaldehyde (1.288g, 2.195 mmol, 6eq), DMF 10 ml, 1% triflic acid, yield: 51%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 9.07 (s, 3H), 8.94 (s, 3H), 7.72 (s, 3H), 7.66-7.68 (d, *J* = 8.0 Hz, 3H), 7.18 (s, 3H), 4.14-4.18 (q, 12H), 1.83-1.92 (m, 12H), 1.44-1.59 (m, 12H), 1.34-1.37 (m, 24H), 1.14-1.21 (m, 120H), 0.76-0.81 (m, 18H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 161.27, 150.45, 149.60, 143.53, 139.28, 132.38, 128.52, 127.93, 125.34, 124.15, 119.99, 116.52, 114.07, 113.98, 113.70, 69.62, 69.54, 33.83, 31.63, 29.79, 29.77, 29.71, 29.66, 29.57, 29.56, 29.49, 29.40, 29.36, 26.21, 26.18, 22.71, 22.68, 14.13, 14.11. Elemental analysis: C, 86.33; H, 11.43; N, 2.24 (calcd.); C, 86.07; H, 11.49; N, 2.32 (expt.).

**Compound 4d:** (0.100g, 0.365mmol, 1eq), 3,4,5-tris(dodecyloxy)benzaldehyde (1.822g, 2.195 mmol, 6eq), DMF 10 ml, 1% triflic acid, yield: 59%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 9.39 (s, 3H), 9.23-9.25 (d, 3H), 7.40 (s, 6H), 4.20-4.21 (m, 18H), 1.88-1.94 (m, 18H), 1.58-1.62 (m, 18H), 1.52-1.56 (m, 18H), 1.25-1.40 (m, 198H), 0.86-0.91 (m, 27H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 161.74, 153.49, 143.59, 139.52, 139.26, 134.50, 128.65, 128.15, 125.43, 124.82, 120.21, 114.23, 114.07, 109.77, 73.76, 69.54, 33.83, 32.25, 31.96, 31.93, 31.64, 31.44, 30.54, 30.04, 29.90, 29.87, 29.84, 29.83, 29.80, 29.78, 29.72, 29.67, 29.59, 29.54, 29.42, 29.37, 29.17, 28.96, 26.30, 26.27, 22.72, 22.69, 14.43, 14.13, 14.11. Elemental analysis: C, 86.15; H, 12.21; N, 1.65 (calcd.); C, 85.98; H, 12.25; N, 1.74 (expt.).

### 3.5. <sup>1</sup>H and <sup>13</sup>C NMR spectra



Figure 3.17 <sup>1</sup>H (top) and <sup>13</sup>C NMR (bottom) spectra of compound 4



Figure 3.18  $^{1}$ H (top) and  $^{13}$ C-NMR (bottom) spectra of compound 5



Figure 3.19 <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 6a



Figure 3.20  $^{1}$ H (top) and  $^{13}$ C-NMR (bottom) spectra of compound 6b



Figure 3.21 <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 2-i


Figure 3.22 <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 3-i



Figure 3.23 <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 3,4bis(dodecyloxy)benzaldehyde



Figure 3.24 <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 3,4,5tris(dodecyloxy)benzaldehyde



Figure 3.25 <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 3,4bis(hexadecyloxy)benzaldehyde



Figure 3.26 <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 3,4,5tris(hexadecyloxy)benzaldehyde



Figure 3.27 <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 4a



Figure 3.28 <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 4b



Figure 3.29  $^{1}$ H (top) and  $^{13}$ C-NMR (bottom) spectra of compound 4c



Figure 3.30 <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 4d

# **3.6. References**

- 1. Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nature Materials* 6, 183–191 (2007).
- Baldridge, K. K. & Siegel, J. S. Of graphs and graphenes: Molecular design and chemical studies of aromatic compounds. *Angewandte Chemie - International Edition* (2013) doi:10.1002/anie.201300625.
- Stępień, M., Gońka, E., Żyła, M. & Sprutta, N. Heterocyclic Nanographenes and Other Polycyclic Heteroaromatic Compounds: Synthetic Routes, Properties, and Applications. *Chemical Reviews* 117, 3479–3716 (2017).
- 4. Narita, A., Wang, X. Y., Feng, X. & Müllen, K. New advances in nanographene chemistry. *Chemical Society Reviews* (2015) doi:10.1039/c5cs00183h.
- Wu, J., Pisula, W. & Müllen, K. Graphenes as Potential Material for Electronics. *Chemical Reviews* 107, 718–747 (2007).
- 6. Zhang, Q. *et al.* Facile bottom-up synthesis of coronene-based 3-fold symmetrical and highly substituted nanographenes from simple aromatics. *Journal of the American Chemical Society* (2014) doi:10.1021/ja413018f.
- Kumar, S. Chemistry of Discotic Liquid Crystals. Chemistry of Discotic Liquid Crystals (CRC Press, 2016). doi:10.1201/b10457.
- Kumar, S. Self-organization of disc-like molecules: chemical aspects. *Chem. Soc. Rev.* 35, 83–109 (2006).
- 9. Wöhrle, T. *et al.* Discotic Liquid Crystals. *Chemical Reviews* (2016) doi:10.1021/acs.chemrev.5b00190.
- Rohr, U. *et al.* Liquid crystalline coronene derivatives with extraordinary fluorescence properties. *Angewandte Chemie - International Edition* (1998) doi:10.1002/(SICI)1521-3773(19980605)37:10<1434::AID-ANIE1434>3.0.CO;2-P.
- Rohr, U., Kohl, C., Müllen, K., van de Craats, A. & Warman, J. Liquid crystalline coronene derivatives. *Journal of Materials Chemistry* 11, 1789–1799 (2001).

- Herwig, P., Kayser, C. W., Müllen, K. & Spiess, H. W. Columnar mesophases of alkylated hexa-peri-hexabenzocoronenes with remarkably large phase widths. *Advanced Materials* (1996) doi:10.1002/adma.19960080613.
- Watson, M. D., Debije, M. G., Warman, J. M. & Müllen, K. Peralkylated Coronenes via Regiospecific Hydrogenation of Hexa-peri-hexabenzocoronenes. *Journal of the American Chemical Society* 126, 766–771 (2004).
- Fechtenkötter, A., Tchebotareva, N., Watson, M. & Müllen, K. Discotic liquid crystalline hexabenzocoronenes carrying chiral and racemic branched alkyl chains: supramolecular engineering and improved synthetic methods. *Tetrahedron* 57, 3769–3783 (2001).
- Lemaur, V. *et al.* Charge Transport Properties in Discotic Liquid Crystals: A Quantum-Chemical Insight into Structure-Property Relationships. *Journal of the American Chemical Society* (2004) doi:10.1021/ja0390956.
- 16. Feng, X. *et al.* Towards high charge-carrier mobilities by rational design of the shape and periphery of discotics. *Nature Materials* **8**, 421–426 (2009).
- Van De Craats, A. M. & Warman, J. M. Core-size effect on the mobility of charge in discotic liquid crystalline materials. *Advanced Materials* (2001) doi:10.1002/1521-4095(200101)13:2<130::AID-ADMA130>3.0.CO;2-L.
- Boden, N., Bushby, R. J., Cooke, G., Lozman, O. R. & Lu, Z. CPI: A recipe for improving applicable properties of discotic liquid crystals. *Journal of the American Chemical Society* (2001) doi:10.1021/ja003443b.
- Adam, D. *et al.* Fast photoconduction in the highly ordered columnar phase of a discotic liquid crystal. *Nature* 371, 141–143 (1994).
- Pal, S. K., Setia, S., Avinash, B. S. & Kumar, S. Triphenylene-based discotic liquid crystals: recent advances. *Liquid Crystals* (2013) doi:10.1080/02678292.2013.854418.
- Boden, N., Borner, R. C., Bushby, R. J., Cammidge, A. N. & Jesudason, M. V. The synthesis of triphenylene-based discotic mesogens New and improved routes. *Liquid Crystals* 15, 851–858 (1993).

