

REVIEW PAPER

Asymmetric Dimeric Liquid Crystals and Their Application as Fluorescence and Nanohybrid: A Review

Zainab Rabeea Banoon ^{*}, Ali Kareem A. Al-Lami, Ahmed M. Abbas

Department of Chemistry, College of Science, University of Misan, Misan, Iraq

ARTICLE INFO

Article History:

Received 03 September 2022

Accepted 25 December 2022

Published 01 January 2023

Keywords:

Chalcones

Luminescence

Nanoparticles

Quantum Yield

Schiff bases

ZnO

ABSTRACT

Asymmetric dimeric liquid crystals (ADLCs) are fascinating and used in fluorescence and nanohybrids. Due to their intermediate condition between solid crystals and isotropic liquids, liquid crystals are important materials. Asymmetric dimeric liquid crystals exhibit remarkable physical and visual properties due to their unique chemical architectures. It covers ADLC synthesis, characteristics, and behavior. Their structural arrangements, which give them chirality, birefringence, and polarizability, are highlighted. Understanding these features unlocks their full potential in many applications. The latter part of the review focuses on the application of ADLCs in fluorescence and nanohybrid systems. These materials have proven to be promising candidates for fluorescence-based devices, owing to their ability to modulate light emission through molecular alignment. Additionally, the incorporation of ADLCs into nanohybrid structures has opened up new avenues in nanotechnology and materials science. Their compatibility with other nanomaterials and their tunable properties makes them suitable for designing novel nanocomposites with enhanced functionalities. Furthermore, the review discusses the challenges and future prospects associated with ADLCs. It highlights the current gaps in research and proposes potential directions for further exploration and development of these fascinating materials. The current review underscores the significance of asymmetric dimeric liquid crystals as a captivating field of study with immense potential in various applications, particularly in fluorescence-based devices and nanohybrid systems. The comprehensive understanding presented here can serve as a valuable resource for researchers and scientists working in liquid crystal chemistry, materials science, and nanotechnology.

How to cite this article

Banoon Z R., Al-Lami A K A., Abbas A M. Asymmetric Dimeric Liquid Crystals and Their Application as Fluorescence and Nanohybrid: A Review. J Nanostruct, 2023; 13(1):274-295. DOI: 10.22052/JNS.2023.01.028

INTRODUCTION

Liquid crystals can be described as an intermediate state that exists between solids, wherein molecules are constrained to a three-dimensional grid with a well-defined molecular structure, position, and direction. On the other hand, in the liquid phase, molecules move freely

and randomly, lacking a specific arrangement. Fig. 1 illustrates how liquid crystals possess unique properties distinct from both solids and liquids, despite sharing some characteristics with each [1, 2].

The specific intermediate state obtained is determined by the thermal energy required to

^{*} Corresponding Author Email: zainabrabeea09@uomisan.edu.iq



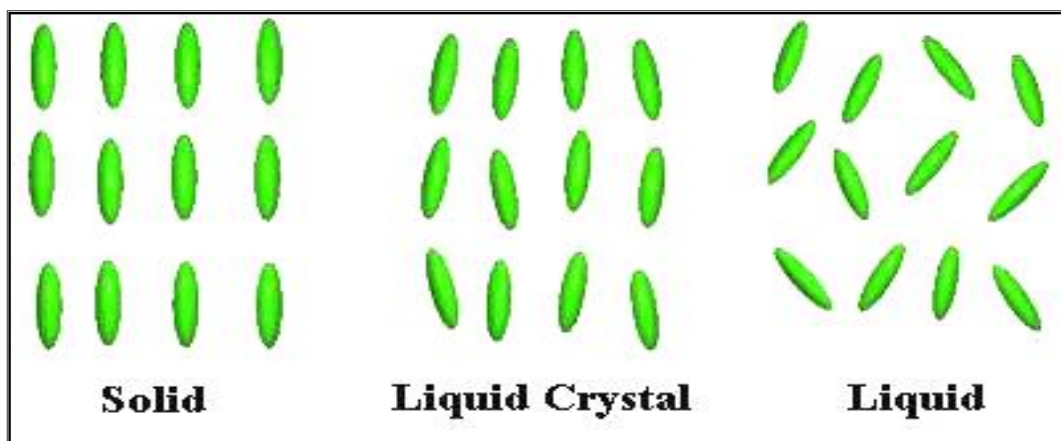


Fig. 1. Molecular arrangement of solid, liquid crystal and liquid [5].

disrupt the parallel arrangement of molecules within the crystal grid. As the temperature rises, the forces between molecules weaken, causing one dimension of the crystal grid to break down and form a two-dimensional system known as the Smectic phase. Further heating will then disrupt the forces in another dimension, resulting in the formation of a one-dimensional system called the nematic phase [3, 4].

In 1888, Friedrich Reinitzer, an Austrian botanist, made an intriguing observation regarding cholesteryl benzoate (shown in Fig. 2). He noticed that it displayed a peculiar fusion behavior with two separate melting points. When heated, the substance transforms into a noxious liquid at 145.5 °C, and upon further heating to 178.5 °C, it undergoes a complete disappearance and turns into a pure liquid (a phenomenon known as isotropy)[6].

Reinitzer was sent to Otto-Lehman, where the world identified a new and distinct state of matter with the help of the polarized microscope and confirmed the existence of the new physical state of the substance [7]. In 1890 he proposed the term “liquid crystalline” for the new intermediate situation and launched an introduction entitled “Fluid crystals” or “Liquid crystals” containing observations on the noxious liquids.

In 1908 Vorlander studied a methodology to determine the relationship between molecular structure and liquid crystal properties [8], providing several research to systematically modify the structure of the aromatic nucleus and study several homogeneous chains, and finding that these changes in transport temperature were always occurring in the series [9, 10], and in 1922 the French scientist Freidel launched the term mesophases on the three liquid crystals (Nematic,

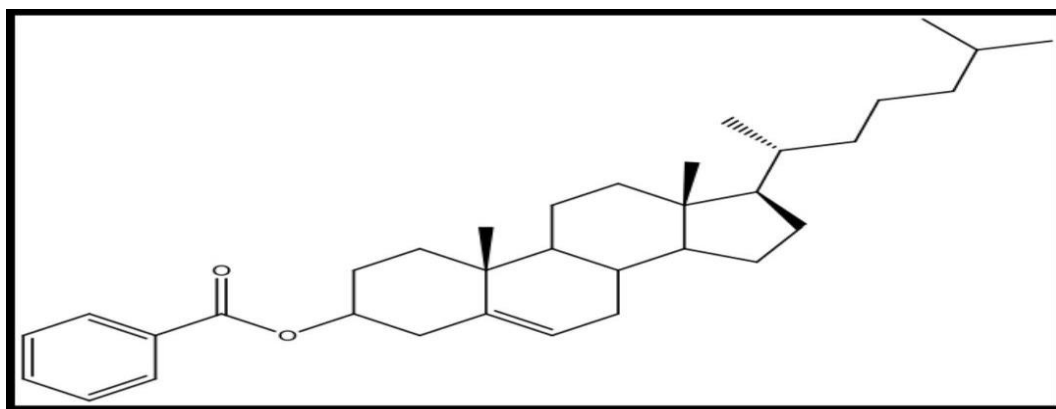


Fig. 2. Structure of cholesteryl benzoate [6].

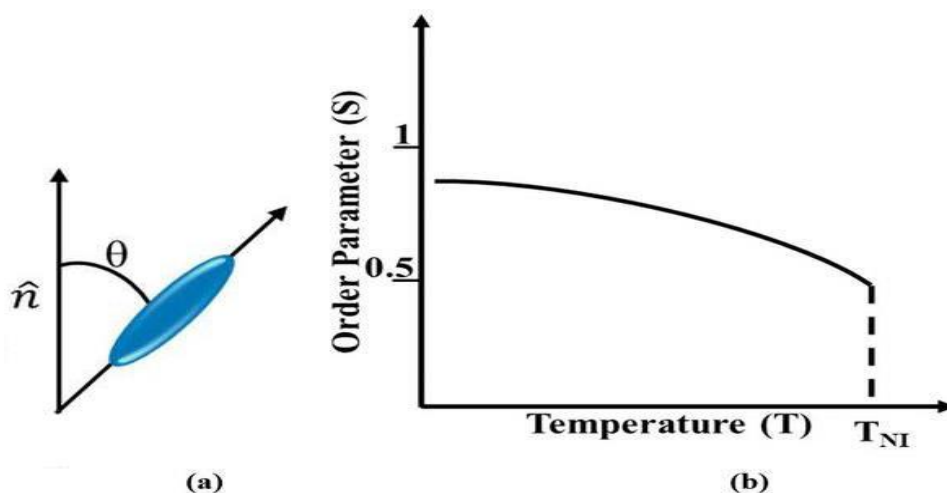


Fig. 3. (a) Liquid crystal director and (b) temperature dependence of order parameter [16].

Smectic, Cholestric) to distinguish them from the rest of the substance, using the polarized optical microscopy and microscopy of textures [11].

Despite these discoveries, liquid crystals were not popular among scientists in the 20th century, but after World War II Gray at Hull University was able to prepare several mesogenic compounds. This work has helped to draw the attention of many scientists to the preparation of compounds that possess mesogenic characteristics and study the relationship between molecular structure and the meogenic characteristics [12].

