SYNTHESIS AND CHARACTERIZATION OF SOFT CONDENSED MATERIALS CORED BY SUBSTITUTED PHENYL AND NAPHTHALENE MOIETIES

NUR AMANINA JUNIASARI BINTI TUN NUR ISKANDAR

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by

NUR AMANINA JUNIASARI BINTI TUN NUR ISKANDAR

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Å	Angstrom
b	Broad
$C_nH_{2n+1}Br$	Bromoalkane
^{13}C-NMR	Carbon nuclear magnetic resonance
CHN	Carbon, Hydrogen and Nitrogen
δ/ppm	Chemical shift in part per million unit
COSY	Correlation spectroscopy
J	Coupling constant
Cr	Crystal
Cr_1	Crystal 1
Cr_2	Crystal 2
°C	Degree celcius
°C min^{-1}	Degree celcius per minute
$CDCl_3$	Deuterated chloroform
$M_{dia}(H)$	Diamagnetic moment
χ_{dia}	Diamagnetic susceptibility
DCM	Dichloromethane
DSC	Differential scanning calorimetry
DMAP	Dimethylaminopyridine
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide-d_6
n	Director
DEPT	Distortionless enhancement by polarization transfer
d	Doublet
emu g^{-1}	Electromagnetic unit per gram
ΔH	Enthalpy change
ΔS	Entropy change

EtOH	Ethanol
^{19}F-NMR	Flourine nuclear magnetic resonance
FT-IR	Fourier transform infrared
FT-NMR	Fourier transform nuclear magnetic resonance
HMBC	Heteronuclear multiple bond correlation
HMQC	Heteronuclear multiple quantum correlation
$M(H)$	Isothermal magnetization
$\Delta M(H)$	Isothermal magnetization change
I	Isotropic
kJ mol^{-1}	kiloJoule per mole
kOe	kilooersted
LCs	Liquid Crystals
H	Magnetic field
M	Magnetization
m	Medium
MHz	Megahertz
l	Molecular length
MW	Molecular weight
m	Multiplet
DCC	*N*, *N*-Dicyclohexylcarbodiimide
N	Nematic phase
n	Number of carbon atoms at terminal alkoxy chains
1D-NMR	One-dimensional nuclear magnetic resonance
o	*Ortho*
p	*Para*
ppm	Part per million
%	Percentage
π-π interaction	Pi-pi interaction
POM	Polarizing optical microscopy

K_2CO_3	Potassium carbonate
KOH	Potassium hydroxide
KI	Potassium iodide
^{1}H-NMR	Proton nuclear magnetic resonance
q	Quartet
Si	Silicon
s	Singlet
SmC	Smectic C phase
Sm	Smectic phase
s	Strong
SQUID	Superconducting quantum interference device
T	Temperature
TMS	Tetramethylsaline
t	Triplet
2D-NMR	Two-dimensional nuclear magnetic resonance
v/cm^{-1}	Wavenumber in centimeter unit

SINTESIS DAN PENCIRIAN BAGI BAHAN LEMBUT TERTUMPAT YANG BERTERASKAN KUMPULAN FENIL DAN NAFTALENA YANG TERTUKARGANTI

ABSTRAK

Empat siri homolog baru bagi bahan lembut tertumpat yang terdiri daripada sistem bifenil yang disambungkan pada sistem teras yang berbeza, iaitu fenil dan naftalena telah berjaya disediakan dan dicirikan. Pengukuran fizikal dan analisis unsur (mikroanalisis CHN), teknik spektroskopik FT-IR, 1D dan 2D-NMR digunakan untuk mengenalpasti struktur molekul sebatian yang disintesis. Sifat hablur cecair dan kelakuan termal bagi kesemua sebatian tajuk telah dijalankan melalui POM dan DSC. Homolog dalam siri pertama terdiri daripada gelang fenil yang dihubungkan oleh unit bifenil dengan pelbagai rantai alkoksi terminal, OC_nH_{2n+1} (n = 7-12) pada satu hujung dan hujung yang lain digabungkan dengan imina aromatik dengan penukargantian terminal *p*-metoksi. Siri kedua merupakan analog bagi siri pertama yang berbeza dari segi kehadiran penukarganti etoksi persisian yang terletak pada kedudukan *orto* pada gelang fenil pusat. Bagi siri ketiga, sebatian **6X** menyerupai homolog dalam siri kedua di mana pelbagai penukarganti terminal X (X = OCH_3, F, Cl, Br dan I) diperkenalkan pada kedudukan *para* dalam kumpulan imina manakala rantai alkoksi terminal dalam unit bifenil dikekalkan dengan tujuh atom karbon. Semua sebatian sasaran bagi ketiga-tiga siri ini memaparkan fasa nematik (N) enantiotropik. Sifat mesomorfik sangat dipengaruhi oleh panjang rantai alkoksi di mana kestabilan termal bagi sebatian tajuk daripada siri pertama dan kedua akan berkurang sekiranya rantai alkoksi terminal meningkat dari n = 7 hingga n = 12. Kajian ini juga mendedahkan bahawa suhu lebur

dan suhu jelas yang lebih tinggi dapat diperhatikan bagi sebatian **3a-3f** dalam siri pertama berbanding sebatian **5a-5f** daripada siri kedua, dan kehadiran penukarganti terminal yang berkutub dalam siri ketiga menyebabkan pengurangan dalam suhu lebur dan suhu jelas. Dalam siri keempat, 2,6-naftalenadiol diperkenalkan sebagai teras pusat di mana dua lengan sisi lanjutan terdiri daripada sistem bifenil dengan pelbagai rantai alkoksi terminal, OC_nH_{2n+1} (n = 7-12) yang dihubungkan kepadanya. Homolog dengan ahli yang lebih pendek (n = 7 hingga n = 10) didapati mempamerkan fasa N semasa proses penyejukan dan pemanasan. Terbitan naftalena dengan panjang rantai alkoksi terminal yang lebih tinggi bagi terbitan undesiloksi dan dodesiloksi didapati menunjukan fasa N enantiotropik dengan kemunculan fasa smektik C (SmC) monotropik. Kewujudan ketegaran dan kebolehkutuban naftalena sebagai teras pusat nampaknya meluaskan julat suhu peralihan fasa N. Sebagai tambahan, julat suhu fasa SmC meningkat apabila rantai alkoksi terminal memanjang dari n = 11 hingga n = 12. Tingkah laku magnet yang tidak dijangka dapat diperhatikan dalam semua homolog organik tulen kecuali bagi sebatian **7a-7f** walaupun bahan ini tidak mempunyai sebarang spesies magnetik seperti unsur logam atau radikal.