- Gupta, R. K. & Sudhakar, A. A. Perylene-Based Liquid Crystals as Materials for Organic Electronics Applications. *Langmuir* (2019) doi:10.1021/acs.langmuir.8b01081.
- Van De Craats, A. M. *et al.* The mobility of carriers in all four phases of the columnar discotic material hexakis(hexylthio)triphenylene: Combined tof and PR-TRMC results. *Advanced Materials* (1996) doi:10.1002/adma.19960081012.
- 24. Iino, H. *et al.* Very high time-of-flight mobility in the columnar phases of a discotic liquid crystal. *Applied Physics Letters* (2005) doi:10.1063/1.2056608.
- Cook, M. J. 1,4,8,11,15,18,22,25-octasubstituted phthalocyanines: the contrasting effects of alkyl and alkoxy substituents on molecular self-assembly. *Journal of Materials Science: Materials in Electronics* 5, (1940).
- Ahmida, M. M. & Eichhorn, S. H. Measurements and Prediction of Electronic Properties of Discotic Liquid Crystalline Triphenylenes and Phthalocyanines. *ECS Transactions* (2019) doi:10.1149/1.3314449.
- 27. Ohta, K. *et al.* Discotic liquid crystalline semiconductors. in *Molecular Crystals and Liquid Crystals* (2003). doi:10.1080/714965592.
- Fechtenkötter, A., Saalwächter, K., Harbison, M. A., Müllen, K. & Spiess, H. W. Highly ordered columnar structures from Hexa-peri-hexabenzocoronenes- synthesis, X-ray diffraction, and solid-state heteronuclear multiple-quantum NMR investigations. *Angewandte Chemie - International Edition* (1999) doi:10.1002/(SICI)1521-3773(19991018)38:20<3039::AID-ANIE3039>3.0.CO;2-5.
- Pieterse, K. *et al.* An electron-deficient discotic liquid-crystalline material. *Chemistry of Materials* (2001) doi:10.1021/cm010181j.
- Segura, J. L., Juárez, R., Ramos, M. & Seoane, C. Hexaazatriphenylene (HAT) derivatives: from synthesis to molecular design, self-organization and device applications. *Chemical Society Reviews* 44, 6850–6885 (2015).
- Bock, H., Babeau, A., Seguy, I., Jolinat, P. & Destruel, P. Electron-Deficient Columnar Plastic Crystals. *ChemPhysChem* 3, 532 (2002).

- 32. Fogel, Y. *et al.* Electron-Deficient N-Heteroaromatic Linkers for the Elaboration of Large, Soluble Polycyclic Aromatic Hydrocarbons and Their Use in the Synthesis of Some Very Large Transition Metal Complexes. *Journal of the American Chemical Society* 129, 11743– 11749 (2007).
- Bisoyi, H. K. & Kumar, S. Discotic nematic liquid crystals: Science and technology. Chemical Society Reviews (2010) doi:10.1039/b901792p.
- Lehmann, M. *et al.* High Charge-Carrier Mobility in π-Deficient Discotic Mesogens: Design and Structure-Property Relationship. *Chemistry - A European Journal* 11, 3349– 3362 (2005).
- 35. Kestemont, G. *et al.* Discotic mesogens with potential electron carrier properties. *Chemical Communications* (2001) doi:10.1039/b107135c.
- Imamura, K., Takimiya, K., Aso, Y. & Otsubo, T. Triphenyleno[1,12-bcd:4,5-b'c'd':8,9-b'c'd']trithiophene: The first bowl-shaped heteroaromatic. *Chemical Communications* (1999) doi:10.1039/a905860e.
- Furukawa, S., Kobayashi, J. & Kawashima, T. Development of a sila-Friedel-Crafts reaction and its application to the synthesis of dibenzosilole derivatives. *Journal of the American Chemical Society* (2009) doi:10.1021/ja906566r.
- Jiang, W., Qian, H., Li, Y. & Wang, Z. Heteroatom-annulated perylenes: Practical synthesis, photophysical properties, and solid-state packing arrangement. *Journal of Organic Chemistry* (2008) doi:10.1021/jo8012622.
- Jiang, W., Li, Y. & Wang, Z. Heteroarenes as high performance organic semiconductors. *Chemical Society Reviews* (2013) doi:10.1039/c3cs60108k.
- He, B. *et al.* A divergent route to core- and peripherally functionalized diazacoronenes that act as colorimetric and fluorescence proton sensors. *Chemical Science* (2015) doi:10.1039/c5sc00304k.

- Wei, J. *et al.* 1,5,9-triazacoronenes: A family of polycyclic heteroarenes synthesized by a threefold pictet-spengler reaction. *Angewandte Chemie International Edition* 49, 8209–8213 (2010).
- Tan, Q., Chen, H., Xia, H., Liu, B. & Xu, B. Parent and trisubstituted triazacoronenes: Synthesis, crystal structure and physicochemical properties. *Chemical Communications* (2016) doi:10.1039/c5cc08853d.
- Liu, B. *et al.* Triazacoronene Derivatives with Three peri -Benzopyrano Extensions: Synthesis, Structure, and Properties. *European Journal of Organic Chemistry* 2018, 869– 873 (2018).
- Zhang, Y. *et al.* N-type organic semiconductor bisazacoronene diimides efficiently synthesized by a new type of photocyclization involving a Schiff base. *RSC Advances* (2012) doi:10.1039/c2ra22488g.
- 45. Li, Y. *et al.* Synthesis, characterization, and self-assembly of nitrogen-containing heterocoronenetetracarboxylic acid diimide analogues: Photocyclization of N-heterocyclesubstituted perylene bisimides. *Chemistry - A European Journal* (2006) doi:10.1002/chem.200600605.
- Tan, Q., Chen, H., Xia, H., Liu, B. & Xu, B. Parent and trisubstituted triazacoronenes: synthesis, crystal structure and physicochemical properties. *Chem. Commun.* 52, 537–540 (2016).
- He, B. *et al.* Thiophene fused azacoronenes: Regioselective synthesis, self-organization, charge transport and its incorporation in conjugated polymers. *Chemistry of Materials* (2014) doi:10.1021/cm5018272.
- Tokita, S., Hiruta, K., Kitahara, K. & Nishi, H. Diels-Alder Reaction of Dialkyl Diazenedicarboxylates with Perylenes; A New Synthesis of Polycyclic Aromatic Pyridazines. Synthesis 1982, 229–231 (1982).
- 49. Schlichting, P., Rohr, U. & Müllen, K. New synthetic routes to alkyl-substituted and functionalized perylenes. *Liebigs Annales* (1997) doi:10.1002/jlac.199719970218.

- 50. Schlichting, P., Rohr, U. & Müllen, K. Easy synthesis of liquid crystalline perylene derivatives. *Journal of Materials Chemistry* (1998) doi:10.1039/a804332i.
- Göltner, C., Pressner, D., Müllen, K. & Spiess, H. W. Liquid-Crystalline Perylene Derivatives as "Discotic Pigments." *Angewandte Chemie International Edition in English* 32, 1660–1662 (1993).
- Pressner, D., Gültner, Chr., Spie
  ß, H. W. & Müllen, K. Liquid Crystalline Perylene Derivatives: Orientation and Phase Variation of Discotic Dyes. *Berichte der Bunsengesellschaft für physikalische Chemie* (1993) doi:10.1002/bbpc.19930971030.
- Müller, G. R. J., Meiners, C., Enkelmann, V., Geerts, Y. & Müllen, K. Liquid crystalline perylene-3,4-dicarboximide derivatives with high thermal and photochemical stability. *Journal of Materials Chemistry* (1998) doi:10.1039/a705910h.
- 54. Chen, L. et al. Hexathienocoronenes: Synthesis and Self-Organization. Journal of the American Chemical Society 134, 17869–17872 (2012).
- 55. Takase, M. *et al.* Pyrrole-fused azacoronene family: The influence of replacement with dialkoxybenzenes on the optical and electronic properties in neutral and oxidized states. *Journal of the American Chemical Society* (2013) doi:10.1021/ja402371f.
- Kumar, S., Manickam, M., Balagurusamy, V. S. K. & Schonherr, H. Electrophilic aromatic substitution in triphenylene discotics: Synthesis of alkoxynitrotriphenylenes. *Liquid Crystals* 26, 1455–1466 (1999).
- 57. Zhang, Q. *et al.* Facile bottom-up synthesis of coronene-based 3-fold symmetrical and highly substituted nanographenes from simple aromatics. *Journal of the American Chemical Society* (2014) doi:10.1021/ja413018f.
- Thomas, M. Surfactant Polyelectrolyte complexes: Structure and Interactions. (Jawaharlal Nehru University, 2019).
- Veerabhadraswamy, B. N., Dambal, H. K., Rao, D. S. S. & Yelamaggad, C. V. s-Triazine-Based Functional Discotic Liquid Crystals: Synthesis, Mesomorphism and Photoluminescence. *ChemPhysChem* 17, 2225–2237 (2016).