It was thought that the possibility of preparing liquid crystal phase in polymeric materials was difficult to form, because the polymer chain was usually in coil form while the liquid crystal phases had a long-range orientational order and/or a positional order. In 1956, Paul Flory first proposed the ability of highly degree of order polymers to exist in the liquid crystal state through his studies of the thermodynamic properties of solutions of polymers. Thus, the liquid crystalline behavior of polymeric materials has now received considerable attention because of many different and distinct characteristics, and thus liquid polymers, such as polyazomethines, are considered to be one of the most important liquid crystalline polymeric material produced and their widespread applications in high-performance polymer fibers, optics, energy storage, etc., whose composition can be influenced by the chemical structure of the polymer backbone, mesogenic unit, flexible spacers and the surrounding alkyl

tail [5, 13]. Studies and discoveries of liquid crystal compounds continued, helping to develop and flourish in industrial applications such as computers, clocks, telephones, many electronics, electrons, temperature measures and medicine, as well as their use in liquid crystal display devices (LCD) [14]. To describe the order of molecules within the liquid crystal lattice, it is necessary to clarify two basic concepts:

Director

The Director can be described as the guiding force that represents the collective molecular orientations at each intermediate point. It operates along the visual axis of the phase and can exhibit specific tendencies and possibilities, which may vary from one point to another within the intermediate state. These variations can lead to the emergence of malignancy or unfavorable characteristics, as shown in Fig. 3a.

Order parameter

The order parameter was introduced by the Zwetkow used to describe the degree of molecular alignment with respect to director, and it is given by following equation (1) [15]:

$$S = 1/2(3 \cos^2 \theta - 1) \quad (1)$$

where the angle θ between the director and the long axis of each molecule. The brackets denote an average overall of the molecules in the sample. In an isotropic liquid, the average of the cosine

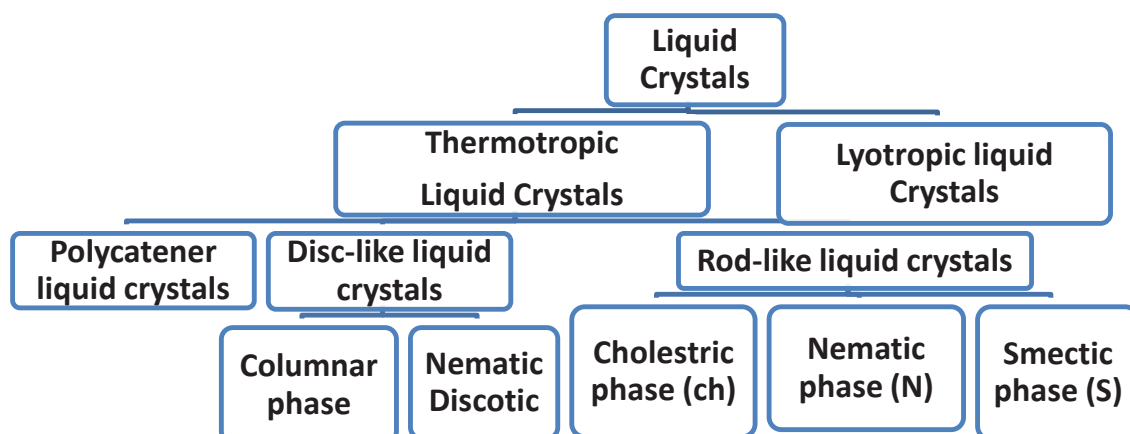


Fig. 4. Types of Liquid Crystals.

terms is zero, and therefore the order parameter is equal to zero. For a perfect crystal, the order parameter evaluates to one. Typical values for the order parameter of liquid crystal range between 0.3 and 0.9, and the exact value is a function of temperature, as a result of kinetic molecular motion. This is illustrated below for a nematic liquid crystal materials. The order parameter is usually found to decrease with increasing temperature and vanishes suddenly at the isotropic transition temperatures [16] as shown in Fig.3b.

TYPES OF LIQUID CRYSTALS

The most widely employed categorization of liquid crystals is depicted in Fig.4.

Lyotropic liquid Crystals

Amphiphilic molecules have the striking property of presenting two antagonistic characteristics within the same molecule, i.e., hydrophobicity and hydrophilicity. In contact with polar and/or nonpolar liquids, under proper temperature and relative concentration conditions, they form lyotropic liquid crystalline phases [17]. The effect of these polar solvents (e.g., water or alcohol) on the combined forces of these compounds consists of a series of lyotropic mesophases, the appearance of which lies between solid and liquid conditions by increasing the concentration of the solvent, i.e., at high concentrations and with enough amphiphilic liquid crystals, the composition of the solvents (Micelles) will be combined. In the case of low concentrations, these liquid crystals do not take any composition, such liquid crystals are of particular importance in biological systems and in

the diagnosis of diseases. A well-known biological example for lyotropic lamellar structures is the lipid bilayers of cell membranes [18, 19] as shown in Fig. 5 a and b, it's an example of a liquid lyotropic crystal Sodium dodecyl Sulfate (SDS) compound Fig. 5c [20].

Thermotropic Liquid Crystals

Thermotropic liquid crystal is temperature dependent. Thermotropic liquid crystal can be characterized by the various phase transitions that occur during heating, displaying temperature transitions between the crystal and the liquid (isotropic) phases and called such compounds polymorphous. If the increase in temperature is too large, all molecular forces will be destroyed and lead to the formation of the isotropy phase as in Fig. 6. The temperature of the transition from crystal to the liquid crystal phase is known as the melting temperature (T_m), while the temperature of the substance from liquid crystal phase to an isotropic liquid is known as the clearing temperature (T_c) [21]. There are two types of thermotropic liquid crystals in which mesophases are shown by heating solid matter and refrigerating liquid inversely called enantiotropic. The other type shows liquid crystals only during cooling, so when the crystals are heated, they melt directly into isotropic liquid and when they are cooled, they show liquid crystals and are called monotropic [22].

The Thermotropic liquid crystals are classified according to the order of the molecules into three categories:

1. Rod-like liquid crystals

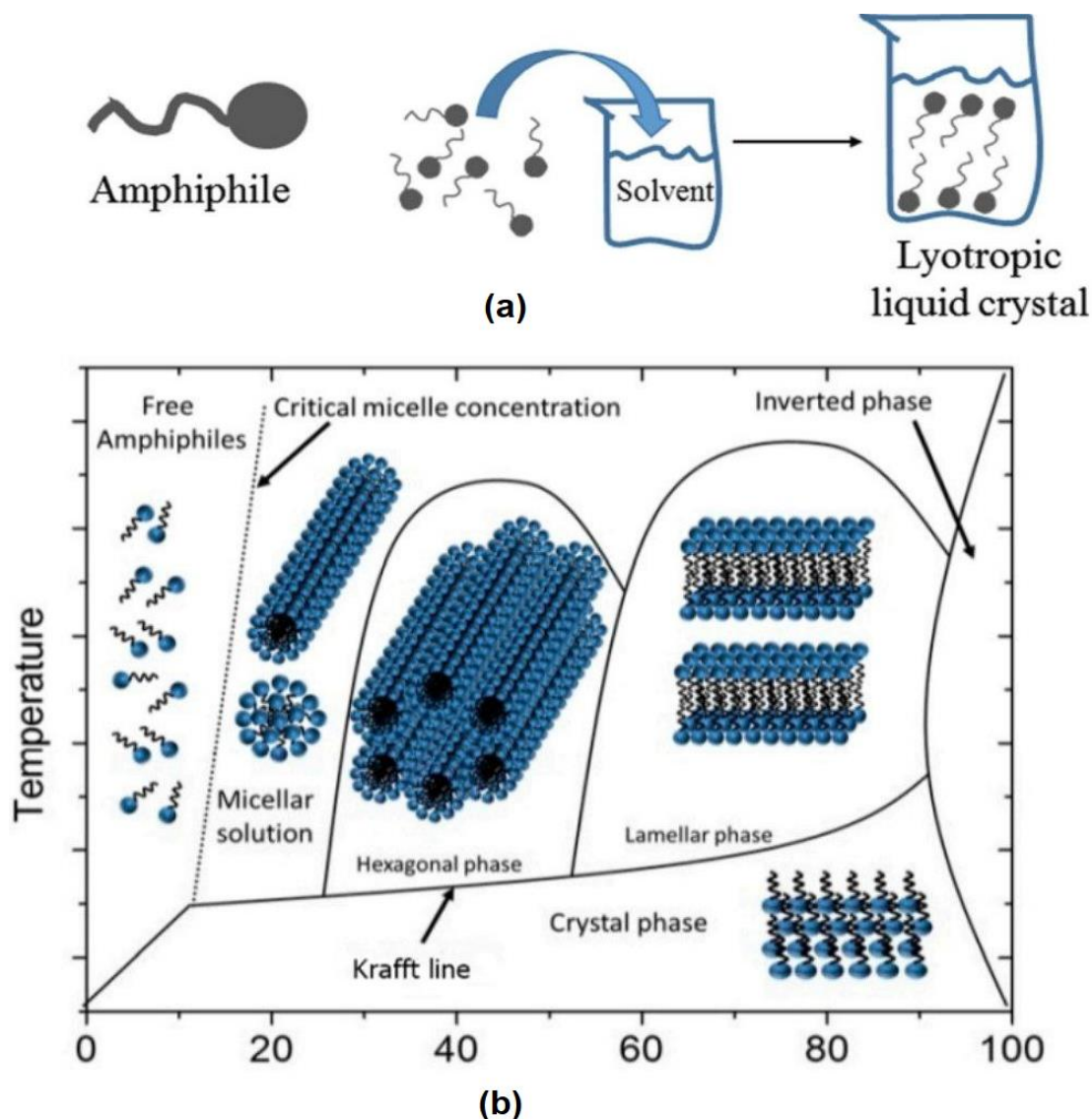


Fig. 5. A, B- A scheme that represents amphiphilic molecules and water affected by changes in concentration and temperature[18].
C- Sodium dodecyl Sulfate as lyotropic liquid crystal[20].