SYNTHESIS AND CHARACTERIZATION OF SOFT CONDENSED MATERIALS CORED BY SUBSTITUTED PHENYL AND NAPHTHALENE MOIETIES

ABSTRACT

Four new homologues series of soft condensed materials consisting of biphenyl unit connected to different core systems, namely phenyl and naphthalene have been successfully prepared and characterized. The physical measurement and elemental analysis (CHN microanalysis), FT-IR, 1D and 2D-NMR spectroscopic techniques were employed to elucidate the molecular structures of the synthesized compounds. The liquid crystal properties and thermal behavior of all title compounds were conducted by POM and DSC. The homologues in the first series comprising a phenyl ring armed by a biphenyl unit with various flexible terminal alkoxy chains, OC_nH_{2n+1} (n = 7-12) at one end and the other end was attached by aromatic imine with terminal *p*-methoxy substituent. The second series are the analogues of first series which differ in term of the presence of peripheral ethoxy substituent located at the *ortho* position in the central phenyl ring. As for the third series, compounds **6X** resemble the homologues in the second series wherein the various terminal substituents X (X = OCH_3, F, Cl, Br and I) were introduced in the *para* position of the imine fragment while the terminal alkoxy chain in the biphenyl unit was retained at seven carbon atoms. All target compounds in these three series display enantiotropic nematic phase. The mesomorphic property is strongly influenced by the length of alkoxy chains wherein the thermal stability of title compounds from the first and second series will be decreased if the terminal alkoxy chains increased from n = 7 to n = 12. The study

also reveals that higher melting and clearing temperatures were observed for compounds **3a-3f** in the first series than the compounds **5a-5f** from the second series, whilst the presence of terminal polar substituents in the third series led to a reduction in the clearing and melting temperatures. In the fourth series, 2,6-naphtalenediol was introduced as a central core wherein two extended side arms made up by biphenyl systems with various terminal alkoxy chains, OC_nH_{2n+1} (n = 7-12) were connected to it. The homologues with shorter members (n = 7 to n = 10) were detected to exhibit N phase upon cooling and heating processes. The naphthalene derivative with higher terminal alkoxy chain lengths for undecyloxy and dodecyloxy derivatives were found to show enantiotropic N phase with the emergence of monotropic smectic C (SmC) phase. The existence of the rigidity and polarizability of naphthalene as central core seems to broaden the N phase transition temperatures range. In addition, the SmC phase temperature range increased when the terminal alkoxy chains lengthen from n = 11 to n = 12. The unexpected magnetic behavior was observed in all purely organic homologues except compounds **7a-7f** even though these materials do not possess any magnetic species like metal or radical elements.

CHAPTER 1 – INTRODUCTION

1.1 State of Matter

Matter is described as any substance that occupies space and has mass as well as exists in different stable states relying on the volume, temperature and pressure of the surroundings. The most fundamental states of matter are solid, liquid and gas (Eliezer *et al.*, 2001; Griffin, 2018). Generally, the distinction among the state of matter is based on the particles arrangement in different geometrical configuration under different thermodynamic conditions (Rizvi, 2003). In solid state, the particles are packed closely together, therefore, cannot be compressed easily. Solid has a rigid shape and volume. This is due to the strong intermolecular forces acting on the molecules that make the molecules unable to move freely but only vibrate and rotate at a fixed position and orientation. In the liquid state, the molecules are closely packed together but with no fixed arrangement. Molecules of liquid are held together by strong intermolecular forces (Tabor, 1991; Griffin, 2018; Khachan, 2018). Therefore, they can vibrate, move freely, slide over each other and able to fill the shape of the containers. Liquid is much easier to compress in comparison to solid. Whilst in the gas state, they are highly compressible because of widely spaced molecules having sufficient empty space among them. The molecules are very far apart in a random manner. Hence, the intermolecular interaction between their molecules are negligible.

In addition, the wide range of materials in the state of matter that cannot be classified merely as simple liquids or crystalline solids, commonly referred to soft condensed material which is also known as soft matter or complex fluid (Jones, 2002). More details on this soft condensed material will be discussed further in the next section.

1.2 Soft Condensed Material

Pierre-Gilles De Gennes, a Noble Prize-winning was one of the first to identify the soft condensed material. He stated that soft condensed material as a convenient term of materials that showed a ‘large response to small perturbation’. This means that it is generally described as the material that is structurally modified or deformed easily under an external stimulus such as electricity, magnetic fields, thermal or mechanical deformations (Hirst, 2012). This material can be classified into some distinctive features, namely length scales among atomic sizes and macroscopic scales, universality (most aspects of soft material interactions and structures does not rely on the particular chemistry but more on the topological implications) and fluctuations that occur in any thermal systems (Jones, 2002).

Several notable example of soft condensed material are liquid crystals, polymers, colloids, surfactants, foams, gels, granular materials and others (Hirst, 2012; Doi, 2013; Selinger, 2015). In more precise terms, the soft condensed materials we are focusing in this thesis include the fourth unique state of matter which is liquid crystal. A general overview of liquid crystals will discuss in the later section.

1.3 A general overview of Liquid Crystals

Liquid crystals (LCs) can be referred as the substance that show the intermediate state, called mesophases which exist between crystalline solid and isotropic liquid (Mohanty, 2003). The molecules of crystalline solid have highly ordered structure with no translational freedom. In liquid state, the molecules are mobile and have no orientational order but with translational freedom. On the other hand, liquid crystal phases have high orientational order with low positional order but these mesophases have certain degree of positional arrangements (Singh *et al*., 2002). They merely tend to point along a common axis, called as a director, *n*. The molecular arrangement among crystalline solid, liquid crystal and isotropic liquid are illustrated in Figure 1.1.

The unique features of LCs property offer a variety of potential applications that have been widely applied in the industrial and scientific areas, such as liquid crystal displays (LCDs), liquid crystal thermometer, optical imaging, liquid crystal sensors and others. Lin and co-workers reported the preparation of liquid crystalline graphene oxide to study the rheological property and their application in optoelectronics and LCDs (Lin, 2015). Furthermore, LCDs exploit the technological advances from the past decade to the present as they are extensively used in television, computer monitors, GPS devices and smartphones. They are compact, thin and flat electronic panel displays which used light modulation in its primary source of operation systems and they consist of a huge number of pixels or picture elements, based on twisted nematic (TN) or various super-twisted nematic (STN) liquid crystals. (Schadt, 1997; Schadt, 2018). In addition, LCDs show tremendously high resolution, produce excellent color and images, as well as energy efficiency which only used low power consumption to run (Briere, 2015).

For every advantages, there are also disadvantages found in these liquid crystal displays, wherein they have difficulty in reproducing black and very dark gray images. Besides, they are not suitable for used in high temperature or brightly environments as a large amount of light in LCDs are absorbed and the backlight shines through the LCs are utilized by LCDs (Briere, 2015).

Liquid crystal remain the focus of this research and therefore it will be further discussed in the upcoming chapter.