# **Chapter 4**

# Synthesis and Characterization of Novel Chromenonaphthophenanthridine DLCs



This chapter discusses the synthesis of novel  $\pi$ -extended chromenonaphthophenanthridine discotic liquid crystals through tandem Pictet-Spengler cyclization and ipso-aromatic substitution in one pot. The compounds are characterized by spectral and elemental analysis, and their structural and mesomorphic behavior were investigated. These molecules exhibited enantiotropic columnar mesophase over a wide temperature range and remained stable till room temperature on cooling. X-ray diffraction analysis of these derivatives indicated the hexagonal ordering of the columns, and a more ordered plastic columnar phase was found in the derivative with a shorter alkyl chain around the core. Compounds showed high thermal stability beyond the mesomorphic range, and photophysical studies suggested a blue emission around 470 nm.

# **4.1. Introduction**

Extended polycyclic heteroaromatic molecules, otherwise known as heterocyclic nanographene, are fascinating materials for applications in organic electronics as functional chromophores and organic semiconductors<sup>1</sup>. Extending the ring structure and replacing the carbon atoms with other heteroatoms at selected positions is a versatile strategy to fine-tune the electronic, self-assembly, and charge carrier properties of polycyclic aromatic hydrocarbons (PAHs)<sup>2,3</sup>. Incorporating several main group elements into these fused  $\pi$  conjugated systems enhances the optoelectronic behavior while maintaining structural similarities. Most reported heteroaromatic  $\pi$ conjugated systems contain five to six-membered nitrogen or sulfur incorporated aromatic rings. A substantial amount of effort has been directed towards synthesizing larger heteroaromatics containing boron, phosphorous, and chalcogens<sup>4-6</sup>. However, oxygen-containing heterocycles are less explored in comparison, and most of the reported molecules are five-membered furan fused heterocycles such as tetraoxa[8]circulene (1)<sup>7,8</sup>, benzofurans (2 & 3) (Figure 4.1)<sup>9,10</sup>. Nitrogen incorporated structural analogues of tetraoxa[8]circulenes, known as azatrioxa[8]circulene (4) and diazadioxooxa[8]circulene (5) derivatives were synthesized from dihydroxycarbazoles. Photophysical properties of these heterocyclic circulenes were compared and realized that replacing one or two oxygen with nitrogen atoms improves the quantum yield and is better suited for blue OLED applications<sup>11,12</sup>. Substituted tetraoxa[8]circulene derivatives (6) have been synthesized by acid-catalyzed tetramerization of dialkylbenzoquinones and reported to exhibit columnar mesomorphism for the first time<sup>13</sup>.

However, the six-membered oxygen-containing pyran-based heterocycles are limited due to their restricted reaction pathways to form a pyran ring as the critical step. Benzodixanthane and anthradichromene analogues (7) containing sulfur and nitrogen atoms instead of oxygen were synthesized from anthraquinone derivatives<sup>14</sup>. Photophysical studies of these compounds revealed a red-shifted absorption for derivatives containing nitrogen compared to the oxygen and sulfur analogue. Oxygen-doped aromatics such as peri-xanthenoxanthene (8) are characterized for charge-transport properties, easy processability, and high thermal stability<sup>15–17</sup>.  $\pi$  -extended larger O-doped nanographenes (9) have been achieved from a key ring closer strategy of intramolecular C-O bond formation favoring stepwise planarization and remarkable columnar  $\pi$ - $\pi$  stacking<sup>18</sup>.



1













Figure 4.1. Oxygen-doped polycyclic aromatic hydrocarbons and nanographenes.

# 4. Synthesis and Characterization of Novel Chromenonaphthophenanthridine DLCs

Furanyl and pyranopyranyl fused extended PAHs were synthesized using acid catalyzed and oxidative Cu-catalyzed planarization reactions, respectively<sup>19</sup>. Photophysical and electrochemical characterization showed that the complementary absorption and redox properties can be tailored through fine-tuning of ring extension and the type of oxygen linkage (furanyl or Pyranopyranyl). Dialkoxyphenyl substituted dicyanotetraoxapentacene derivatives (**10**) (**Figure 4.2**) exhibited columnar hexagonal mesophases and displayed enhanced emission properties in solution and thin films<sup>20</sup>. Heteroatoms incorporated pentacene derivatives (**11**) were synthesized from nucleophilic aromatic substitution reaction<sup>21</sup>. X-ray crystallography revealed that the oxygen and nitrogen-containing derivatives are highly planar and exhibit effective  $\pi$  -stacking than sulfur compounds.

Several derivatives of the oxygen and nitrogen-bridged azadioxatriangulene and its cationic derivatives were synthesized, and their physicochemical properties were investigated<sup>22</sup>. Benzofuran and benzopyran fused fluorescent dyes based on symmetric polycyclicphenazines (**12** & **13**) were synthesized and characterized for their absorption and emission properties. The benzopyran-linked derivatives have red-shifted absorption and larger stokes shift compared to the furan-based phenazines<sup>23,24</sup>. Several benzopyranoacridine derivatives (**14**) that possess a fused ring system containing xanthene skeleton were synthesized by cyclization of xanthone intermediates<sup>25</sup>. In addition, the effect of chalcogen atoms in the electronic property of naphthodiazole based polymers (**15**) has been studied. It is found that the oxygen incorporated naphthobisoxadiazole has deeper frontier orbital energy levels compared to the other chalcogen atoms like sulfur and selenium, which allows ambient ambipolar charge transport behavior in transistor devices<sup>26</sup>.

Benzopyran derivatives, commonly known as chromenes, are an important class of heterocycles found in many natural products. Recently there have been many reports on the synthesis of chromene derivatives that displayed remarkable pharmacological and biological properties<sup>27,28</sup>. The condensation reaction of structurally diverse salicylaldehydes and molecules with active methylene groups such as malononitrile followed by intramolecular substitution resulted in various chromene and azachromene derivatives **16** (Figure 4.3)<sup>29,30</sup>. In addition, chromenopyridine based molecules having potential biological activities such as cancer chemopreventive, antibacterial, antihistamic etc., were developed through an efficient one-pot synthesis<sup>31</sup>. Facile and highly efficient synthesis of chromenopyridinone derivatives was achieved

by piperidine mediated [3+3] cyclization involving intramolecular nucleophilic additionaromatization sequence<sup>32</sup>. Synthesis of some chromenonaphthyridine (17) derivatives using a onepot multicomponent reaction was reported and found to show high corrosion inhibition efficiency and antimicrobial activity<sup>33,34</sup>. Polycyclic fused phenanthridine derivatives and chromenophenanthridine derivatives (18) were successfully synthesized from benzotriazole moiety followed by ring closure in multistep reaction pathway under mild reaction conditions<sup>35</sup>.













12

Figure 4.2. Heteroatom incorporated pentacene, phenazine, benzopyran derivatives.



Figure 4.3. Some biologically active azachromene derivatives.

Thermotropic liquid crystals were derived from simple etherification or esterification of natural products such as ellagic acid, flavellagic acid, or coruleoellagic acid knowns as chromenochromene-diones, with appropriate long alkyl chains. A homologous series of benzotrisfuran based disc-shaped molecules with various peripheral substitutions was reported from the condensation of phloroglucinol with benzoin and subsequent esterification<sup>36</sup>. The shorter alkyl chain esters were found to show ordered columnar mesophase over the longer chains. Several attempts have been made to lower the LUMO frontier molecular orbital level, a necessary criterion for better electron transport performance by replacing the carbon with heteroatoms such as nitrogen and oxygen in the ring system<sup>37,38</sup>. Soluble and air-stable n-type diazadioxaacenes (**19**) (**Figure 4.4**) and triphenodioxaazines (**20**) were synthesized, and their photophysical, electronic, and charge transport properties were analysed<sup>39–41</sup>. The electron mobility of triphenodioxaazines derivatives is two orders of magnitude higher than that of all carbon pentacene congeners.



Figure 4.4. Structures of some nitrogen and oxygen-containing acenes, triazacoronenes, and chromenopentaazacoronenes.

Wei et al. have successfully synthesized benzopyran fused triazacoronenes (21) through tandem Pictet-Spengler cyclization and  $K_2CO_3$  catalyzed ipso-aromatic substitution in one pot<sup>42</sup>.