2. Discotic liquid crystals
3. Polycatener liquid crystals

Rod-like liquid crystals

The mesogens in this category possess elongated shape, longitudinally shaped molecules, which are accountable for the manifestation of anisotropic properties., i.e., the variation in the significant physical properties in the molecular form of thermotropics, in order to achieve a phased thermal meltdown of the mesogen, the

molecular implied forces must vary in the physical properties to an appropriate extent, resulting from the fact that the length of the molecule (l) is significantly greater than the molecular breadth (b) called calamitic liquid crystals, as shown in Fig. 7. A typical calamitic mesogen consists of a rigid central core, since it must remain elongated to produce directional interaction. In addition to the flexible side chains which provide a stabilizing effect, there are also rigid linking groups. The rigid core is essentially aromatic, but it may also

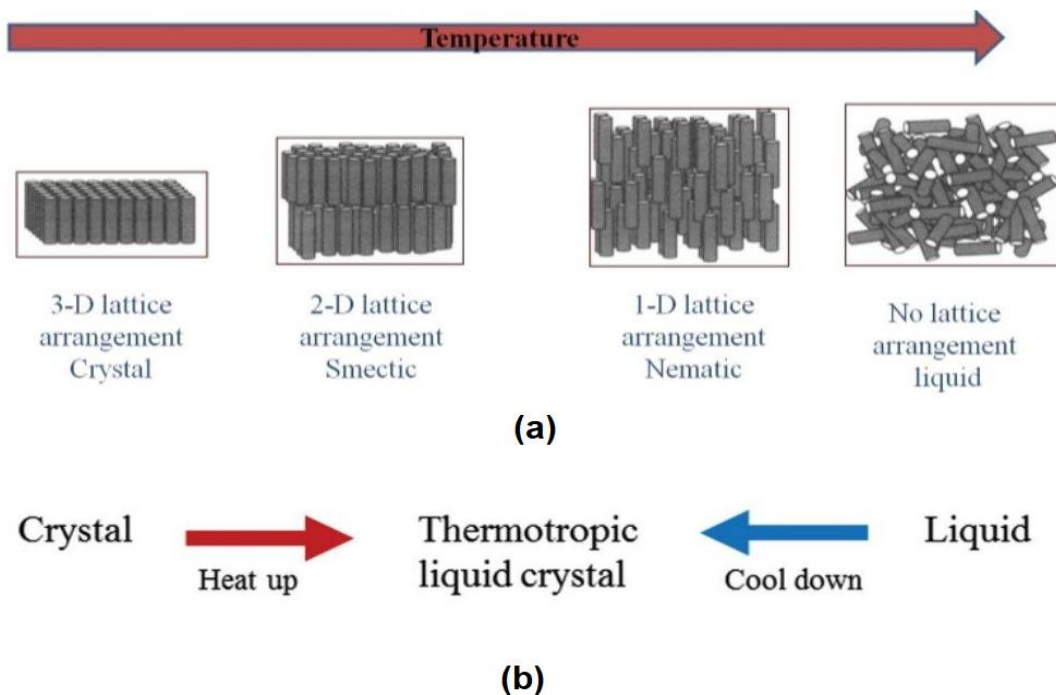


Fig. 6. A-Thermotropic Liquid Crystals[23], B- Mechanism of formation Thermotropic Liquid Crystals.

be alicyclic, and the polar group is also commonly used. Most of these compounds consist of two or more aromatic rings that are directly related to each other or connected by a linking group [23, 24].

The calamitic liquid crystals can be classified depending on the arrangement of the molecules in different mesophase into Smectic phase (S), Nematic phase (N), and Cholestric phase (ch).

Smectic phase (S)

The word “Smectic” is derived from the Greek

word Smectose, which means soap, created by Fridel because the compounds of this phase are a think turbid liquid with soapy properties [25]. Of all the liquid crystal phases, this is the most orderly phase, where molecules at this phase take the order of the class as a result of the parallel alignment of the linear axes of the molecules with each other, adding to the ability of these molecules to sort their end together by placing their weight at the same level, thus having these molecules in the directional order (Long range orientation order) and the positional order. This is characterized by

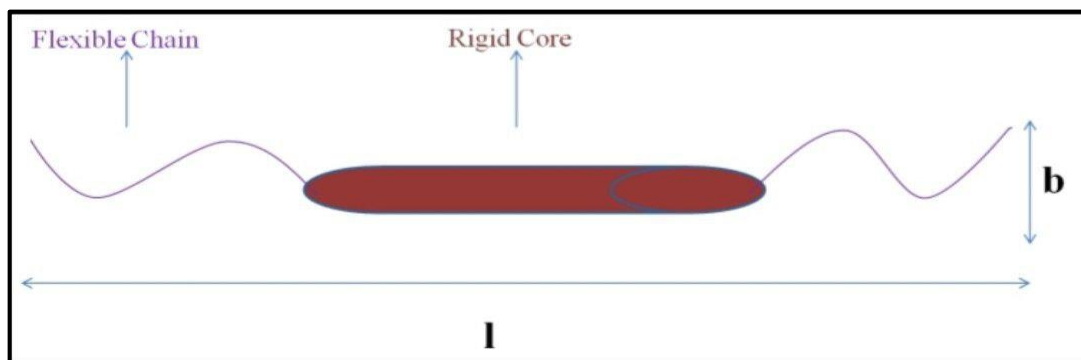


Fig. 7. Calamitic liquid crystals [23].

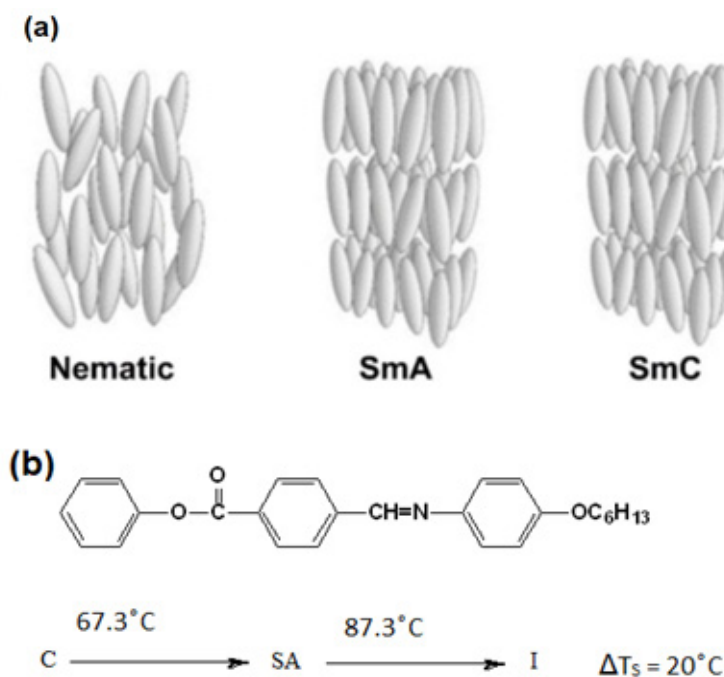


Fig. 8. A-Smectic liquid crystals[13], B- compound in Smectic phase [27].

the free sliding of the layers above each other and by the high viscosity because of the high order of the molecules within the layer that makes the longitudinal movement limited.

Smectic liquid crystals can be classified according to the molecular axle slope for the type of layer, namely SmA, SmB, SmC, SmF, SmI and others, and the most studied Smectic phases are SmA and SmC as shown in Fig. 8a.

In the Smectic-A, the molecules of each layer are arranged vertically, and the centre is unequally arranged such that in a liquid state. The lateral forces between the molecules are strong with respect to the inter layer attraction. Consequently, these layers can glide relatively easily. As a result, this phase has fluid properties. The Smectic-C is tilted from of smectic-A. The molecules are inclined with respect to the layer [23, 26]. It's an example of a Smectic phase as in the compound of Fig. 8b.

Nematic phase (N)

The name of the phase is derived from the Greek word «nema», which means thread since the phase has a thread-like schlieren texture and is characterized by a wide range of directional order (Long range orientational order) while there is no

positional order as a result of the parallel alignment of the longitudinal axes of the molecules and their endpoints overlapped in a finger, where there is no relationship between the centers of the weight of the molecules. In addition, the ability of the molecules to slide freely above each other so that it is least ordered than the Smectic phase when observed under the polarized optical microscopy (POM) shows the Nematics compound the threaded texture, as shown in Fig. 9b [26, 28]. The discovery of the twist-bend nematic phase (N_{TB}) is a milestone within the field of liquid crystals that have a helical structure with a repeat length of a few nanometers, and is therefore chiral, even when formed by achiral molecules, where this discovery has been made into the synthesis and characterization of dimeric and oligomeric liquid crystalline [29], as shown in Fig. 9a.