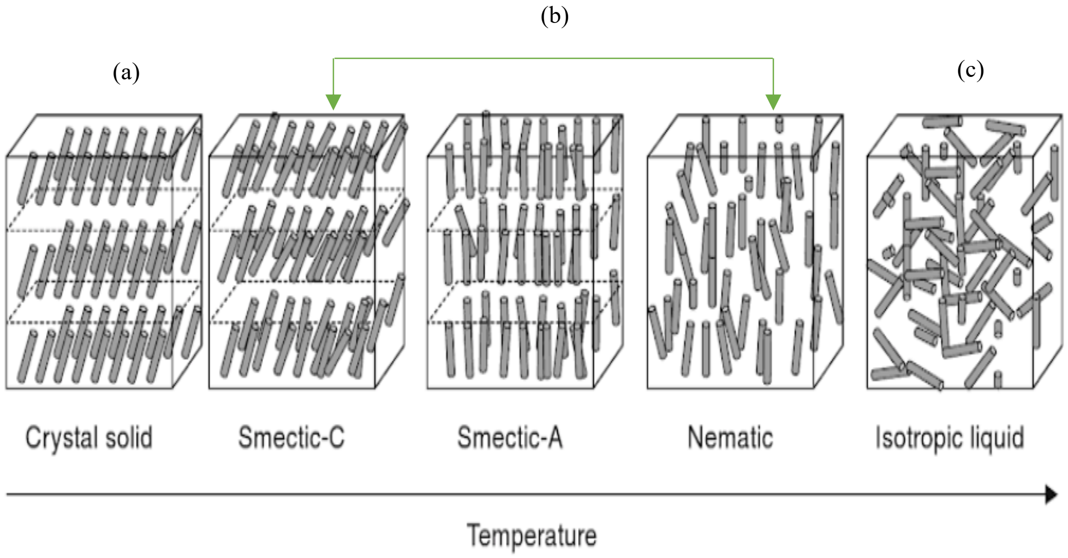


Figure 1.1. Molecular arrangement in (a) crystalline solid, (b) liquid crystal state: smectic C (SmC), smectic A (SmA), nematic (N) and (c) isotropic liquid (Yang, 2014).

1.4 Problem Statements

There are several drawbacks found in the previously reported soft condensed materials comprising biphenyl unit as the mesogenic group connected to rigid core system where their drawbacks have drawn our interest to create some structural modifications to these materials. One of the issues that emerges from the reported soft materials containing biphenyl unit carried out by Ito and co-workers is the phase transition of the compounds that can only be observed during the heating cycle (Ito *et. al.*, 2013). In the present study, the methoxy substituent at the aromatic imine will be introduced to ensure the compound shows the phase transition during cooling and heating cycles. Other weakness of soft condensed materials in early research undertaken by Ito and co-workers is the N phase temperature range observed in these materials is small (Ito *et. al.*, 2013). In the present work, various terminal alkoxy chains at the biphenyl system or different terminal halogen substituents at the aromatic imine group as well as *o*-ethoxy peripheral substituent in the central phenyl core will be employed to broaden the temperature range of N phase. The other shortcoming which was found to be very common in earlier reported soft condensed materials containing biphenyl groups was that it only exhibited a single mesophase (Prajapati, 2001; Zugenmaier *et. al.*, 2006; Alshargabi *et. al.*, 2013). Therefore, the structural modification will be employed in this research by introducing 2,6-dihydroxynaphthalene to the biphenyl system to enhance the mesomorphic properties as naphthalene derivatives exhibit rich mesomorphism and higher order structure.

1.5 Research Objectives

The objectives of this research are as follows:

(a) To synthesize and characterize new soft condensed materials comprising of biphenyl units connected to different core systems using various spectroscopic techniques along with thermal and optical analyses.

(b) To investigate the influence of different number of carbon atoms at terminal alkoxy chains and the effect of various terminal substituents X (in which X = OCH_3, F, Cl, Br and I) as well as lateral substituents (o-OCH_2CH_3) on the thermal stability, optical and magnetic behaviors.

(c) To investigate the effect of different core systems on the liquid crystalline properties of the synthesized compounds.

1.6 Research Scopes

The overall organizational structure of this thesis consist of five chapters and each chapter provides specific information on research interest as stated in the research objectives in the preceding section.

- ⇒ **Chapter 1** is an introduction which addresses a general overview of LCs, problem statements, research objectives and research scopes.
- ⇒ **Chapter 2** is devoted to describe the fundamental theory of soft condensed materials, classification and chemical constitution of LCs of prior research related to the present study. A short review on additional feature of LCs is also presented.
- ⇒ **Chapter 3** briefly describes the chemical reagents and research methodology used for this study. This is followed by synthesis and characterization of synthesized compounds. A general experimental procedure of magnetic behavior measurement also described in this chapter. The research work described in this chapter involves four new series of soft condensed materials based on biphenyl unit in the different mesogenic cores, namely phenyl and naphthalene.
  - The compounds presented in the first series possess biphenyl moiety with different flexible terminal alkoxy chains, OC_nH_{2n+1} (n = 7-12) and aromatic imine fragment possessing *p*-methoxy substituent connected by central phenyl core.
  - The second series contains peripheral ethoxy substituent attached to the phenyl center of imine group at the *ortho* position.
  - For the members in the third series, which are analogous to the second series, they possess the terminal substituent X (X = OCH_3, F, Cl, Br

and I) at the *para* position of aromatic imine fragment and heptyloxy terminal chains at the biphenyl moiety.

- The last series consists of naphthalene core with extended side arm made up by biphenyl system and the terminal alkoxy chains, OC_nH_{2n+1} varied from n = 7 to 12.

⇒ **Chapter 4** discusses the molecular structures for the synthesized compounds are elucidated using CHN microanalysis and various spectroscopic techniques such as fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR). The texture of liquid crystals are observed by polarizing optical microscopy (POM). Differential scanning calorimetry (DSC) is used to determine the phase transition temperatures and associated enthalpy values of the synthesized compounds. The magnetic behaviors of all the title compounds are investigated by the direct method using permanent magnet. Magnetic interaction of representative compounds are substantiated by the superconducting quantum interference device (SQUID) magnetometer. The research work in this thesis involves the study of various terminal alkoxy chains or terminal substituents on the thermal stabilities, liquid crystalline properties and magnetic interaction. These studies are then compared with their analogous compounds containing *o*-ethoxy substituent. Moreover, this research also covers the influence of two different core systems on the mesomorphic behaviors of the synthesized compounds. Furthermore, the liquid crystalline and structural properties relationship for all target compounds in each series will be further investigated.

⇒ **Chapter 5** summarizes the entire findings in connection with the objectives of this thesis and recommendations of future works have been presented.

CHAPTER 2 – LITERATURE REVIEW

2.1 History and Development of Liquid Crystals

The discovery of liquid crystals (LCs) began in 1888 by an Austrian botanist, Friedrich Reinitzer. He found two distinct phase transition temperatures of cholesteryl benzoate extracted from carrots (Figure 2.1). He spotted that the white fine cholesteryl benzoate melted into a cloudy fluid at 145.5 ˚C. At first, he assumed the turbidity of the reported compound is due to the existence of the impurities but additional studies had ruled out this assumption. On further heating, the cloudiness suddenly faded and became a clear transparent liquid at 179 ˚C (Kawamoto, 2002). He also observed the appearance of violet and blue colors which vanish immediately with the sample leaving the lactescent, turbid but fluid. The continuous cooling had demonstrated the reformation of violet and blue colors and subsequently the sample crystallized. In 1889, this phenomenon had been carried out in detail by Otto Lehmann, a German physicist. He discovered the optical anisotropy of the opaque phase exhibited a double refraction effect, characteristic of a crystal in Reinetzer's sample. Then, he began to name this mesomorphic state as "fliessende krystalle" which is also known as liquid crystal (Kawamoto, 2002).