The core enlarged aromatic molecules have the phenyl rings knitted with them, which favors the self-assembling properties that could lead to improved charge transport properties and broad liquid crystalline phases. They have also reported the synthesis of chromenopentaazacoronenes (22) by incorporating two diazine and one imine groups in the bay region of methoxy substituted triphenylene-1,5,9-triamine<sup>43</sup>. These molecules exhibited enhanced packing and red-shifted emission due to the extension of the  $\pi$  system that prompted us to explore the liquid crystallinity of these molecules. In addition, Mastalerz et al. have synthesized several  $\pi$  extended benzopyran fused nitrogen-containing PAHs (23 & 24) following the similar strategy of Pictet-Spengler cyclization and thermally induced ipso-aromatic substitution<sup>44</sup>. The resulted molecules have extended delocalization due to planarization of phenyl groups during C-O bond formation, thus favoring a tight  $\pi - \pi$  stacking.

In the N-annulated triphenylene and triazacoronene derivatives discussed in the previous chapters, the phenyl rings present in the periphery have a torsional angle with the  $\pi$  -planes, which is evident from the energy minimized structures. This out of plane phenyl rings could hinder the  $\pi$  -delocalization and adequate molecular packing in crystal and liquid crystalline states. There have been many strategies to planarize the molecule, among which the effective way is to connect the phenyl ring with the central core through a chalcogen like oxygen or sulfur<sup>45,46</sup>. We have employed a similar approach by planarizing the phenyl ring of naphthophenanthridine moiety through oxygen linkage and synthesized chromenonaphthophenanthridine derivatives from various hexaalkoxytriphenylene-amines and studied their structure-property relationship. The final compounds have one less alkoxy chain due to the intramolecular substitution reaction; hence we used monoamine instead of triphenylene triamine, which would eventually be remained with just three alkoxy chains around the core. Here, we report the synthesis and characterization of a series of novel chromenonaphthophenanthridine based DLCs.

# 4.2. Results and discussion

# 4.2.1. Synthesis



Scheme. 4.1 Synthesis of chromenonaphthophenanthridine derivatives 6a-6d.

The synthetic strategy of the targeted compounds follows the scheme given in **Scheme 4.1**. Compounds **2-5** were synthesized following the literature procedure and well-characterized for their purity using elemental and spectral analysis before the final step<sup>47,48</sup>. Compounds **6a-6d** were prepared using a modified reaction condition reported previously<sup>49</sup>.  $\pi$ -extended naphthophenathridines **6** were synthesized through triflic acid-catalyzed tandem Pictet-Spengler cyclization followed by ipso-aromatic substitution in one pot. All the final compounds were characterized for their purity, thermal stability, and structural confirmation was carried out using a combination of spectral and elemental analysis. The synthetic methods and representative spectra are given in section **2.3.1.2** (intermediates **2-5**) and in section **4.4.2** (final compounds **6a-d**).

# 4.2.2. Mesophase characterization

The liquid crystalline behavior of all the compounds was analyzed using a combination of polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction studies. The samples were placed between untreated glass substrates and examined under crossed polarizer in POM to determine the mesophase type and transition temperature. All the compounds show liquid crystallinity having both fluidity and birefringence, and the photomicrographs taken while cooling from the isotropic liquid phase under crossed polarizer are given in Figure 4.5. Compound 6a on cooling from the isotropic phase at 250 °C started to form a circular domain followed by a dark dendritic texture with hexagonal symmetry, which is characteristic of homeotropically aligned columns in-between the glass. This texture remained stable up to 160 °C before it changed into a mosaic-like texture with rectilinear defects on the homeotropic region, suggesting a columnar phase with higher order<sup>50–52</sup>. These phase transitions were further validated using DSC. The DSC thermograms of all the compounds are shown in Figure 4.6, and corresponding enthalpy changes associated with the phase transition are given in Table 4.1. DSC traces of 6a obtained at the rate of 10 °C min<sup>-1</sup> display three endothermic peaks on heating at 80, 160, and 252 °C, and two exothermic peaks on the cooling cycle. The first transition at 80 °C with a high enthalpy value is associated with the crystal to a highly ordered columnar phase. At 160 °C, 6a enters into another mesophase type and clears to the isotropic liquid at 252 °C. In the cooling cycle, 6a exhibits two peaks at 249 and 157 °C suggesting two different columnar mesophases, and the crystallization was not observed. The remaining compounds were also enantiotropic, showing only one columnar mesomorphism in both the heating and cooling

# 4. Synthesis and Characterization of Novel Chromenonaphthophenanthridine DLCs

cycle. Compound **6b** upon cooling from isotropic liquid forms dendritic-like fingerprint textures of columnar mesophase at 200°C that stays stable well below the room temperature as evident from the DSC thermogram (**Figure 4.6**). Compounds **6c** and **6d** show similar microscopic behavior, exhibiting homeotropic mosaic-like textures with rectilinear defects suggesting an ordered columnar phase. As expected, the increasing alkoxy chain length around the core significantly decreases the phase transition temperatures hence reducing the mesophase range.



Figure 4.5. POM images of compounds 6a-6d on cooling from the isotropic phase. a) dendritic textures with homeotropically aligned domains of 6a at 250°C, b) dendritic texture of 6b at 200°C, c) & d) mosaic textures of 6c at 115°C and 6d at 125°C.



Figure 4.6. DSC thermograms of compounds 6a-6d.

Table 4.1. Phase transition temperatures in °C and enthalpy values in (kJ/mol).

Compour	nd Heating	Cooling
6a	Cr 80 (20.7) Col <sub>hp</sub> 160 (6.5)	Iso 249 (6.5) Col <sub>h</sub> 157(6.4) Col <sub>hp</sub>
	Col <sub>h</sub> 252 (6.7) Iso	
6b	Cr 45 (21.2) Col <sub>h</sub> 224 (5.7) Iso	Iso 220 (5.3) Col <sub>h</sub>
6c	Cr 40 (30.3) Col <sub>h</sub> 197 (3.2) Iso	Iso 193 (3.5) Col <sub>h</sub> -10 (16.2) Cr
6d	Cr 51 (46.7) Col <sub>h</sub> 141 (0.5) Iso	Iso 135 (0.8) Col <sub>h</sub> 9 (29.3) Cr



Figure 4.7. Intensity vs. 2θ profile of compounds 6a (180°C on heating), 6b (100°C on heating),6c (45°C on cooling), and 6d (100°C on heating).

X-ray diffraction experiments were carried out on unoriented samples to characterize the exact arrangement of these columns in the 2D lattice, and the scattering profiles are shown in **Figure 4.7**. XRD profile of **6a** at 180°C on heating shows a sharp dominant reflection accompanied by few less intense peaks in the small-angle region whose d-spacing values are in the ratio of  $1:1/\sqrt{3}:1/2:1/\sqrt{7}$ , implying a hexagonal arrangement of columns (Col<sub>h</sub>) with the lattice parameter of 18.66 Å. These peaks correspond to the (10), (11), (20) and (21) planes of the hexagonal lattice. There are two peaks in the wide-angle regime. The peak at 4.27Å arises from fluid-like arrangement of alkyl chains and the peak at 3.66Å corresponds to core-core ordering within the columns. The X-ray diffractograms of all the compounds are shown in **Figure 4.7** and the lattice parameters calculated are given in **Table 4.2**. Compound **6b** at 100°C on the heating cycle displays

two small-angle peaks corresponding to (10) and (20) planes whose d-spacing ratios are  $1:1/\sqrt{3}:1/2$ . The amorphous packing of alkoxy chains causes the halo in the wide-angle region, and the broad ordered peak at 3.56 Å marks the intracolumnar ordering of discs. Compounds **6c** and **6d** have similar XRD profiles with d values in the ratio of a hexagonal lattice, thereby confirming the hexagonal columnar mesophase in concurrence with POM and DSC analysis.