The nematic phase is very close in its attributes to the isotropic fluid as a one-dimensional system, but it can change in the absence of external steering forces, such as the electric or magnetic fields of the electrotropic state, which makes this phase highly liquid and less liquid for a Smectic phase, and this characteristic is very useful for liquid crystal displays (LCD) [30]. Example of liquid crystals showing a nematic phase in the compound

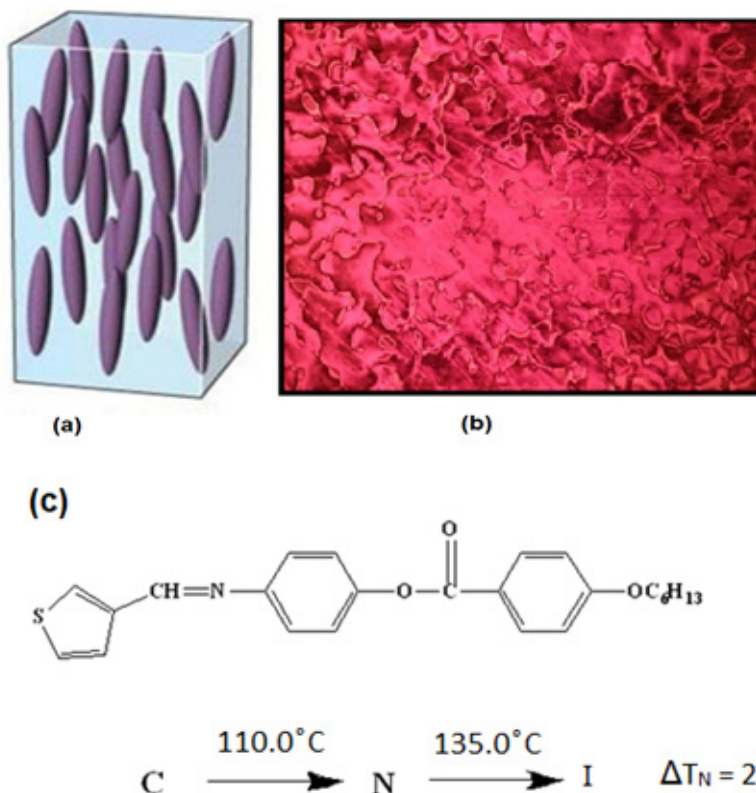


Fig. 9. a-Alignment in a nematic Phase[32], b- Thread-like texture of nematic phase [23], c-compound in nematic phase [31]

in Fig. 9c [31].

Cholestic phase (ch)

The initial discovery of this phase occurred in cholesterol derivatives. The molecules in this phase align parallel to one another, resembling the nematic phase with a broad directional organization. However, unlike the nematic phase, there is no extensive in-plane arrangement where the molecules are organized in a flat configuration. Instead, the director's direction changes in what is known as the cholesteric pitch, giving rise to a helical-like structure commonly referred to as the Twisted Nematic phase. An important physical characteristic of the cholesteric phase is the phenomenon of selective reflection, which is characterized by its brightness and is one of the most important characteristics of the Cholesteric phase. These colors are the first phenomena in the detection of the intermediate phase of liquid crystals, and the absence of colors in some of the cholesterical liquid crystals does not mean that there is no cholesterical phase because the

selective reflection occurs in the red zone of the spectrum or the molecules may be in a particular state of alignment so that they do not lead to the selective reflection. Consider this phase optically active due to possessing helical structure, which rotates the level of bulbing of falling light [16, 33], as appears in Fig. 10.

Discotic liquid crystals

Mesogens with a disc-shaped are known as discotic liquid crystals. In 1977, the Indian scientist S. Chandrasekhar et al. first discovered the disc-shaped mesophase. Typically, discoid mesogens usually consists of a central aromatic functionalized core with three to eight flexible chains. These chains can either be directly attached to the aromatic ring or linked through an ether, ester, or thioether bond. [34, 35]. Disk liquid crystal molecules are characterized by the fact that their diagonal axis is greater than the longitudinal axis, as (d) represents the diagonal axis of the molecule and (t) the thickness of the molecule, as shown in Fig. 11a.

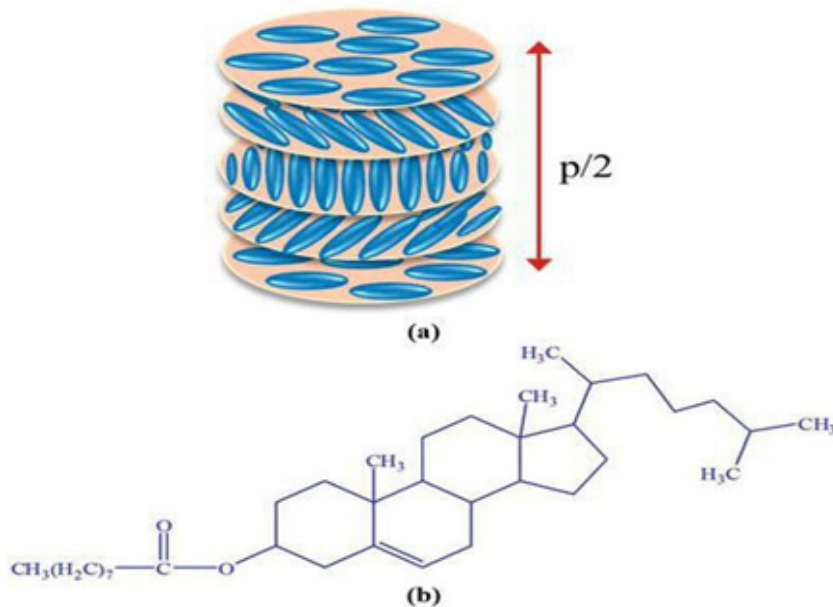


Fig. 10. (a) Molecular arrangement and (b) example of cholesteric liquid crystal phase [16].

There are two main types of discotic liquid crystals:

Disc Nematic phase

The nematic disc phase, represented by (N_D) , is the least ordered mesophases and typically occurs at higher temperatures. This phase exhibits orientational order but no positional order, as the

molecules intersect with each other horizontally and stack in a parallel manner. The discotic nematics has a similar structure to the calamitic nematics, although in this case, the axis of the disc is more or less in the same direction.

Columnar phase

It is denoted by the symbol (C_o) . The columnar

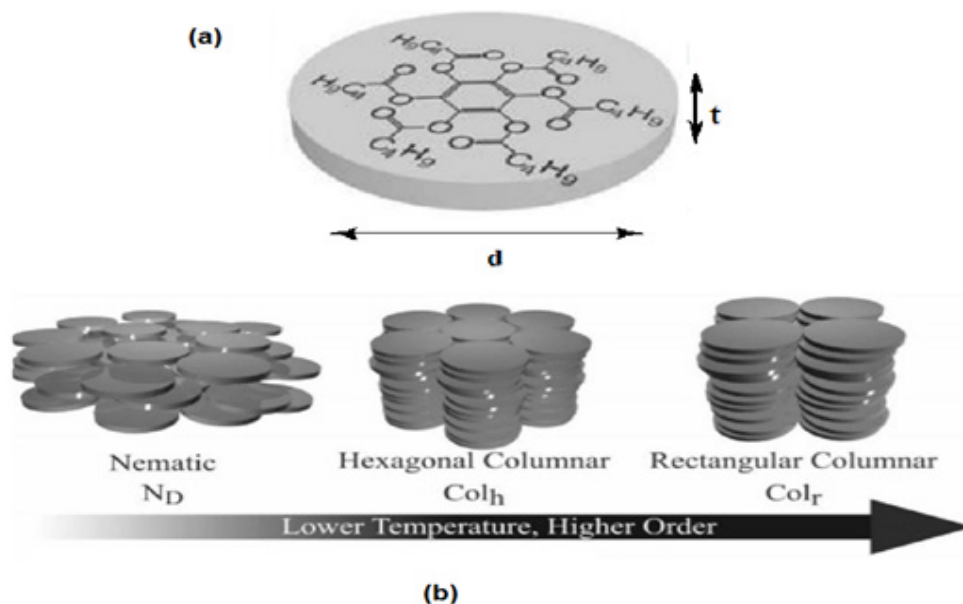


Fig. 11. (a) Discotic liquid crystals[35], (b) Type of Discotic liquid crystals [37].

(or disk) liquid crystals differ from the previous types, where the molecules are stacked into columns, the columns then being organized in a two-dimensional lattice. Molecules in such a phase have a positional order in two dimensions and are disordered in the third. Columnar phases are very rich and are normally classified at three levels; according to the symmetry of the two-dimensional array, the orientation of the core with respect to the column axis, and finally the degree of order within the column. The columnar phase divided into hexagonal and rectangular columnar phases, as shown in Fig. 11b [36, 37].

Polycatenar liquid crystals

Polycatenar liquid crystals are intriguing substances composed of elongated, rod-like cores that contain between three and six terminal chains. These chains are often, but not always, arranged symmetrically around the core. Two common examples are shown (a 'tetracatenar' and a 'hexacatenar' system) [38].

Dimeric Liquid Crystals

For many years it was considered that the liquid crystals of low molar mass should consist of molecules containing a semi-rigid core usually joined by a flexible spacer and attached to which were one or two alkyl chains, alkoxy, thioalkyl, halogens, cyano, and so on. However, this is no longer held to be true, as it was found that there are many molecular compounds that have the ability to show liquid crystalline properties, as the dimeric liquid crystals consist of molecules containing two semi-rigid mesogenic/ non-mesogenic unit connected via a flexible spacer,

which forms an alkyl chain, which is characterized by showing Liquid crystal properties at low temperatures, and this can be seen through the relationship between the molecular structure and liquid crystal properties in many studies[39-41].