In 1889, L. Gatterman and A. Ritschke synthesized the first synthetic liquid crystal of *p*-azoxyanisole. A French mineralogist, Georges Friedel developed a classification of liquid crystals (nematic, cholesteric and smectic) based on their structural properties. He also reported the orienting effects of electrical and magnetical fields (Keller, 1988; Castellano, 2005). The correlation principles between molecular structures and the presence of the liquid crystalline state has been explored by D. Vorländer (Demus, 2001). Pierre-Gilles de Gennes, who was awarded with the Nobel Prize in Physics 1991, revealed the ordering of molecules in liquid crystals and polymers. He also observed the relations between liquid crystals and superconductors in addition to the magnetic materials (de Gennes, 1972; de Gennes, 1992; de Gennes, 1992).

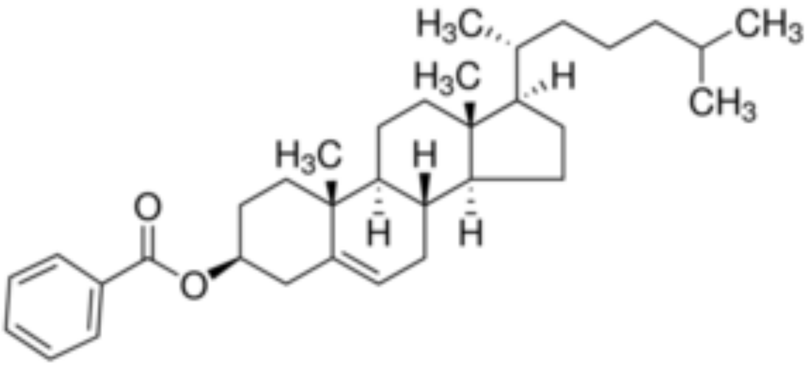


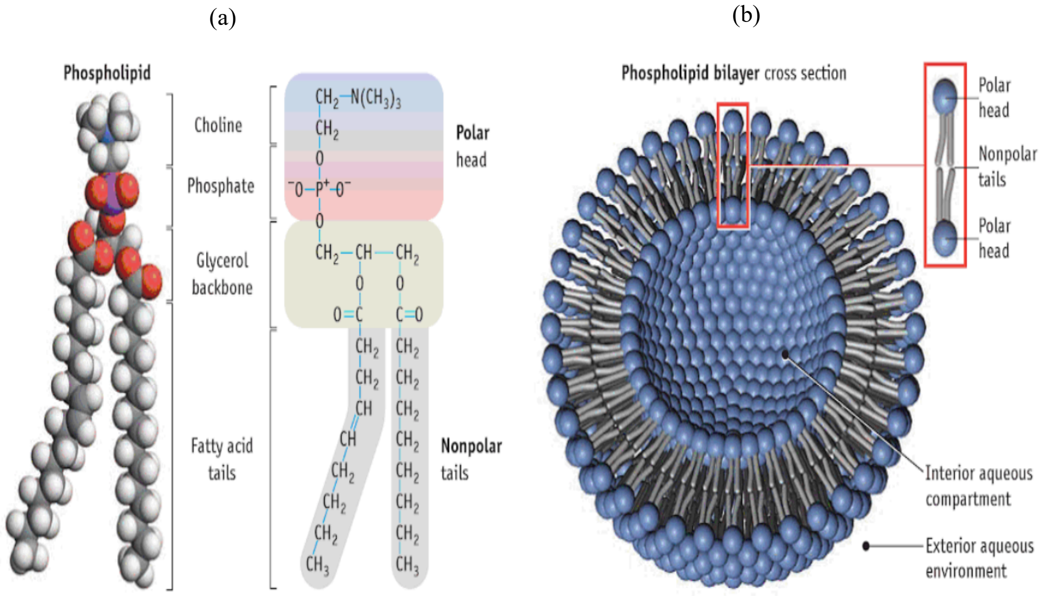
Figure 2.1. Molecular structure of 5-cholesten-3-yl benzoate (cholesteryl benzoate) (Chester *et al*., 2013; Goodby *et al*., 2014).

2.2 Types of Liquid Crystals

Liquid crystals (LCs) are generally categorized into two types which are lyotropic and thermotropic liquid crystals. The fundamental distinction between them can be distinguished by their molecular composition structure, molecular size and the formation of liquid crystalline phase.

2.2.1 Lyotropic Liquid Crystals

Lyotropic LCs is comprised of two or more components where the mesophases are induced by the influence of certain concentration range in the isotropic solvent on the amphiphilic compounds. The compounds usually consist of two different moieties, which are hydrophobic tail (saturated or unsaturated hydrocarbons) and hydrophilic head (ionic or non-ionic) group (Figure 2.2). In lyotropic phases, the space of the compounds are surrounded by the solvent molecules which contribute to the fluidity of the system (Jameson *et al*., 2007). Under the critical micelle concentration (cmc), the molecules act independently and the molecular orientation are dispersed randomly throughout the water or other solvents. As the concentration increases, the size of micelles molecules will be increased which leads to the LCs formation (Barzic and Ioan, 2016; Zhou, 2017).


(a)

(b)

Figure 2.2. (a) The chemical structures of phospholipid molecule and (b) a cross-section of phospholipid bilayer composed of hydrophilic head (water lover region) with polar chemical groups and hydrophobic tails (water haters region) consist of saturated or unsaturated hydrocarbons which are in the interior of bilayer (Kotz *et al*., 2009).

2.2.2 Thermotropic Liquid Crystals

The single component systems which display liquid crystalline behavior within a certain temperature range is referred as thermotropic LCs (non-amphiphilic anisometric mesogen). The thermotropic LCs are usually formed by compounds comprising of rigid core (aromatic and non-aromatic) and flexible terminal moiety (aliphatic chains). The introduction of the flexible terminal chains on the rigid unit are very useful in promoting the mesomorphic properties. This thermotropic LCs occurred due to the anisotropic dispersion forces among the molecules, as well as the stacking interactions between the molecules (Gopal Rai, *et al*., 2010). The transition temperature at which crystalline solid (Cr) changed to mesophase is known as melting point while the clearing point (isotropization) can be defined as the transition temperature of liquid crystal phase which transformed to the isotropic liquid.

Thermodynamically stable mesophase which formed upon both heating and cooling cycles are documented as enantiotropic phase whereas the thermotropic metastable mesophase that can only be observed during cooling or heating cycle is termed as monotropic liquid crystal. Thermotropic LCs can be classified into two general groups based on the molecular shape of the constituent molecules which are conventional liquid crystal and non-conventional liquid crystal.