Compound	Phase	<b>d</b> observed	d calculated	Miller indices	Parameters	
		(Å)	(Å)	(h,k)		
6a	Col <sub>h</sub>	16.16	16.16	10	a = 18.66 Å	
	180°C	9.32	9.33	11	$S_h = 301.74 \text{ Å}^2$	
		8.05	8.08	20	$V_h = 1104.36 \text{ Å}^3$	
		6.11	6.11	21	Z = 0.9	
		4.27 (h <sub>a</sub> )				
		3.66 (h <sub>c</sub> )				
6b	Col <sub>h</sub>	18.08	18.04	10	a = 20.83 Å	
	100°C	9.02	9.02	20	$S_h = 375.78 \ \text{\AA}^2$	
		4.58 (h <sub>a</sub> )			$V_h = 1337.79 \text{ Å}^3$	
		3.56 (h <sub>c</sub> )			Z = 0.9	
6c	Col <sub>h</sub>	20.14	20.13	10	a = 23.25 Å	
	45°C	11.61	11.62	11	$S_h = 468.36 \text{ Å}^2$	
		10.07	10.07	20	$V_h = 1639.27 \text{ Å}^3$	
		4.52 (h <sub>a</sub> )			Z = 1.0	
		3.50 (h <sub>c</sub> )				
6d	Col <sub>h</sub>	23.19	23.20	10	a = 26.80 Å	
	100°C	13.39	13.39	11	$S_h = 622.04 \text{ Å}^2$	

Table 4.2. The layer spacings and lattice parameters calculated from X-ray diffractogram

	11.61	11.61	20	$V_h = 2202.02 \text{ Å}^3$
	4.60 (h <sub>a</sub> )			Z = 1.0
	3.54 (hc)			

(a = lattice parameter =  $\sqrt{(4/3) \times d_{10}}$ ; lattice area  $S_h = a^2 \sin 60^\circ$ ; lattice volume  $V_h = a^2 \sin 60^\circ \times h_c$ ( $h_a$  if  $h_c$  is not observed); No of molecules per slice of column ( $\mathbf{Z}$ ) = ( $\sqrt{3} \times N_a \times \rho \times a^2 \times h$ )/2M;  $N_a$ =Avogadro number;  $\rho$  =Density in Kg/m<sup>3</sup>; a=lattice parameter;  $h_c$  =core-core peak ( $h_a$  = alkyl-alkyl chain peak, if  $h_c$  is not observed); M=molecular weight in Kg/m<sup>3</sup>).

In addition to the Col<sub>h</sub> phase, compound **6a** shows another phase in the lower temperature region. There is no change in the POM texture across this transition, but DSC traces show a peak at 160 °C, with an enthalpy change of 6.4 kJmol<sup>-1</sup>. In order to get an insight into the structure of this phase, X-ray diffraction measurements were carried out, and the intensity vs 20 profile is shown in **Figure 4.8**. At 110°C, the reflections attributed to the hexagonal phase remain unchanged. However, the broad peak corresponding to the core-core order split into two sharp peaks at 3.59 Å, and 3.51 Å, which were assigned to (002) and (102) planes of the three-dimensionally ordered columnar hexagonal plastic phase (Col<sub>hp</sub>)<sup>53,54</sup>. The lattice parameter (18.46 Å) of the Col<sub>hp</sub> is found to be slightly lower than that of the Col<sub>h</sub> mesophase. This plastic phase remained stable till room temperature without crystallization for a long time. Three-dimensional order and spontaneous alignment make these compounds prime candidates as organic electronic materials.



Figure 4.8. POM image and the X-ray diffraction pattern observed for compound 6a at 110°C.

Table 4.3. The laver	spacing and 1	attice parameters	calculated from	the X-rav	diffractogram
	spacing and I	attice parameters	culculated from	i une i i i uj	amactogram

Compound Phase		<b>d</b> observed	<b>d</b> calculated	Miller indices	Parameters
		(Å)	(Å)	(h,k)	
6a	$\operatorname{Col}_{hp}$	15.99	15.99	100	a = 18.46 Å
	110°C	9.25	9.22	110	c = 7.18  Å
		7.99	7.99	200	$S_h = 293.11 \text{ Å}^2$
		6.03	6.04	210	$V_h = 1035.86 \text{ Å}^3$
		4.63	4.61	220	Z = 1
		3.59	3.59	002	
		3.51	3.46	102	

The thermal stability of all the compounds was analyzed using thermogravimetric analysis. The TGA profile of all the derivatives is shown in **Figure 4.9**. All the compounds showed good thermal stability up to 380 °C before 5% weight loss was observed. This temperature is much higher than the clearing temperature of all the synthesized compounds, which excludes any possible decomposition during the mesophase characterization.



Figure 4.9. TGA thermogram of compounds 6a-d.

### 4.2.3. Photophysical properties and DFT studies

The photophysical properties of compounds **6a-d** were studied using UV-visible and emission spectroscopy in their micromolar concentration. **Figure 4.10** shows the identical absorption and emission profile of all the compounds. The absorption spectra show peaks ranging from 260 nm to 430 nm, with the strongest peak at 260 nm and other peaks at 285, 348 and two weaker peaks in the lower energy region at 420 nm and 440 nm. Absorption between 260 nm to 285 nm is assigned to the  $\pi$ - $\pi$ <sup>\*</sup> transition of the central core. There are broad featureless peaks between 420 and 440 nm in the visible region for all the compounds, possibly due to the intramolecular charge transfer (ICT) process<sup>55–57</sup>. Molar extinction coefficient values of compounds **6a-d** are 2.09 X 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>, 2.12 X 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>, 1.98 X 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>, 2.10 X 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> respectively. The optical energy gap was calculated from the intersection of the extrapolate tangent of the longest wavelength absorption peak and found to be 2.68 eV. Emission spectra of all the compounds are recorded at an excitation wavelength of 348 nm and found to have emission maxima of 466 nm with a shoulder peak on the lower energy side at 490 nm. The structural changes accompanied by electronic excitation could lead to larger stokes shift values of about 200 nm.



Figure 4.10. UV-vis and emission spectra of compounds 6a-d in chloroform solution  $(7 \times 10^{-6} \text{ M})$ 

concentration).



**Figure 4.11**. Energy minimized structures and frontier orbital electron density of compound **6a** obtained from Gaussian.

Density functional theory (DFT) calculations were performed for compound **6a** using the GAUSSIAN-09 program with a Becke's three-parameter functional and Lee, Yang, and Parr correlation functional (DFTB3LYP) by using the 6-311G (d, p) basis set. **Figure 4.11** displays the energy minimized structure, the electron density distribution of frontier molecular orbitals, and the HOMO – LUMO energy level diagrams of **6a** obtained from computations. The HOMO orbitals are evenly spread over the central core, but the LUMO orbitals are mainly focused in the extended core region towards the nitrogen and oxygen fused rings. The theoretical energy level of compound **6a** was found to be around 3.36 eV.

# 4.3. Conclusion

A series of oxygen and nitrogen incorporated chromenonaphthophenanthridine derivatives were synthesized through N-annulation and ipso-aromatic substitution. Planarization of pheripheral phenyl ring via oxygen atom resulted in enhanced delocalization evident from photophysical and density functional theory calculations. The thermal and mesomorphic properties of all the compounds were studied using TGA, POM, DSC, and X-ray diffraction experiments. The synthesized compounds exhibited stable hexagonal columnar mesophase over a wide temperature range. A highly ordered columnar plastic phase was observed for a derivative with a shorter butoxy alkyl chain around the core. The theoretical bandgap of 3.36 eV was obtained from Gaussian, and the optical band gap value of 2.68 eV was calculated from absorption studies for all the compounds.

# 4.4. Experimental section

# 4.4.1. Reagents and Instruments

Reagents and instruments used are the same as in Section 2.1.3.1

# 4.4.2. Synthetic procedures and spectral data of compounds 6a and 6b

All the intermediates and final compounds are synthesized following literature procedures<sup>47,49,58</sup>. The synthetic process and spectral data of compounds **2-5** are given in **Section 2.1.3.2**.

### General synthetic procedure for compound 6

A mixture of compound **5** (1eq) and salicylaldehyde (2 eq) is dissolved in NMP and was added 1% triflic acid. The reaction mixture was heated at 120°C for 12 hours under nitrogen.  $K_2CO_3$  (2eq) was added to this reaction mixture after 12 hours, and the reaction was monitored using TLC for the appearance of a yellow-greenish spot in 350 nm. The mixture was cooled to room temperature after completion, water was added and alkalized with 15% NaOH solution, extracted with chloroform, and washed with brine. The combined organic layer was evaporated. The crude was subjected to column chromatography using silica gel and 5% ethyl acetate in hexane as eluent and recrystallized in methanol to give compound **6** as a yellow solid.