The pointed materials are further classified into two broad classes:

Symmetric Liquid Crystal Dimers

The interest in liquid crystalline dimers can be traced back to the scientist Griffin and Britt in 1980 AD suggested that they can be used as model compounds for a semi-flexible main chain liquid crystalline polymers of technological importance[42], while its discovery was several decades ago by the scientist Vorlander has been largely ignored[43]. This type consists of two mesogenic units are the same that contain the structural features found in mesogenic compounds of low molar mass and are linked to each other by a flexible spacer normally, but not always, an alkyl chain. These compounds were called dimers and prepared the first dimeric series that showed liquid crystal properties α,ω -bis(4-n-alkylanilinebenzylidene-4'-oxy)alkanes,[44, 45] which took the following structure (Fig. 12).

Nonsymmetric Liquid Crystal Dimers

They are unconventional liquid crystal dimers that have attracted a lot of attention due to the unique liquid crystal properties that these dimers possess, which include two asymmetric mesogenic groups that are linked together by alkyl chains (CH_2)_n through flexible spacers[40, 41], and the lack of The homogeneity of the skeleton structure of these compounds will have an impact on the thermal and mesomorphic properties, where the

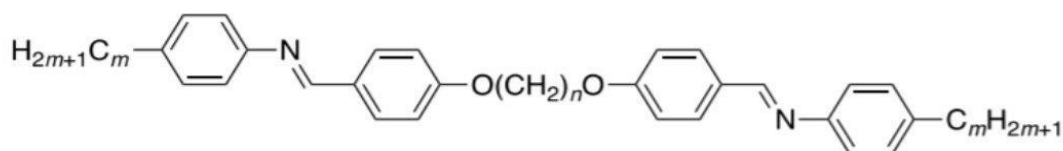


Fig. 12. α,ω -bis(4-n-alkylanilinebenzylidene-4'-oxy)alkanes[44].

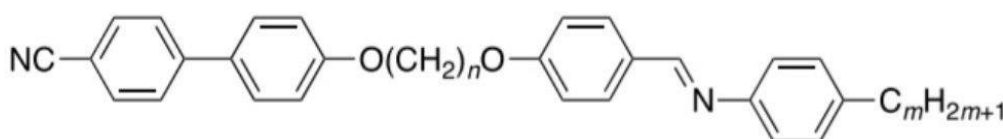


Fig. 13. α -(4-cyanobiphenyl-4'-yloxy)- ω -(4-n-alkylanilinebenzylidene-4'-oxy)alkanes [50, 51].

thermal properties and mesomorphic behaviors of the liquid crystal dimers are affected by several factors, including the composition, the size of the mesogenic units, the length of the spacer and the terminal chains, and that these asymmetric liquid crystal dimers have a high potential to show a wide range of phases. Compared to symmetrical dimers, it has a tendency to form few phases [46-49]. To verify this interesting possibility, many studies were conducted on several asymmetric crystalline dimers, but these studies were much less than it is compared to symmetric crystalline dimers. Among these studies are the following α -(4-cyanobiphenyl-4'-yloxy)- ω -(4-n-alkylanilinebenzylidene-4'-oxy) alkanes, as shown in the general structure (Fig. 13) [50, 51].

In which n and m refer to the number of carbon atoms in the spacer and terminal chains, respectively. During the study of differential scanning calorimetry and the polarized optical microscopy, it was found that the length of the terminal chain, as well as the length of the flexible spacer, had a clear effect on the appearance and type of liquid crystalline characteristics, as such dimers give the nematic phase. When the length of the chain is short and medium, and as the length of the terminal chain increases, as well as the length of the flexible spacer, the probability of the appearance of the smectic-A phase increases [52], and although a number of problems are still not fully identified, which have been discussed recently in many studies [53-56].

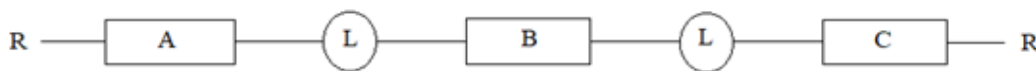
Chalcone Liquid Crystalline

The chalcone consists of two aromatic rings, which are linked together by a bond group consisting of three carbon atoms of the α,β -unsaturated carbonyl system. The chalcone is also known by other names: benzacetophenone,

benzylideneacetophenone and 1,3-diphenyl-2-propene-1-one, which It contains a ketoethylenic group (-CO-CH=CH-), that is, the chromophore group, and this is why these compounds are colored [57].

The chalcone group is considered an intermediate group consisting of an odd number of carbon atoms, which leads to the formation of a central structure that has the shape W, and this leads to an increase in the molecular width, which makes this group less inclined to show crystalline properties. However, chalcone linkage has been used in liquid crystalline compounds due to its geometrical shape, rigidity, and thermal stability. In addition, charge transfer property by π -bond conjugation of chalcone linkage plays important role in fluorescence, dielectric properties of molecules, and also polymerisation process. The liquid crystal properties of molecules containing chalcone linkages can be improved by incorporating other central linkages that enhance the appearance of liquid crystalline properties such as imine. (Schiff's base), ester or azo along with it [58], as it was present in many studies of liquid crystalline compounds that include in their composition the aromatic rings, which are considered the core structure of liquid crystalline compounds that are linked to each other by central linkages -N=N-, COO-, -CH=N- and compensators at the Para or Meta site, groups may be halogen atoms, NO₂, CN, or alkyl or alkoxy chains. These studies show that the appearance of liquid crystalline phases and their thermal stability depend on the nature of the molecules [59-61].

There are different ways to prepare chalcone, but the most suitable method is the Claisen-Schmidt by condensation of ketone with aldehyde in the presence of aqueous alkaline bases or in the presence of alcoholic alkali [62, 63].



R, R': terminal units (alkoxy chains, OH, CN, NO₂ and so on)

A, B, C: Ring system (phenyl, cyclohexyl, heterocyclic)

L: Linking units (C=N, N=N, C=C, and so on)

Fig. 14. The general formula for liquid crystalline particles [45].

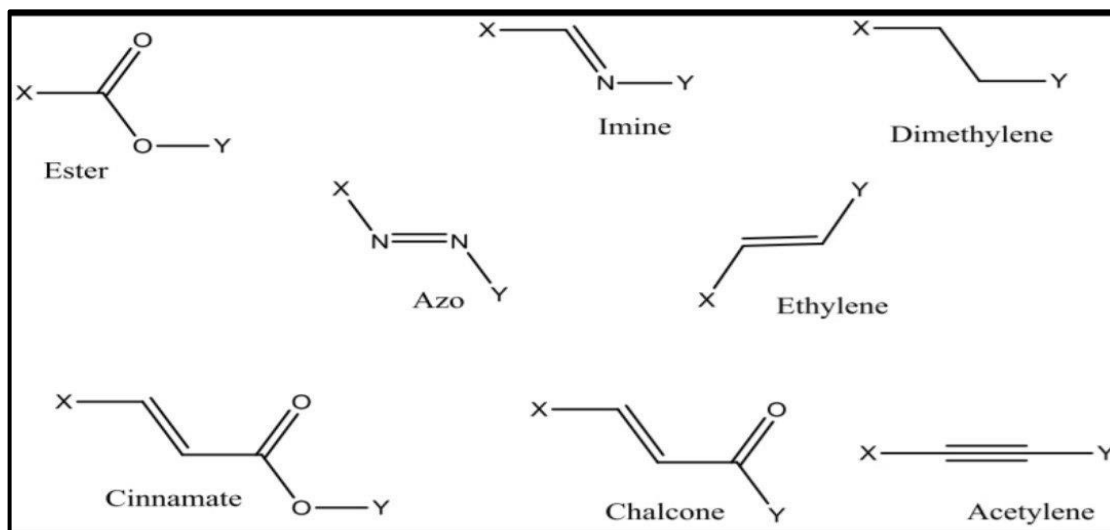


Fig. 15. Different linking groups [23].

Schiff's Bases

Schiff bases are among the most important reactions that are used in the preparation of compounds with liquid crystalline characteristics for many reasons, including the ease of chemical preparation and the fact that they give a more rigid model, which makes them possess high stability over a wide range of temperatures due to the presence of the double bond between carbon and nitrogen $-C=N-$ Which makes studying the physical properties of these compounds at the liquid crystalline phase easy [64, 65].

They are generally prepared through a condensation reaction between carbonyl compounds and primary amines or amino acids to form an azomethine group [66]. The stability of Schiff bases depends on the type of amine and the type of aldehyde or ketone used, as Schiff bases prepared from aromatic aldehyde and aromatic amine are the most stable among bases. This is due to the increase in resonance stability, and the aldehydes are more effective towards nucleophile addition with amines compared to ketones due to the inductive effect of the attached alkyl groups (donor effect) in addition to the approach of the attacking nucleophile to the carbon atom faces steric hindrance, especially if the alkyl groups are large. Upon the discovery of 4-methoxybenzylidene-4'-butyl aniline (MBBA) that appears as a mesophase at room temperature, Schiff bases were studied repeatedly [67], and many studies show that liquid crystals

containing the azomethine group form the core structure and can be used as linking groups to form different types of liquid crystal compounds [68]. The linking unit between ring systems increases the length of the molecules, as well as altering the polarizability and flexibility of the molecules. Linking units can impart polarity or act as non-polar groups and, hence, increase or decrease polarizability, and a variety of molecules with Schiff base units have been synthesized and their liquid crystal properties were determined [69, 70]. In the study [71], an asymmetric dimeric chain was prepared from chalcones and Schiff bases, which are characterized by their liquid crystal properties, the effect of alkyl chain lengths on the behavior of liquid crystals was studied, and mixing liquid crystal compounds with zinc oxide nanoparticles. Photoluminescence of compounds was examined and the results indicated that the emission in the blue region reveals that material has blue light emission properties.