2.3 Geometrical Shapes of Thermotropic Liquid Crystals

2.3.1 Non-conventional Liquid Crystals

In recent years, much work on the designing and synthesizing different molecular architectures in which the anisometric shape of the molecules is different from the conventional LCs of calamitic or discotic molecules that are known as non-conventional liquid crystals have gained a lot of attention by the researchers (Demus, 1989; Tschierske, 1998; Pathak *et al*., 2016; Wöhrle *et al*., 2016). Non-conventional LCs are formed by the self-assembly system with covalent complex molecules tethering of several mesogenic (anisometric) segments through discrete molecular fragment namely flexible components either chains or spacers. Many studies have been reported that the shape anisotropic molecules of non-covalent LCs have a prominent influence on the mesomorphic behaviour in which these molecules stabilized the liquid crystallinity (Ooi *et al*., 2013). These LCs molecules are compensated by the nano-segregation of physically or chemically incompatible molecular fragments and the propensity towards the efficient space filling in the condensed matter (Skoulios *et al*., 1988; Pegenau *et al*., 1999; Tschierske *et al*., 2001; Achalkumar *et al*., 2011). Some non-conventional LCs are oligomers, dimers, dendrimers, dendrons, bent-core molecules, multi-armed mesogens, rod-coil molecules, metallomesogens and hydrogen-bonded mesogens (Chunxiu Zhang, 2008;

Lehmann, 2008; Ooi *et al*., 2013; S.K. Gupta *et al*., 2013; Imrie *et al*., 2014; Yeap *et al*., 2013; S.K. Pathak *et al*., 2016).

2.3.2 Conventional Liquid Crystals

The anisometric discotic (oblate) molecules or calamitic (prolate) molecules commonly formed the conventional LCs. These states of soft matter occurred due to the steric packing of the molecules (Ha *et al*., 2010).

2.3.2(a) Discotic Liquid Crystals

The first systematic study of hexa-n-alkanoyloxybenzenes based on disc-like molecular architecture (discotic) that displayed mesomorphic properties have been reported (Kumar, 2016). Since then, a considerable amount of literature on the discotic LCs have been published. Further investigation had been confirmed by the French researchers, Dubois and Levelut on the discotic molecules that also capable to show liquid crystalline phase (Schmidt-Mende *et al*., 2001; Paquette, 2012). Discotic molecules show a huge disparity between the thickness (T) of disc and the diameter (breadth) of the molecule wherein the disc thickness is lesser than the molecular diameter. Figure 2.3 shows the general molecular shape of the discotic LCs. Discotic molecules composed of numerous amount of long flexible side chains (paraffinic chains) that are laterally bonded to the relatively flat discotic core. Many variations can be applied to these discotic mesogens depending on their molecular shape and symmetry by changing the central unit, side chains or the type of the connecting groups that lead to the wide range of liquid crystal compounds. The mesophases that exhibited by disc-shaped molecules resulting into two general classes which are nematic discotic (Figure 2.4(a)) and columnar (Figure 2.4(b)). The nematic discotic molecules possess orientational ordering of the disc with no long-range translational order while the columns that are formed by the stack arrangement of disc-shaped molecules are referred to columnar phase. These columns are self-organized in various two-dimensional crystalline array.

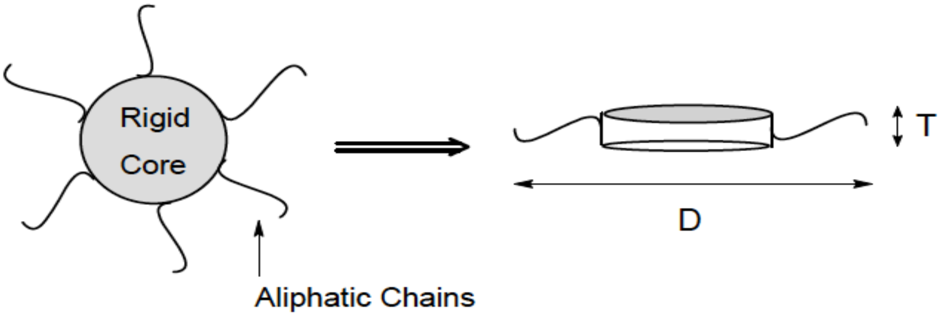


Figure 2.3. The schematic diagram of general molecular shape of discotic liquid crystals (Dawood *et al*., 2015).

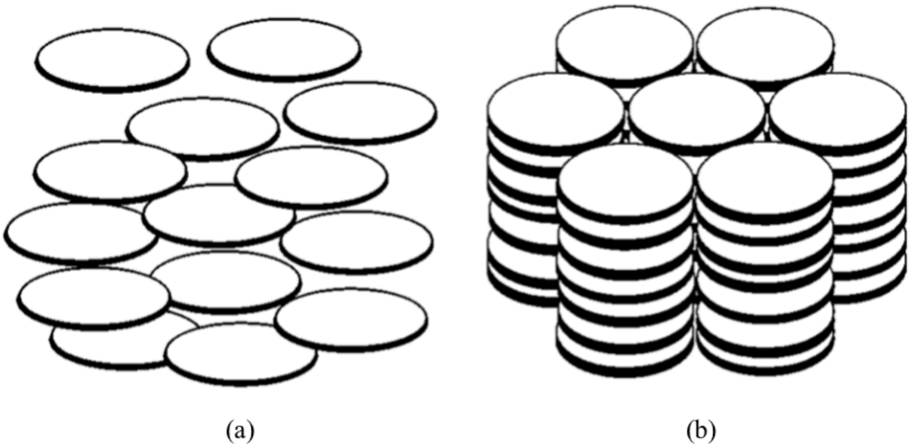


Figure 2.4. The schematic representative of (a) the discotic nematic and (b) columnar phase (Sandeep Kumar *et al*., 2002).

2.3.2(b) Calamitic Liquid Crystals

The molecular geometry of the rod-like (elongated) molecules favor the monomeric calamitic LCs in which the molecular length (l) is significantly greater than the molecular breadth (h) as represented in Figure 2.5. Clearly, the rod-like molecules are packed together in parallel manner to extend the utilization of the space available and to narrow the free volume (J. W. Goodby *et al*., 2015). Calamitic molecule is one of the most influential molecular types in the formation of liquid crystal. These calamitic mesogens typically comprise of rigid central unit system and flexible hydrocarbon chains. Figure 2.6 provides an illustration of calamitic mesogen's template and an example of calamitic LCs.