**Compound 6a**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.77 (d, J = 7.5 Hz, 1H), 8.25 (s, 1H), 7.99 (s, 1H), 7.91 (s, 1H), 7.85 (s, 1H), 7.55 (t, J = 7 Hz, 1H), 7.43 (d, J = 8 Hz, 1H), 7.37 (t, J = 8 Hz, 1H), 4.49 (t, J = 7.5 Hz, 2H), 4.34-4.40 (m, 4H), 4.27 (t, J = 7.5 Hz, 4H), 1.93-2.04 (m, 10H), 1.61-1.77 (m, 10H), 1.06-1.11 (m, 15H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 154.45, 152.32, 149.61, 149.55, 147.60, 144.10, 143.30, 140.88, 138.25, 131.98, 125.32, 124.23, 124.21, 124.12, 123.06, 122.04, 121.42, 120.08, 117.73, 114.99, 113.22, 111.13, 107.28, 106.70, 106.37, 74.68, 70.75, 70.49, 69.25, 69.23, 32.76, 31.86, 31.64, 31.47, 31.44, 19.54, 19.42, 19.39, 19.36, 14.13, 14.01. Elemental analysis: C, 76.78; H, 7.59; N, 1.99 (calcd.); C, 77.01; H, 7.83; N, 1.85 (found.).

**Compound 6b**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.75 (d, *J* = 8 Hz, 1H), 8.12 (s, 1H), 7.92 (s, 1H), 7.83 (s, 1H), 7.74 (s, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 4.47 (t, *J* = 6 Hz, 2H), 4.32 (t, *J* = 6.5 Hz, 4H), 4.23 (t, *J* = 6.5 Hz, 4H), 1.93-2.03 (m, 10H), 1.61-1.66 (m, 10H), 1.43 (m, 20H), 0.96-0.97 (m, 15H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 154.37, 152.13, 149.35, 149.33, 147.34, 143.86, 143.04, 140.48, 138.03, 131.78, 125.25, 124.05, 124.01, 123.83, 122.85, 122.01, 121.15, 119.65, 117.62, 114.75, 112.89, 110.44, 106.94, 106.29, 105.91, 74.95, 70.69, 70.60, 69.39, 69.35, 32.06, 31.80, 31.78, 30.80, 29.85, 29.56, 29.48, 29.45, 26.26, 25.98, 25.94, 25.92, 25.86, 22.86, 22.75, 22.72, 14.21, 14.12, 14.10. Elemental analysis: C, 78.25; H, 8.72; N, 1.66 (calcd.); C, 77.91; H, 9.20; N, 1.36 (found.).

**Compound 6c**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ (ppm) = 8.71 (d, *J* = 7.5 Hz, 1H), 8.19 (s, 1H), 7.93 (s, 1H), 7.85 (s, 1H), 7.79 (s, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 8 Hz, 1H), 7.29 (t, *J*
= 7.5 Hz, 1H), 4.41 (t, J = 6.5 Hz, 2H), 4.31 (t, J = 6.5 Hz, 2H), 4.27 (t, J = 6.5 Hz, 2H), 4.19 (t, J = 6.5 Hz, 4H), 1.87-1.96 (m, 10H), 1.63-1.65 (m, 10H), 1.37-1.40 (m, 40H), 0.82-0.83 (m, 15H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 154.45, 152.31, 149.60, 149.53, 147.55, 144.08, 143.25, 140.83, 138.17, 131.97, 125.36, 124.19, 124.17, 124.09, 123.03, 122.01, 121.39, 120.02, 117.72, 114.94, 113.16, 110.10, 107.26, 106.70, 106.37, 75.03, 71.08, 70.82, 69.57, 69.54, 31.99, 31.91, 31.89, 30.78, 29.88, 29.77, 29.63, 29.54, 29.52, 29.47, 29.41, 29.38, 29.37, 26.54, 26.30, 26.25, 26.19, 22.76, 22.72, 14.14. Elemental analysis: C, 79.30; H, 9.52; N, 1.42 (calcd.); C, 78.93; H, 9.70; N, 1.25 (found.).

**Compound 6d**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 8.76 (d, *J* = 8 Hz, 1H), 8.16 (s, 1H), 7.95 (s, 1H), 7.86 (s, 1H), 7.78 (s, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 4.48 (t, *J* = 6.5 Hz, 2H), 4.33 (q, *J* = 6.5 Hz, 4H), 4.24 (t, *J* = 6.5 Hz, 4H), 1.96-2.04 (m, 10H), 1.58-1.70 (m, 10H), 1.44-1.50 (m, 70H), 0.86-0.89 (m, 15H). <sup>13</sup>CNMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm) = 153.45, 151.35, 148.65, 148.57, 146.65, 143.13, 142.31, 139.95, 137.26, 130.99, 124.36, 123.26, 123.18, 122.09, 121.02, 120.47, 119.16, 116.73, 114.04, 112.27, 110.31, 106.34, 105.81, 105.51, 74.05, 70.18, 69.86, 68.61, 68.56, 30.92, 29.72, 28.83, 28.76, 28.74, 28.70, 28.68, 28.59, 28.55, 28.51, 28.46, 28.42, 28.38, 28.36, 25.50, 25.26, 25.21, 25.14, 21.68, 13.0. Elemental analysis: C, 80.71; H, 10.60; N, 1.11 (calcd.); C, 81.14; H, 10.83; N, 1.09 (found.).

## 4.5. <sup>1</sup>H and <sup>13</sup>C NMR spectra



Figure 4.12 <sup>1</sup>H (top) and <sup>13</sup>C NMR (bottom) spectra of compound 6a

Page | 196



Page | 197



Figure 4.14  $^{1}$ H (top) and  $^{13}$ C NMR (bottom) spectra of compound 6c

Page | 198



## 4.6. References

- Stępień, M., Gońka, E., Żyła, M. & Sprutta, N. Heterocyclic Nanographenes and Other Polycyclic Heteroaromatic Compounds: Synthetic Routes, Properties, and Applications. *Chem. Rev.* 117, 3479–3716 (2017).
- Narita, A., Wang, X.-Y., Feng, X. & Müllen, K. New advances in nanographene chemistry. *Chem. Soc. Rev.* 44, 6616–6643 (2015).
- 3. Wang, X. *et al.* Heteroatom-doped graphene materials: syntheses, properties and applications. *Chem. Soc. Rev.* **43**, 7067–7098 (2014).
- 4. Escande, A. & Ingleson, M. J. Fused polycyclic aromatics incorporating boron in the core: fundamentals and applications. *Chem. Commun.* **51**, 6257–6274 (2015).
- Wang, X.-Y., Wang, J.-Y. & Pei, J. BN Heterosuperbenzenes: Synthesis and Properties. Chem. – A Eur. J. 21, 3528–3539 (2015).
- 6. Wu, W., Liu, Y. & Zhu, D. π-Conjugated molecules with fused rings for organic field-effect transistors: design, synthesis and applications. *Chem. Soc. Rev.* **39**, 1489–1502 (2010).
- Erdtman, H. & Högberg, H.-E. Cyclooligomerisation of quinones. *Tetrahedron Lett.* 11, 3389–3392 (1970).
- Nielsen, C. B. *et al.* Organic Light-Emitting Diodes from Symmetrical and Unsymmetrical π-Extended Tetraoxa[8]circulenes. *Chem. – A Eur. J.* 16, 13030–13034 (2010).
- 9. Wang, S. *et al.* Synthesis, Photophysics, and Self-Assembly of Furan-Embedded Heteroarenes. *Chem. A Eur. J.* **21**, 14791–14796 (2015).
- 10. Prakash Rao, H. S. & Vijjapu, S. Synthesis and photochromic properties of benzofuran– phenanthrene and benzofuran–pyrene hybrids. *RSC Adv.* **4**, 25747–25758 (2014).
- Nielsen, C. B. *et al.* Azatrioxa[8]circulenes: Planar Anti-Aromatic Cyclooctatetraenes. *Chem. – A Eur. J.* 19, 3898–3904 (2013).
- Hensel, T. *et al.* Diazadioxa[8]circulenes: Planar Antiaromatic Cyclooctatetraenes. *Chem. A Eur. J.* 19, 17097–17102 (2013).