THE RELATIONSHIP BETWEEN STRUCTURE PROPERTY AND THERMOTROPIC LIQUID CRYSTAL.

Core

In order to clarify the molecular structure relationship in thermotropic liquid crystalline organic compounds, the general formula for liquid crystalline molecules that have the ability to show mesogenic properties [45] was developed, which is represented in Fig. 14.

The molecular anisotropy required for its

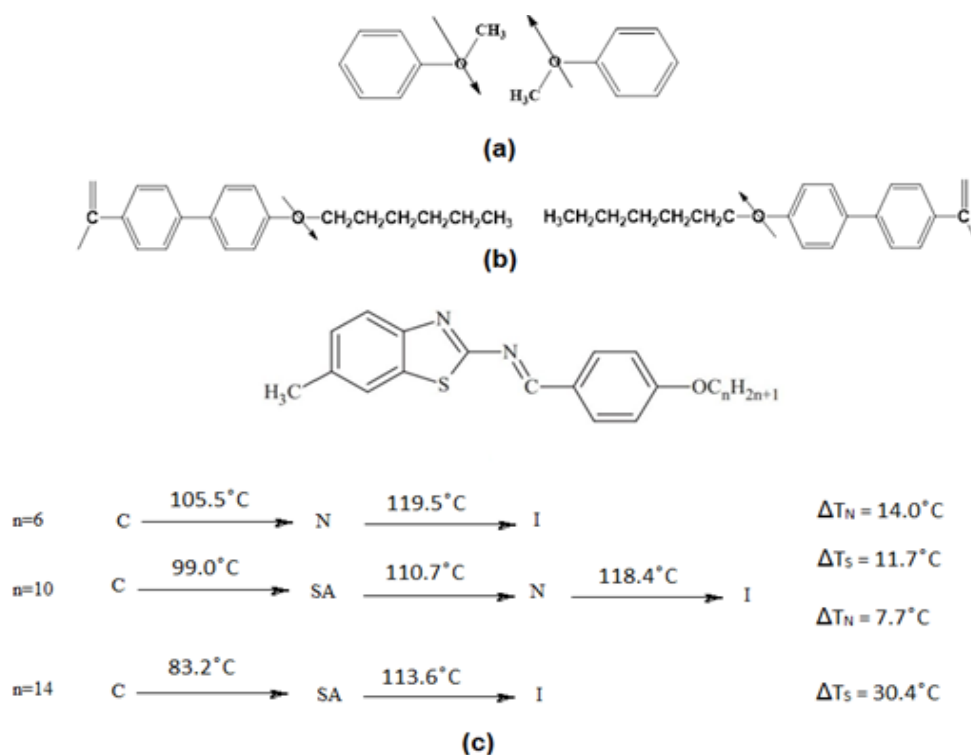


Fig. 16. Effect of Terminal Group [74].

mesogenicity is primarily due to the core, which is also the cause of the comparatively high melting point. The core rings are connected either directly or by linking groups, along with lateral substituent. Calamitic liquid crystals generally have aromatic rings. An increase in aromatic rings will generally result in an increase in the melting point. Furthermore, the mesogenicity of the compound increase as the number of linearly connected rings increases. When the CH group in the ring is replaced by an N atom, the shape of the ring changes little, but the electronic properties change, and a considerable electric dipole is generated, which changes the intermolecular attraction [23].

Linking groups

The linking groups are a structural units that connects one part of the core to another part of a liquid crystal molecule, as the linking groups between aromatic systems increase the length of the molecules while maintaining the linear shape, in addition to increases the polarization anisotropy of the molecular core, and improves the stability

of the liquid crystal phase. The effect of the linking groups of aromatic and non-aromatic rings is significantly different since there is no conjugation effect of the non-aromatic rings. The ester group is considered the most commonly used linking group in liquid crystals because it is relatively stable and easy to prepare and can produce important liquid crystals with low melting points, while the ethylene group is a fully conjugated linking group that can improve longitudinal polarization and lengthen the molecule while preserving linearity, while acetylene maintains rigidity, Linear shape, polarization of the core and increases the length of the molecule. The rules of the functional group (CH=N) are widely used as a linking group to increase the rigid and high stability and promote the formation of mesophases, although it produces a staggered central structure [65]. Fig. 15 shows the different linking groups used in liquid crystal molecules.

Terminal Group

The terminal groups type and the dipole moment type that these substituted groups have

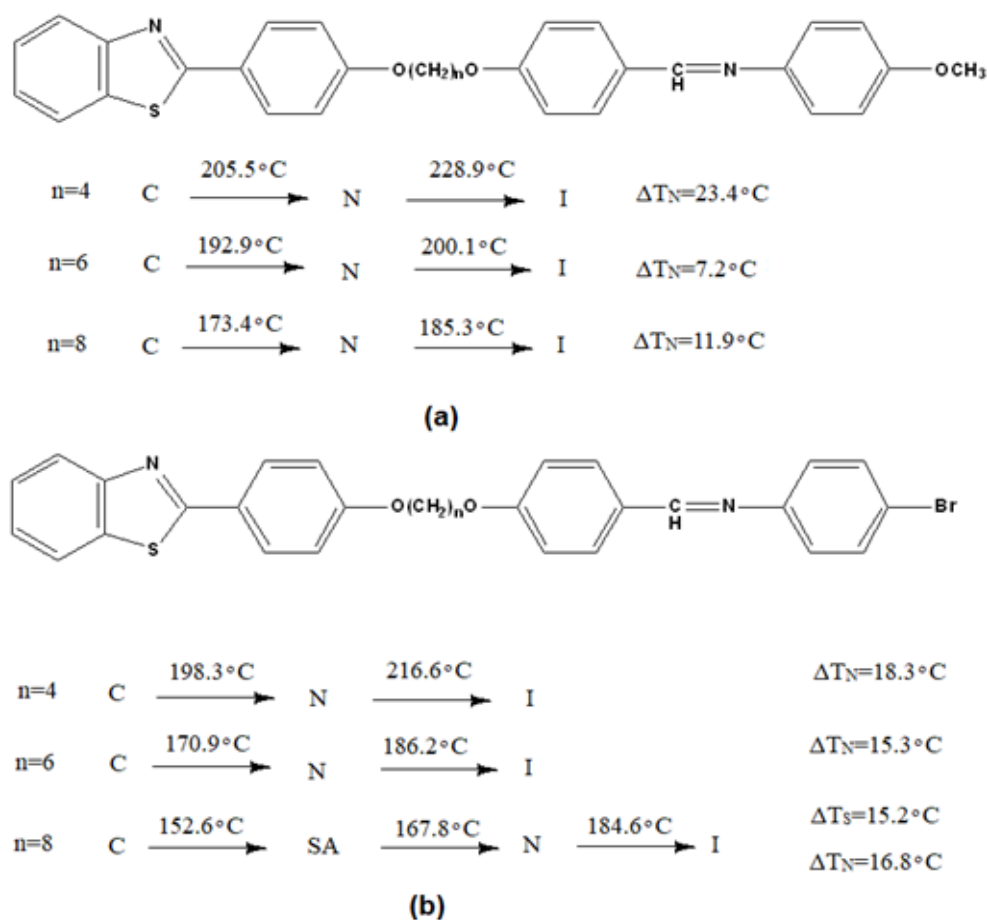


Fig. 17. Example of the effect of Terminal Group [75].

at the terminal of the molecule are the most important factors affecting the thermal stability of mesogenic compounds and the type of liquid crystal phase.

Where studies were conducted on the effect of the terminal chain length on the mesogenic properties, it was found that the compounds that contain an terminal substituted are more stable mesophases than the non-substituted mesogenic compound, whether the alkyl chain or the alkoxy chain. The choice of end groups is critical for the formation of a particular type of liquid crystalline phase. The theory of Mayer and Saupe [72] showed that the transition temperature from the nematic phase to the isotropic of a compound is related to the molecular polarization of the molecule, and the molecular polarization is always related to the terminal group and its influence on the intramolecular conjugation. Sometimes Smectic

liquid crystals reduce the thermal stability of some terminal groups. In the short alkyl chains, the nematic phase appears only because the terminal attractive forces are high, as the separation between the aromatic rings compensated by terminal groups is small, and this can be explained in the compound in Fig. 16a.

Increasing the length of the chain leads to the appearance of the smectic and nematic phases together because of the increase in the attractive forces between the sides of the molecules resulting from the polarization of the CH_2 groups added at the end of the molecule. While the very long chains show the smectic phase only because of increasing the separation between the ends of the molecules, and this leads to a great weakening of the peripheral attractive forces and the transition to the smectic phase occurs directly without going through the nematic phase [2, 73] as in Fig. 16b,

and as in compound in Fig. 16c [74].