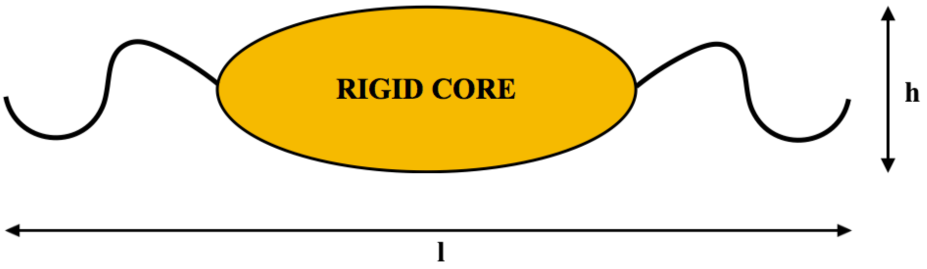
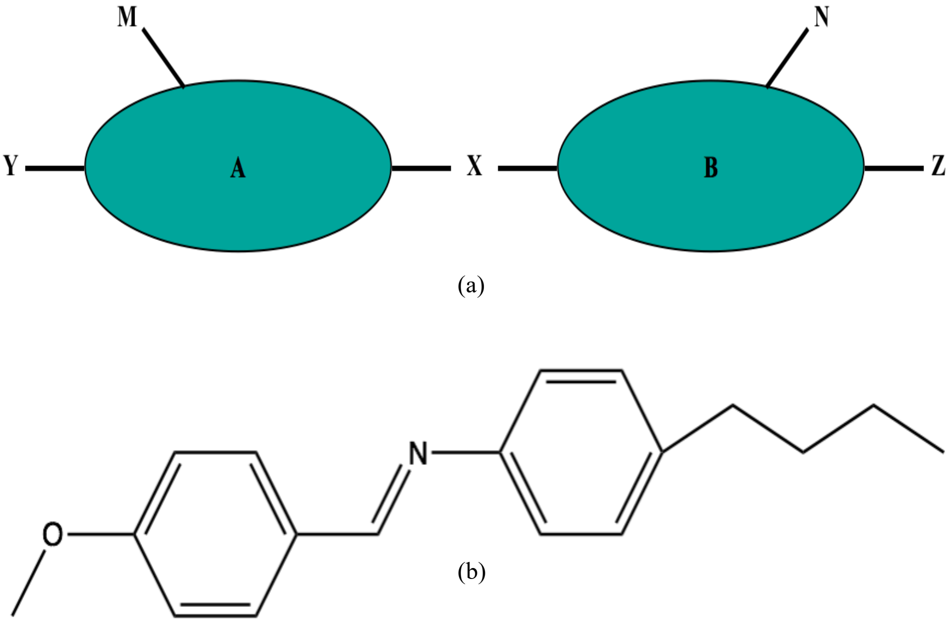


Figure 2.5. Illustration of calamitic LCs, where length (l) >> breadth (h) (Goodby *et al*., 2014).



(a)

(b)

Figure 2.6. (a) General structural template of rod-like LCs and (b) representative example of calamitic LCs (Collings and Hird, 1997).

The terms A and B usually encompass core unit such as aromatic or alicyclic cores which are interconnected through linking group comprising of covalent bonds. The linking groups, X may have contributed to the increase in the length and flexibility of the molecules. The abbreviations Y and Z will be used to refer to the terminal moieties. Hydrocarbon chains (alkyl or alkoxy) and polar terminal substituents (halogen, cyano, acyloxyl and nitro groups) are the most frequently used terminal moieties. M and N are used to describe the lateral substituents (hydroxy, alkoxy, alkyl, cyano or nitro groups).

2.4 Calamitic Mesophase Structures

Friedel stated that mesophases exhibited by rod-liked molecules are primarily of two types which are nematic (N) and smectic (Sm) phases.

2.4.1 Nematic phase

Nematic phase has been identified as the most disordered mesophase with highest symmetry which is the closest to the isotropic liquid state. Hence, the molecules are self-aligned along the same direction known as director, n to have spontaneous long-range directional order. Thus, the molecules do not show any positional order in which the molecular mass center of the molecules are randomly distributed. Furthermore, the nematogenic LCs can be identified as small droplets and the schlieren textures under the polarizing optical microscope (POM). Figure 2.7 depicts the molecular arrangement and optical texture of nematic phase.

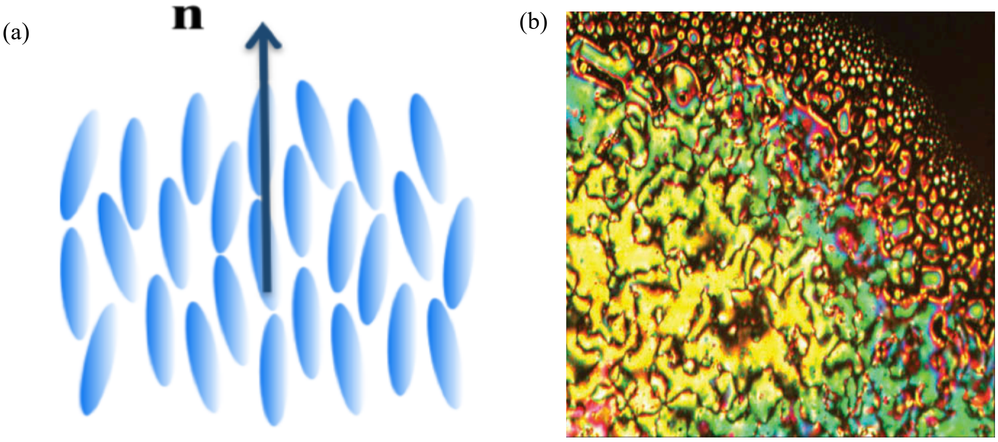


Figure 2.7. The schematic depiction of (a) the molecular alignment of nematic phase (Singh *et al*., 2015) and (b) the schlieren texture of N phase (Heng *et al*., 2014).

2.4.2 Smectic phase

The study of the mesomorphic behavior of the smectic phase was first discovered by D. Vorländer in 1908 (Demus, 2001). Smectic phase has been regarded as being more complex and ordered phase compared to the nematic LCs. The Sm phases display orientational order and they also possess higher degree of positional order than nematogenic phase. The Sm LCs occur at lower temperature range than nematic LCs. Hence, the molecules are able to align and organize themselves into well-defined layers that can slide to one another that can be observed like a soap. Generally, Sm phase tend to occur at the temperature lower than nematic LCs (Kelker and Hatz, 1980). The smectic phase can be classified according to the packing formation and the order in the layer system into smectic A (SmA) and smectic C (SmC) phases.

The molecules in the SmA phase has been acknowledged as the least order among all types of Sm phases wherein the molecules are parallel to each other and they are organized in the diffuse layers with the orientation of the long axes perpendicular to the layer plane (Figure 2.8a). In addition, the fluidity property of the SmA phase is much viscous than the nematic phase. This phenomenon could be attributed to the feeble attractions of interlayer and strong lateral forces among the molecules that allow the molecules to slide easily among each other (Chandrasekhar, 1983; Chandrasekhar, 1992).

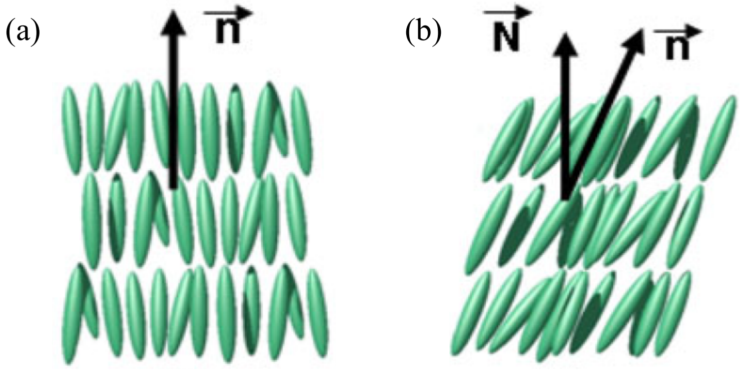


Figure 2.8. Molecular arrangement in (a) SmA and (b) SmC phases (Barois *et al.*, 2012).