- Eskildsen, J., Reenberg, T. & Christensen, J. B. Substituted Tetraoxa[8]circulenes New Members of the Liquid Crystal Family. *European J. Org. Chem.* 2000, 1637–1640 (2000).
- Tokita, S., Watanabe, T., Fujita, Y., Iijima, H. & Terazono, S. Molecular Design and Synthesis of Novel Analogues of Benzodixanthene and Anthradichromene. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A. Mol. Cryst. Liq. Cryst.* 297, 269–276 (1997).
- Lv, N. *et al.* Synthesis, Properties, and Structures of Functionalized peri-Xanthenoxanthene. *Org. Lett.* 15, 2382–2385 (2013).
- Wang, L., Duan, G., Ji, Y. & Zhang, H. Electronic and Charge Transport Properties of peri-Xanthenoxanthene: The Effects of Heteroatoms and Phenyl Substitutions. *J. Phys. Chem. C* 116, 22679–22686 (2012).
- 17. Kobayashi, N., Sasaki, M. & Nomoto, K. Stable peri-Xanthenoxanthene Thin-Film Transistors with Efficient Carrier Injection. *Chem. Mater.* **21**, 552–556 (2009).
- Stassen, D., Demitri, N. & Bonifazi, D. Extended O-Doped Polycyclic Aromatic Hydrocarbons. *Angew. Chemie Int. Ed.* 55, 5947–5951 (2016).
- Miletić, T. *et al.* Tailoring Colors by O Annulation of Polycyclic Aromatic Hydrocarbons. *Chem. – A Eur. J.* 23, 2363–2378 (2017).
- Hiscock, L. K. *et al.* Synthesis and Characterization of Liquid-Crystalline Tetraoxapentacene Derivatives Exhibiting Aggregation-Induced Emission. *Chem. – A Eur.* J. 25, 1018–1028 (2019).
- Hiscock, L. K., Yao, C., Skene, W. G., Dawe, L. N. & Maly, K. E. Synthesis of Emissive Heteroacene Derivatives via Nucleophilic Aromatic Substitution. *J. Org. Chem.* 84, 15530– 15537 (2019).
- W. Laursen, B. & C. Krebs, F. Synthesis, Structure, and Properties of Azatriangulenium Salts. *Chem. – A Eur. J.* 7, 1773–1783 (2001).
- Ooyama, H. E. *et al.* Photophysical properties and photostability of novel symmetric polycyclicphenazine-type fluorescent dyes and the dye-doped films. *Dye. Pigment.* 94, 103–112 (2012).

- Ooyama, H. E. *et al.* Photophysical properties and photostability of novel unsymmetric polycyclicphenazine-type D-π-A fluorescent dyes and the dye-doped films. *J. Photochem. Photobiol. A Chem.* 230, 38–46 (2012).
- FUJIWARA, H. & KITAGAWA, K. Synthesis of [1]Benzopyrano[2, 3, 4-kl]acridin-3-ol and Its Analogues as Pentacyclic Compounds. *Chem. Pharm. Bull. (Tokyo).* 48, 1380–1383 (2000).
- Kawashima, K., Osaka, I. & Takimiya, K. Effect of Chalcogen Atom on the Properties of Naphthobischalcogenadiazole-Based π-Conjugated Polymers. *Chem. Mater.* 27, 6558– 6570 (2015).
- Kulkarni, M. V, Kulkarni, G. M. & Sun, C.-H. L. and C.-M. Recent Advances in Coumarins and 1-Azacoumarins as Versatile Biodynamic Agents. *Current Medicinal Chemistry* vol. 13 2795–2818 (2006).
- Yu, D., Suzuki, M., Xie, L., Morris-Natschke, S. L. & Lee, K.-H. Recent progress in the development of coumarin derivatives as potent anti-HIV agents. *Med. Res. Rev.* 23, 322–345 (2003).
- Costa, M., Areias, F., Abrunhosa, L., Venâncio, A. & Proença, F. The Condensation of Salicylaldehydes and Malononitrile Revisited: Synthesis of New Dimeric Chromene Derivatives. J. Org. Chem. 73, 1954–1962 (2008).
- O'Callaghan, C. N., McMurry, T. B. H. & O'Brien, J. E. Synthetic reactions of 2-(2-amino-3-cyano-4H-[1]benzopyran-4-yl)propane-1,3-dinitrile with reactive methylene compounds. *J. Chem. Soc. Perkin Trans. 1* 417–420 (1995) doi:10.1039/P19950000417.
- Evdokimov, N. M. *et al.* One-Step Synthesis of Heterocyclic Privileged Medicinal Scaffolds by a Multicomponent Reaction of Malononitrile with Aldehydes and Thiols. *J. Org. Chem.* 72, 3443–3453 (2007).
- Zhang, D., Luo, N., Gan, J., Wan, X. & Wang, C. Piperidine-Mediated [3 + 3] Cyclization of 2-Amino-4H-chromen-4-ones and 2-Benzylidenemalononitriles: To Access 2-Aminochromeno[2,3-b]pyridine Derivatives. J. Org. Chem. 86, 9218–9224 (2021).
- 33. Gohil, J. D., Patel, H. B. & Patel, M. P. Synthesis and evaluation of new chromene based

[1,8]naphthyridines derivatives as potential antimicrobial agents. *RSC Adv.* **6**, 74726–74733 (2016).

- 34. Salman, M. *et al.* Chromeno naphthyridines based heterocyclic compounds as novel acidizing corrosion inhibitors: Experimental, surface and computational study. *J. Mol. Liq.*322, 114825 (2021).
- Katritzky, A. R., Du, W., Matsukawa, Y., Ghiviriga, I. & Denisenko, S. N. Polycyclic fused phenanthridines: An alternative approach from benzotriazoles. *J. Heterocycl. Chem.* 36, 927–932 (1999).
- Destrade, C., Tinh, N. H., Gasparoux, H. & Mamlok, L. Preliminary Communications. Benzotrisfuran derivatives A new series of disc-like liquid crystals. *Liq. Cryst.* 2, 229–233 (1987).
- Wolf, R. & Marvel, C. S. Polymers with quinoxaline units. V. Polymers with quinoxaline and dioxin units. J. Polym. Sci. Part A-1 Polym. Chem. 7, 2481–2491 (1969).
- Ames, D. E. & Ward, R. J. [1,4]Benzodioxinopyridazines. J. Chem. Soc. Perkin Trans. 1 534–538 (1975) doi:10.1039/P19750000534.
- Schaffroth, M., Lindner, B. D., Vasilenko, V., Rominger, F. & Bunz, U. H. F. Alkynylated Diazadioxaacenes: Syntheses and Properties. *J. Org. Chem.* 78, 3142–3150 (2013).
- 40. Nicolas, Y. *et al.* TIPS-triphenodioxazine versus TIPS-pentacene: Enhanced electron mobility for n-type organic field-effect transistors. *Org. Electron.* **13**, 1392–1400 (2012).
- 41. Di, C. *et al.* Trifluoromethyltriphenodioxazine: Air-Stable and High-Performance n-Type Semiconductor. *Org. Lett.* **10**, 3025–3028 (2008).
- 42. Liu, B. *et al.* Triazacoronene Derivatives with Three peri -Benzopyrano Extensions: Synthesis, Structure, and Properties. *European J. Org. Chem.* **2018**, 869–873 (2018).
- 43. Sun, Y. *et al.* 1,2,5,6,9-Pentaazacoronenes (PACs) and  $\pi$ -Extended PAC Derivatives: Synthesis, Crystal Structure, and Optical and Redox Properties. *Org. Lett.* acs.orglett.1c01574 (2021) doi:10.1021/acs.orglett.1c01574.
- 44. Elbert, S. M., Reinschmidt, M., Baumgärtner, K., Rominger, F. & Mastalerz, M.

Benzopyrano-Fused N-Heterocyclic Polyaromatics. *European J. Org. Chem.* 2018, 532–536 (2018).

- 45. Shivakumar, K. I. *et al.* Photoconductive bent-core liquid crystalline radicals with a paramagnetic polar switchable phase. *J. Mater. Chem. C* **8**, 1083–1088 (2020).
- Kaszyński, P., Constantinides, C. P. & Young Jr., V. G. The Planar Blatter Radical: Structural Chemistry of 1,4-Dihydrobenzo[e][1,2,4]triazin-4-yls. *Angew. Chemie Int. Ed.* 55, 11149–11152 (2016).
- Kumar, S., Manickam, M., Balagurusamy, V. S. K. & Schonherr, H. Electrophilic aromatic substitution in triphenylene discotics: Synthesis of alkoxynitrotriphenylenes. *Liq. Cryst.* 26, 1455–1466 (1999).
- 48. Bushby, R. J. *et al.* Helical geometry and liquid crystalline properties of 2,3,6,7,10,11hexaalkoxy-1-nitrotriphenylenesElectronic supplementary information (ESI) available: calculation of dipolar interactions, details of syntheses and analytical data, DSC data, and full deta. *J. Mater. Chem.* **13**, 470–474 (2003).
- 49. Liu, B. *et al.* Triazacoronene Derivatives with Three peri-Benzopyrano Extensions: Synthesis, Structure, and Properties. *European J. Org. Chem.* **2018**, 869–873 (2018).
- Kumar, S. Self-organization of disc-like molecules: chemical aspects. *Chem. Soc. Rev.* 35, 83–109 (2006).
- 51. Laschat, S. *et al.* Discotic Liquid Crystals: From Tailor-Made Synthesis to Plastic Electronics. *Angew. Chemie Int. Ed.* **46**, 4832–4887 (2007).
- 52. Ribeiro, A. C. *et al.* Rectangular to hexagonal columnar phase transition exhibited by a biforked mesogen. *Eur. Phys. J. E* **10**, 143–151 (2003).
- 53. Glüsen, B., Kettner, A. & Wendorff, J. H. A Plastic Columnar Discotic Phase. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A. Mol. Cryst. Liq. Cryst.* **303**, 115–120 (1997).
- Prasad, S. K., Rao, D. S. S., Chandrasekhar, S. & Kumar, S. X-RAY Studies on the Columnar Structures of Discotic Liquid Crystals. *Mol. Cryst. Liq. Cryst.* 396, 121–139 (2003).