The compound shown in Fig.16c is compensated for by the alkoxy terminal groups of the nematic and smectic phases with different temperature ranges and according to the compensated terminal groups.

The replacement of the OCH₃ alkoxy group in the aromatic ring provides a dipole moment across the longitudinal axis of the molecule, which promotes the emergence of the nematic phase only, but when replaced by the (Br) group, it leads to the appearance of the smectic phase. This is evident from the difference in liquid crystalline properties and the thermal range shown by compounds in Fig 17a and b [75].

The melting point and thermal range decrease for both compounds when the length of the flexible spacer is increased.

In the rod-shape aromatic systems that take a linear form, the order of activity of the terminal group of the Smectic phase is as follows [76]:

Ph > -Br > -Cl > -F > -NMe₂ > -Me > -H > -NO₂ > -OMe > -CN

While the effect of the terminal group of the nematic phase is as follows:

-Ph > -NHCOCH₃ > -CN > -OMe > -NO₂ > -Cl > -Br > -NMe₂ > -OMe > -F > -H.

FLUORESCENCE

It is an essential parameter for liquid crystal materials used in display devices [77]. When a beam of electromagnetic radiation with a suitable wavelength is shined on the molecules of the substance in the solution, these molecules absorb an amount of energy and turn into excited particles, and this absorbed energy is often disposed of in the form of visible rays, this phenomenon is called luminescence.

The fluorescence process begins with the absorption of energy by molecules that contain a Fluorophore (which are regions of electronic structure that exhibit fluorescence) at room temperature, then electrons move from the lowest level (ground-state) of electronic energy to the highest level (excited-state) of electronic energy, as this transition takes a short time (10⁻¹⁵) of a second. This is the transition from the lowest vibrational energy level of the ground state to any excited vibrational energy level, usually the first or second excited singlet state, termed S₁ and S₂,

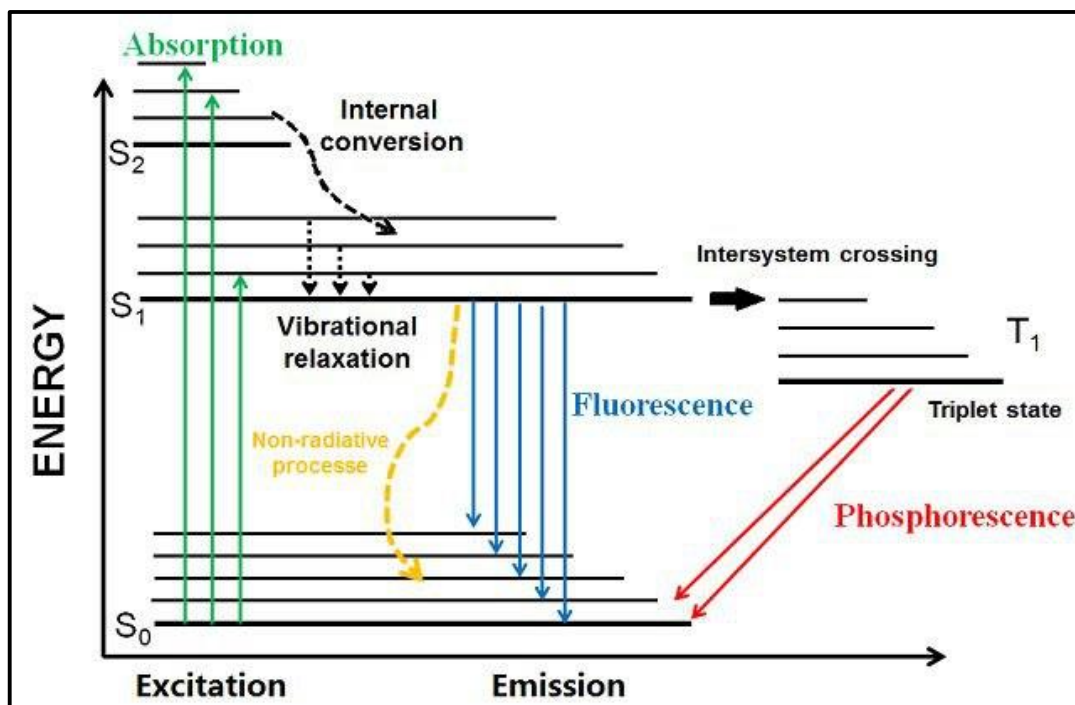


Fig. 18. Jablonski diagram of the various processes associated with the absorption and emission of radiation. Jablonski diagram illustrating the main primary deactivation processes following excitation from the ground electronic singlet state (S₀) to excited electronic singlet states (S₁ and S₂) [79]

respectively. Because the state of excitement does not last for a long time, the electron will lose its energy in several ways, usually in the form of heat or radiation Fig. 18.

In organic molecules, the rotation of electrons in the stable state (the ground state) is Paired ($\downarrow\uparrow$) and the singlet state is called (S_0), while the excited state can have two possibilities for electron rotation:

In the first case, the electron spin is unpaired, which is known as the triplet state and its symbol is T. It is difficult to change the electron spin, as the molecule moves from the stable level S_0 to S_1 and S_2 , then the electron moves to the semi-stable triplet state T_1 by moving across the systems then end to the steady state S_0 and lose excitation energy slowly with the emission of violet or visible light in a time (10^{-3} to 10^{-2}) of a second, represented by phosphorylation.

In the second case, the rotation is double for the excited electron ($\downarrow\uparrow$) and is known as the singlet state, and its symbol is S_1 and S_2 during a time (10^{-9} to 10^{-6}) of a second, and the electron returns to the stable state S_0 and is accompanied by the emission of energy in the form of rays, represented by fluorescence.

It is noted that the processes of fluorescence and phosphorylation always occur from a zero vibrational level for the first monomeric and triplet states, respectively, and it is noted that fluorescence occurs between two similar states in polymorphism, i.e. from one monomeric state to another monomeric state, while phosphorylation occurs between two states that differ in polymorphism from triplet to monomeric, where is The probability of electronic transition between two states of the same plurality is higher than the probability of electronic transition between two different states in plurality. Therefore, the probability of electronic transition depends on the plurality of these two states, so the fluorescence spectrum is of high intensity compared to the phosphorylation spectrum, and the phosphorylation lifetime is longer than the fluorescence lifetime [78]. All major photophysical processes and energy levels can be illustrated by the diagram in Fig. 18.

Determination of emission and excitation spectroscopy

The excitation and emission are two opposite processes, and the excitation process is nothing

but the transition of an electron from a singlet ground state to a singlet excited state, while the emission process is exactly the opposite. Therefore, the emission spectrum is supposed to be a mirror image of the excitation spectrum, as in Fig. 19, but the two spectrums rarely have an identical picture of each other, usually for reasons related to defects in the manufacture of the device, or the presence of impurities that have different properties from the sample. It is important very select the appropriate wavelength for excitation and the appropriate wavelength for measuring fluorescence intensity.

Fluorescence occurs at lower frequencies, that is, at higher wavelengths, where the energy of the emitted radiation is smaller than the energy of the absorbed radiation. This difference between the excitation wavelength and the emission wavelength is called the Stokes shift, after the scientist Stokes, who was the first to notice this phenomenon in 1852 AD. The Stokes shift is expressed by the wavenumber. The emission spectrum is clear and less overlapping with the excitation spectrum as the Stokes shift increases, as in Fig. 20. Thus, the fluorescence spectrum is distinctive in that the absorption wavelength is shorter than the fluorescence wavelength.

Factors affecting the Fluorescence process

There are several factors that positively or negatively affect the intensity of flashing caused by different materials, and these factors include the following:

Effect of molecular structure and conjugation double bonds: Most of the molecules that emit fluorescence are large organic compounds with a ring structure that contain conjugation double bonds with high resonance stability. Aromatic compounds with plane structure and polynuclear aromatic hydrocarbons are ideal for this type of study, in addition to heterocyclic compounds. Increasing the double bond conjugation system in the molecule can shift the absorption and emission

Temperature: Fluorescence is greatly affected by temperature. When the temperature increases, the fluorescence decreases as a result of the increased chance of collision between the molecules of the substance and the molecules of the solvent, i.e., the ease of movement of molecules in the medium in which the temperatures are high, and this leads to energy loss in non-radiative ways, and when the temperature decreases heat can reduce

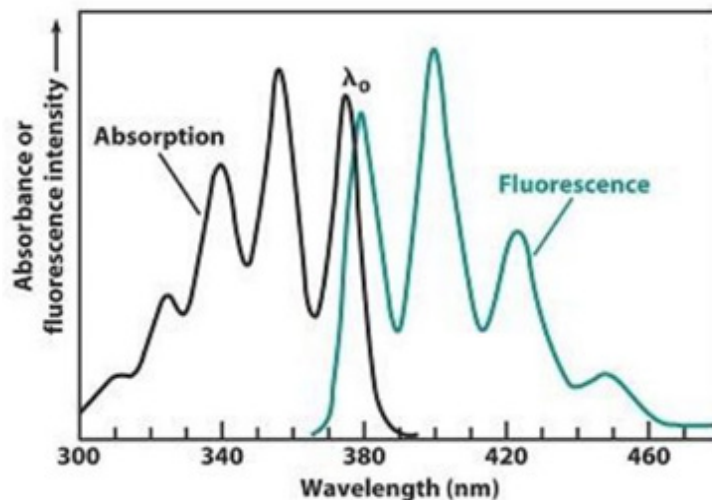


Fig. 19. Emission and excitation spectroscopy[80].

this energy loss.