In SmC phase, the molecules possess similar molecular distribution as in SmA phase in which the molecules are aligned parallel to one another. In contrast to SmA phase, the long axes of SmC phase is not perpendicular to the normal layer but they tilted at an angel, θ with respect to the layer planes (Figure 2.8(b)). The SmC phase in many situations always appear at lower temperatures than the SmA phase, if both phases are observed in the similar compound (Pershan, 1988).

2.5 The Influence of Chemical Constitution on Calamitic Liquid Crystals

The design of specific compounds to generate liquid crystalline behavior involves the selection of core system, linking (connecting) groups, terminal moieties as well as peripheral (lateral) substituents which will be discussed further in the following sections.

2.5.1 Core System

The core system is referred to the rigid fragments that are linearly and directly connected to the aromatic rings or sometimes linked by a connecting group (X). The rigid core units mostly consist of benzene ring, biphenyl, cholesteryl, heterocyclic, naphthalene, thiophene and alicyclic ring in several combinations. These core units play an important role in influencing the thermal stability, optical behavior, bending angle, polarization and reorientational viscosity of the LCs compound. In 1983, Maged A. Osman studied the influence of the structural differences in the rigid core of the molecules on the LCs properties. Besides, Fornasieri and co-workers demonstrated three series of rod-like LCs comprising of a mesogenic core (monophenyl or biphenyl or phenyl benzoate group) bonded to a perflourinated chain through thioester linkage and a hydrocarbon chains with terminal double bond. It has conclusively been shown that with the increase of the aromatic rings in the core structure of the LCs compound as well as elongating the hydrocarbon chains gave significant effects on the mesomorphic behavior and transition temperature wherein the long hydrocarbon chains led to a reduction in the mesomorphic property, while increasing the number of aromatic rings in the core fragments resulted in the increase of the transition temperature (Fornasieri *et al*., 2003). A recent work by Luo and co-workers involved a study of the effects of various core units in a series of menthol-based compounds, in which compound without a conjugated system in three phenyl core showed the widest blue phase temperature range compared to the other compounds with conjugated structures. This phenomenon can be ascribed due to an increase in rigidity and linearity of the core fragments, as well as the increase in the length-to-breadth ratio that occurred in the aromatic ring systems (Luo *et al*., 2018).

2.5.2 Linking Groups

Numerous functional groups have been used as linking groups (common examples: -CH=N=, -N=N-, -COO-, -CH=CH-, $-CH_2-CH_2$ and -C ≡C-) between two or more aromatic rings wherein the presence of the connecting groups help to maintain the molecular linearity and enhance the polarizability anisotropy. As such, it provides high stability of the molecular length and allowing the formation of mesophases (Collings and Hird, 1997). Jankowiak and co-workers published a paper in which they examined the influence of the linking group on the LCs behaviors of several series of isostructural compounds consisting *p*-carborane derivatives and their hydrocarbon analogues. They found that the effectiveness of the linking group in the mesophase stabilization in the *p*-carborane derivatives and their hydrocarbon analogues followed the order of $-CH_2CH_2-$ < -OOC- < $-CH_2O-$ < -COO-. They also discovered that the $-CH_2CH_2-$ and -OOC- linking groups of *p*-carborane derivatives destabilize the mesophase greater than $-CH_2CH_2-$ and -OOC- linking groups of carbocyclic derivatives (Jankowiak et al., 2009). More recent work by Chothani and co-workers investigated the influence of different linking groups on the thermal stability and mesophase temperature range of mesogenic compounds, in which the cinnamate linking group showed higher average mesophase and thermal stability, as well as higher clearing temperature compared to ester linking group. This happened due to the presence of non-coplanarity of cinnamic acid core as a mesogenic fragment that have a tendency to increase the length-to-breadth ratio, which is almost half length of other rod-like (calamitic) cores. Besides, the addition of double bond in the cinnamate linkage leading to an increase in the length and polarizability of rod-like molecules (Chothani et al., 2016).

2.5.3 Terminal Moieties

The rigid core alone has a strong inclination not to show any LCs properties, hence the terminal moiety is introduced to offset the molecular structure to generate the mesophases. A surprising number of terminal substituents have been employed in the LCs system such as flexible terminal chains (alkoxy or alkyl) and polar terminal substituents. Jber *et. al* studied the effect of different terminal alkoxy chains, C_nH_{2n+1} (n = 1 to 8) of the Schiff base esters in which the lengthening of the terminal alkoxy chains resulted in a significant effect on the mesomorphic behaviour (Jber *et al*., 2014). Throughout their observation, the monomers with shorter terminal alkoxy chains (n = 1 and 2) do not possess LCs properties due to the rigidity of molecules, therefore having high melting points and inhibiting their mesomorphic behaviour. The increase of the carbon atoms from n = 7 to n = 8 in the terminal alkoxy chains has suppressed the presence of N phase and led to the formation of Sm phase. Chothani and co-workers reported a series of rod-like molecules comprised of naphthalene moiety having different terminal alkoxy chains and oxadiazole unit with thioalkyl chains (Chothani et al., 2016). They identified that in elongating the terminal chain lengths led to a reduction in clearing and melting temperatures, as well as a decrease in mesophase temperature range. This is due to increase in dipole-dipole interactions that occurred between the terminal chains. The polar terminal groups enabled substantial intermolecular forces to stabilize the molecular orientation as they can form dipoles along or across the molecular axis (Ooi *et al*., 2013). In another work, the influence of terminal polar (cyano) and non-polar (alkyl and alkoxy) substituents on the thermodynamic mesophase stability in relation to their effect on the molecular packing has been explored (Osman, 1983).

2.5.4 Peripheral Substituents

Peripheral (lateral) substituents can be loosely described as one that is not located along the molecular axis which is bonded to the core systems of the molecules. They are frequently used to alter the physical behavior and the LCs morphology, even their presence have led to the disturbance of LCs formation (Collings and Hird, 1997) and bring about to increase the intermolecular interaction. In general, the peripheral substituents are recognized as being the most important role to reduce the phase transition temperatures where in their existence lower the length to breadth ratio as well as the clearing temperatures (Weissflog *et al.*, 2001). Various notable examples of lateral substituents are cyano, nitro, halogens, alkyl, alkoxy and hydroxy groups.

The experiments on the effect of various peripheral substituents on mesogens comprising azo functional group and naphthalene moiety had been reported (Prajapati, 2000; Prajapati and Pandya, 2003; Prajapati *et. al.*, 2004) wherein all title compounds encompassing peripheral substituent exhibited LCs properties. Comparison studies had also shown that the influence caused by the chloro is found to be more pronounced than the lateral methyl and methoxy groups (Prajapati *et al.*, 2003). Previous research has indicated that the increase in size of lateral substituents have been identified as major contributing factors for the decline of the clearing temperatures (Qaddoura *et al.*, 2009). The study on the effect of various lateral substituents on a central benzene ring have been identified to display mesomorphic behavior, where all lateral substituents (-OH, -CH_3, and -Cl) except lateral fluoro substituent only exhibited nematogenic phase, whereas their unsubstituted analog and lateral fluoro substituent showing N and SmC phases. This occurrence can be explained due to length to breadth ratio of lateral fluoro substituent and unsubstituted analog to the terminal attraction forces are high as compared to the other lateral substituents (Al-Hamdani *et al.*, 2010).