- 55. Xi, Y. *et al.* Mechanical stimuli induced emission spectra blue shift of two D-A type phenothiazine derivatives. *Chem. Lett.* (2018) doi:10.1246/cl.180089.
- Eichhorn, S. H. *et al.* A combined study of mesomorphism, optical, and electronic properties of donor-acceptor columnar liquid crystals. in *Liquid Crystals XV* (ed. Khoo, I. C.) 811402 (2011). doi:10.1117/12.893149.
- Paramaguru, G., Solomon, R. V., Jagadeeswari, S., Venuvanalingam, P. & Renganathan, R. Tuning the Photophysical Properties of 2-Quinolinone-Based Donor-Acceptor Molecules through N - versus O -Alkylation: Insights from Experimental and Theoretical Investigations. *European J. Org. Chem.* 2014, 753–766 (2014).
- 58. Bushby, R. J. *et al.* Helical geometry and liquid crystalline properties of 2,3,6,7,10,11hexaalkoxy-1-nitrotriphenylenes. *J. Mater. Chem.* **13**, 470–474 (2003).

## **Chapter 5**

## Summary

This chapter summarizes some of the advances and structure-property relationship of many discotic liquid crystals (DLCs) we have discovered in this thesis work. The thesis deals with "Synthesis and Characterization of Some Novel Discotic Liquid Crystals" in search of the liquid crystalline compounds that self-organizes into columnar mesophase. The primary motive of the thesis revolves around the ring extension of triphenylene moiety by nitrogen and oxygen annulation strategy. We have reported the synthesis of various heterocyclic discotic liquid crystals and discussed the structural, mesomorphic and photo physical properties. The structure-property relationship of the synthesized molecules was investigated by a combination of differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray diffraction techniques. The electronic properties were examined by UV-Vis and fluorescence spectroscopy along with density functional theory (DFT) calculations.

Chapter 1 is an introductory part of the thesis that gives a brief insight on the history, classifications of liquid crystals followed by extended discussions on discotic liquid crystals. The chemistry of discotic liquid crystals in terms of the necessary structural features required to show mesomorphism is discussed. The various mesophases formed by disc-like mesogens and their characterization techniques are discussed in detail. This chapter also contains the many carbocyclic and heterocyclic aromatic rings that are used as cores for designing DLCs. The importance of heterocyclic columnar mesophases as electron-transporting materials is given significant attention. Finally, there is a brief account on the charge transport properties of DLCs along with their applications in organic electronic devices such as liquid crystal displays, organic photovoltaics, organic light emitting diodes.

Chapter 2 deals with the synthesis and thermotropic mesomorphism of a series of naphthophenanthridine discotic mesogens that contain methoxy substituted phenyl, alkyl and various chromophores. Pictet-Spengler cyclization was employed to synthesize the compounds in good yield. All the synthesized compounds are found to show high thermal stability over 350 °C

and exhibit liquid crystallinity and exclusively columnar hexagonal mesophase confirmed by small angle X-ray diffraction studies. Highly ordered columnar plastic like mesophase was found in 2,3,6,7,10,11-hexabutoxy-5-(4-methoxyphenyl)naphthophenanthridine derivative that has a three dimensional order while maintaining certain fluidity which was observed under POM. Ambipolar charge transport properties of butyl substituted naphthophenanthridine was evaluated by time-offlight technique that showed the temperature-independent hole and electron transport behavior in the same order of magnitude. Also, a series of four compounds each bearing a chromophore moiety covalently attached to the naphthophenathridine was synthesized. Pyrene, anthracene, phenothiazine and triphenylamine molecules were used as chromophores. All the derivatives found to exhibit enantiotropic hexagonal columnar mesomorphism and in particular the pyrene functionalized phenanthridine derivative (NP-PY) is found to be room temperature liquid crystal having wide mesophase range. The density functional theory calculations were carried out to investigate the electronic structures and theoretical energy levels of the frontier orbitals. Photophysical properties and optical energy levels were examined using absorption and emission spectroscopy.

Chapter 3 discusses the synthesis and liquid crystalline properties of triazacoronene based discotic derivatives. Here we introduced triazcoronene as a novel core for DLCs for the first time. Hexabutoxytriphenylene-1,5,9-triamine was reacted with shorter chain aliphatic aldehydes to give triazacorone derivatives as yellow solid. This mixed-chain triazacoronenes are non-mesomorphic possibly due to the inadequate balance in core size and shorter hydrocarbon chains. However, the triphenyltriazacoronene peripherally surrounded by longer alkoxy chains exhibited highly ordered columnar mesomorphism for a wide temperature range. Multiple reflections in the small-angle region of X-ray diffractogram suggested the longer intercolumnar correlation and a relatively sharp wide angle peak indicates a strong core-core packing. Spontaneous homeotropic alignment of columns was observed under POM for the derivatives with six alkoxy chains which is an essential criterion for device fabrications.

Finally, in chapter 4 we discuss the synthesis of a series of chromenonaphtophenathridine based DLCs through tandem Pictet-Spengler cyclization followed by ipso-aromatic substitution in one pot. These derivatives are an extension of naphthophenthridine derivatives reported in chapter 2 and the oxygen annulation is achieved by intramolecular nucleophilic substation reaction. The

resulted compounds were characterized using spectral and elemental analysis and confirmed their structure and purity. All the compounds have shown excellent thermal stability and exhibit hexagonal columnar mesophase over a wide temperature range. The mesophase range was found to decrease with increasing alkoxy chain length due to the reduction in isotropic transition temperature. Highly ordered enantiotropic plastic columnar mesophase as confirmed by the derivative with butoxy chains below the hexagonal columnar mesophase as confirmed by the splitting of core-core peak into two sharp reflections in the wide angle region of X-ray diffractogram. Due to the extended delocalization, these derivatives showed red-shifted absorption and emission characteristics. DFT calculations showed that the HOMO orbitals are evenly spread over the core whereas the LUMO are mainly focused on the extended ring system that contains nitrogen and oxygen fused rings.

Overall, the thesis covered some of the heterocylic DLCs and their successful synthesis through Pictet-Spengler cyclization in the bay region of triphenylene derivatives. The effect of extended delocalization in the mesomorphic and electronic properties have been reported. Charge transport properties of some highly ordered and well aligned DLCs reported here will be studied in the future. The Pictet-Spengler strategy will be exploited further to design and synthesis of various other cores to obtain electron deficient DLCs for improved electron transporting properties.

Some of the findings of this thesis work is reported in the following articles.

- Vadivel, M., Kumar, I. S., Swamynathan, K., Raghunathan, V. A. & Kumar, S. Novel Annulated Triphenylene Discotic Liquid Crystals Generated by Pictet-Spengler Cyclization. *ChemistrySelect* 3, 8763–8769 (2018).
- Vadivel, M., Singh, S., Singh, D. P., Raghunathan, V. A. & Kumar, S. Ambipolar Charge Transport Properties of Naphthophenanthridine Discotic Liquid Crystals. *J. Phys. Chem. B* 125, 10364–10372 (2021).
- Vadivel, M., Raghunathan, V. A. & Kumar, S. Highly ordered columnar liquid crystalline triazacoronene: An electron-deficient core and novel addition to the discotic family. (Manuscript under preparation)

- 4. Vadivel, M., Raghunathan, V. A. & Kumar, S. Chromenonaphthophenanthridine: Benzopyrano fused Nitrogen-containing heterocyclic discotic Mesogens. (Manuscript under preparation)
- 5. Vadivel, M., Kumar, S. Synthesis and mesomorphic properties of chromophore-coupled naphthophenathridine discotic liquid crystals. (Manuscript under preparation)