2.6 Additional Features of Monomeric Liquid Crystals

Apart from behaving as liquid crystals, the monomer compounds can also exhibit some unique features including magnetic properties which will be discussed in the forthcoming section.

2.6.1 Magnetic Properties

A large and growing body of literature has investigated the magnetic phenomena in the LCs materials due to their extensive and beneficial potential in the technological developments and scientific areas. The LCs compounds that possess magnetic behaviors are usually related to the rare-earth elements, metal-complex and organic radical compounds. Recently, the experimental studies have shown the unusual intermolecular magnetic interaction in the SmC phase of organic radical compound (Uchida *et al*., 2008). To better understand the effect of the macroscopic structures on the magnetic properties, Umeta and co-workers analyzed the magnetic properties of organic radical fibers aligned self-assembled in the LCs. The organic radicals are anticipated as organic magnetic compounds because of the magnetic moments obtained from the odd electrons (Umeta and Eimura, 2015). Magnetic LCs containing rare-earth complex are attracting widespread interest due to their large magnetic anisotropy, hence the external magnetic field are required to align these paramagnetic LCs (Binnemans *et al*., 2000).

CHAPTER 3 – MATERIALS AND RESEARCH METHODOLOGY

3.1 Overview

This chapter provides description on the research flow chart that gives overall overview of the experimental flow. The information of chemicals, characterization and research methodology used to achieve four new series of soft condensed materials comprising of biphenyl units connected to different core systems, namely phenyl and naphthalene also included in this chapter. A general experimental procedure of magnetic behavior measurement was also reported.

3.2 Research flowchart

The flow of whole research methodology conducted for this research was summarized in flow chart as shown in Figure 3.1.

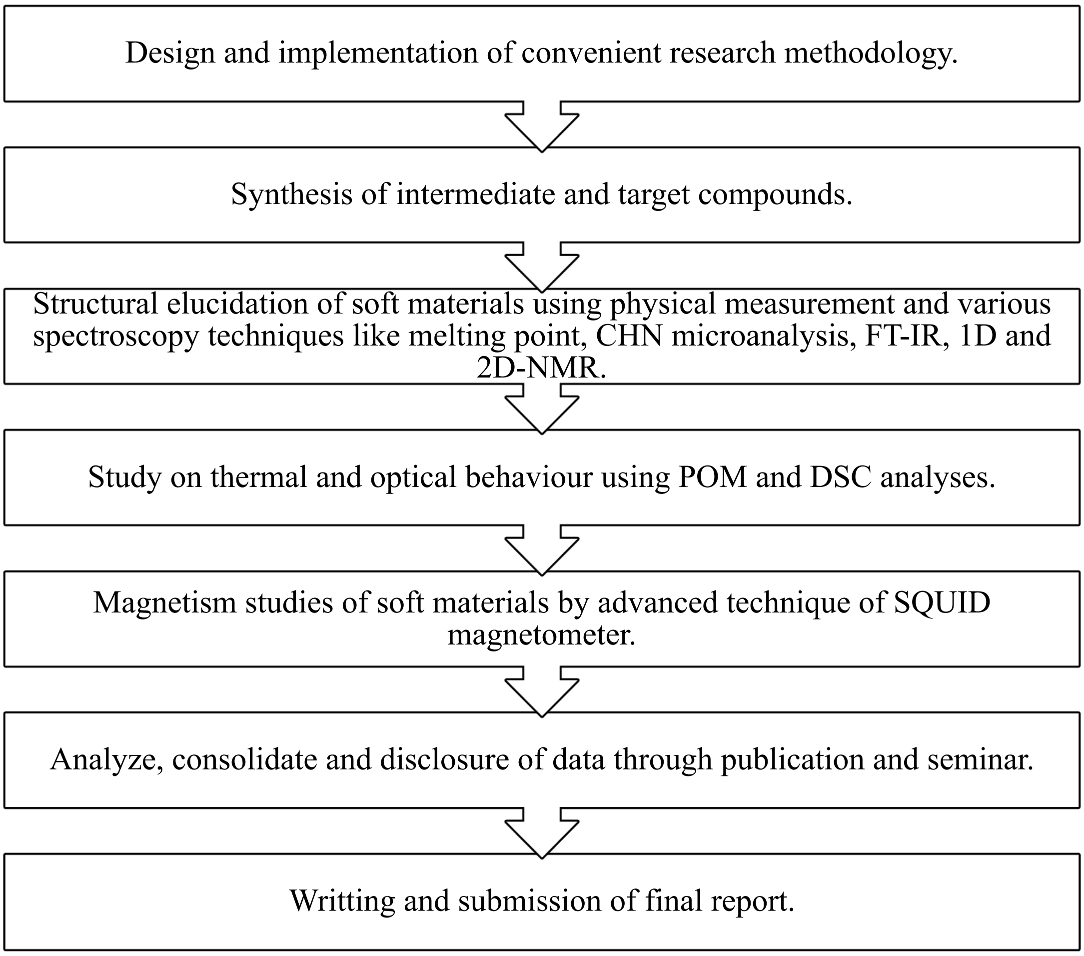


Figure 3.1. General frame work of research flowchart.

3.3 Chemicals

The chemicals reagents with their percentage purity that were used throughout the studies are listed in Table 3.1.

Table 3.1: List of chemical reagents used for the synthesis.

Chemicals	Manufacturer	Percentage purity (%)
Glacial acetic acid	Quality Reagent Chemicals, New Zealand	99.8
Potassium hydroxide	R&M Chemicals, United Kingdom	85.0
Potassium Iodide	R&M Chemicals, United Kingdom	99.5
1-Bromoheptane	Sigma Aldrich, USA	99.0
1-Bromooctane	Sigma Aldrich, USA	97.0
1-Bromononane	Sigma Aldrich, USA	98.0
1-Bromodecane	Sigma Aldrich, USA	98.0
1-Bromoundecane	Sigma Aldrich, USA	98.0
1-Bromododecane	Sigma Aldrich, USA	97.0
4-Methoxyaniline	Sigma Aldrich, USA	98.0
4-Fluoroaniline	Sigma Aldrich, USA	99.0
4-Chloroaniline	Sigma Aldrich, USA	98.0
4-Bromoaniline	Sigma Aldrich, USA	97.0
4-Iodoaniline	Sigma Aldrich, USA	98.0
2,6-Dihydroxynaphthalene	Sigma Aldrich, USA	98.0
4-(dimethylamino)pyridine (DMAP)	Sigma Aldrich, USA	≥ 99.0
4’-Hydroxy-4-biphenylcarboxylic acid	Tokyo Chemical Industry, Japan	98.0
3-Ethoxy-4-hydroxybenzaldehyde	Tokyo Chemical Industry, Japan	> 98.0
4-Hydroxybenzaldehyde	Tokyo Chemical Industry, Japan	> 98.0
N,N’-dicyclohexylcarbodiimide, (DCC)	Tokyo Chemical Industry, Japan	> 98.0