The nature of the solvent and its components: the polarity of the solvent has an important effect on the absorption and emission spectra, in the presence of a polar solvent the probability of transitions improves and this in turn leads to an increase in fluorescence due to the increase in the number of excited particles, because solvents with high polarity lead to a greater displacement in the direction of high wavelengths for emission spectra in fluorescence.

pH: the pH of the solution causes a chemical change in the nature of the compound and turns it into a non-fluorinating molecule, for example, aniline gives blue fluorescence in an acidic medium (PH<5), but with increasing acidity of the solution it turns into an anilinium ion that does not give fluorescence[81].

QUANTUM YIELD

The efficiency of the fluorescence process can be expressed by calculating the ratio of the number of photons emitted through fluorescence, to the number of photons absorbed by the fluorophore. The quantum yield of fluorescence is of great importance because it is a physical property of a substance in a certain state. The values of the quantum yield range from 0 to 1, and the higher the values of the quantitative yield of fluorescence, the brightest emissions and stronger the fluorescence. It is possible to multiply the quantum yield by a hundred and thus obtain

a percentage that is easier for comparisons, in which case it is called the quantum efficiency of fluorescence.

It is also possible to deduce the quantum yield from the rate of processes that occur in the molecules after absorption, so if there are no energy loss processes through fluorescence, then the process is effective, and the quantum yield is large. However, for example, if the transition mechanisms to the triplet state are easy, or the internal or external transition is easy, then the quantum return will decrease. The importance of ϕ_f has been demonstrated in many industries including research, development and evaluation of audiovisual equipment, electrical materials (OLED/LED), dyes/Pigment, and fluorescent probes for biological assays [82].

Numerous studies have been conducted on liquid crystalline compounds about their ability to fluoresce, among these studies: A study [83] in which the compound was presented in the Fig. 21a, the compound shown in Fig. 21a has liquid crystal properties and fluorescence, and the highest emission peak in the fluorescence spectrum was at $\lambda_{max}=349.5\text{nm}$.

Another study [84] in which the compound presented in Fig. 21b showed liquid crystalline properties. The fluorescence properties of this compound were also studied and showed the highest absorption peak in the absorption spectrum at $\lambda_{max}(\text{abs}) = 364\text{nm}$, while the highest peak in the fluorescence spectrum was at λ_{max}

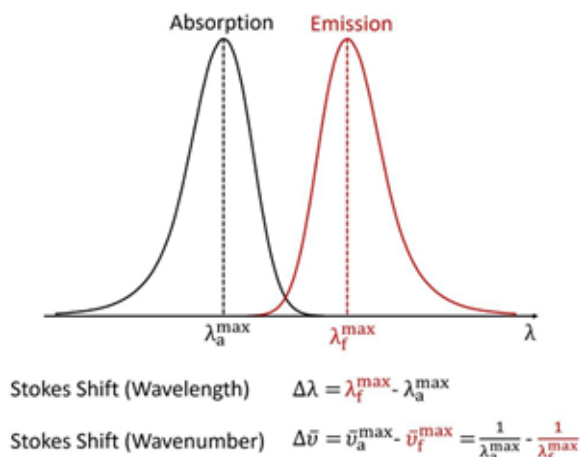


Fig. 20. Definition of the Stocks shift for fluorescence [81].

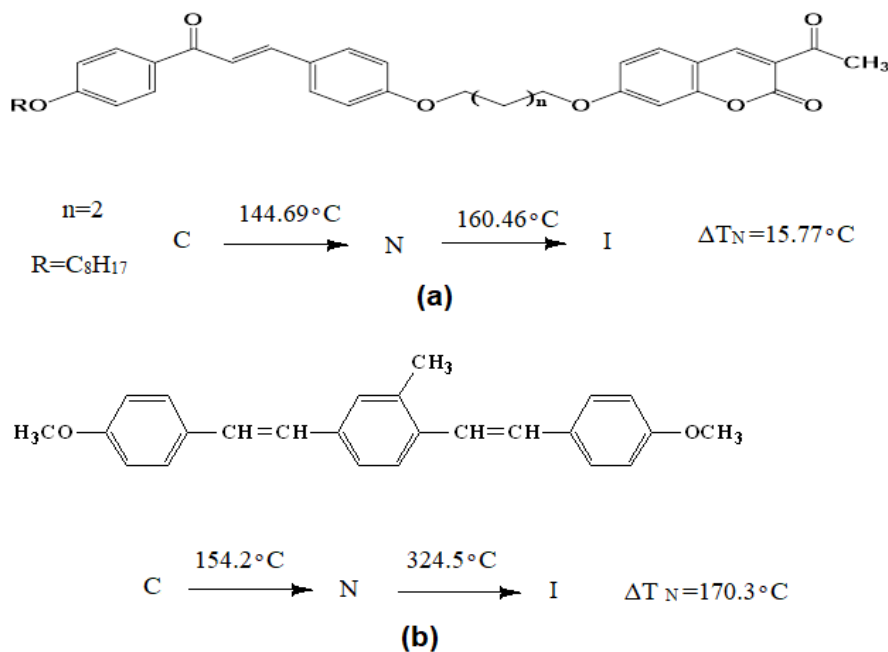


Fig. 21. Compounds with liquid crystal properties and fluorescence [83, 84].

(em) = 414 nm.

LIQUID CRYSTAL NANOPARTICLES

The tremendous progress that has occurred in the field of nanotechnology has stimulated researchers to take advantage of its applications in various fields, as these applications have multiplied in various scientific fields, and thus interfered with all the needs of individuals, as it

was found that the use of nanoparticles from metal oxides has received more attention[85, 86]. These nanomaterials are characterized by their thermal and chemical stability, in addition to their large surface area and unique optical and electrical properties. Among these metal oxide nanoparticles, zinc oxide nanoparticles exhibit superior optical properties such as color absorption in the visible region and UV

absorption. These nanoparticles have a wide range of applications such as catalysts, photocatalysts, drug delivery, environmental remediation, and electronics. Thus, the final properties of ZnO nanoparticles depend on the structural and morphological properties of the prepared ZnO nanoparticles [87]. The morphological and structural properties of zinc oxide nanoparticles were determined by synthesis methods. To date, different preparation procedures have been applied to prepare zinc oxide nanoparticles [88]. Despite their potential benefits, metal oxide nanoparticles also pose potential health and environmental risks. The small size allows these particles to penetrate cells and tissues, which can lead to toxicity and adverse health effects. It is therefore necessary to understand and control the risks associated with exposure to metal oxide nanoparticles to ensure their safe and sustainable use in different applications. The bonding of metal oxide nanoparticles to organic compounds is an important ongoing research area in nanoscience and modern nanotechnology [89].

Previous studies demonstrated the use of nanomaterials to enhance the thermal conductivity of thermotropic liquid crystal compounds. In addition, a study [90] reported that the addition of carbon-based nanoparticles enhanced thermal conductivity, modified phase change, and showed high chemical stability of phase change materials (PCMs).

CONCLUSION

The current review explores the fascinating world of asymmetric dimeric liquid crystals and their applications in fluorescence and nanohybrid systems. Various types of dimeric liquid crystals, including thermotropic liquid crystals, Chalcone liquid crystalline, and Schiff's bases, have been thoroughly investigated and analyzed. The study highlights the significant factors that influence the phases of these liquid crystals, such as the core structure, linking groups, and terminal groups. Moreover, the review emphasizes the role of fluorescence as a fundamental process in liquid crystal materials and explores the utilization of ZnO nanoparticles in practical applications. It was observed that the mesogenic group containing the chalconic bond has limited utility in liquid crystalline compounds due to its W-shaped configuration. However, the presence of linking groups, specifically Schiff

bases, enhances the appearance of liquid crystal properties. Furthermore, the type and size of the terminal group were found to impact the liquid crystalline properties significantly, leading to the emergence of the nematic and smectic phases. Overall, this review provides valuable insights into the potential applications and characteristics of asymmetric dimeric liquid crystals, shedding light on their promising prospects in fluorescence and nanohybrid technologies.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. Singh S. *Liquid crystals: fundamentals*: World Scientific; 2002.
2. Gray GW. *Molecular structure and the properties of liquid crystals*: Academic press; 1962.
3. Pohl L, Demus D, Pelzl G, Finkelmann H, Hiltrop K, Schadt M. *Liquid crystals*: Springer Science & Business Media; 1994.
4. Collings P, Hird M. Chapter 3. *Introduction to Liquid Crystals Chemistry and Physics*. 1997.
5. Hussein MA, Abdel-Rahman MA, Asiri AM, Alamry KA, Aly KI. Review on: liquid crystalline polyazomethines polymers. Basics, syntheses and characterization. *Designed Monomers and Polymers*. 2012;15(5):431-463.
6. Reinitzer F. Beiträge zur kenntniss des cholesterins. *Monatshefte für Chemie und verwandte Teile anderer Wissenschaften*. 1888;9(1):421-441.
7. Lehmann O. Über fließende krystalle. *Z Phys Chem*. 1889;4(1):462-472.
8. Vorländer D. *Kristallinisch-flüssige substanzen*: Enke; 1908.
9. Weygand C, Gabler R. Die höheren Homologen der Azophenol-, Azoxyphenol- und Azomethinphenoläther. *Journal für Praktische Chemie*. 1940;155(10-12):332-341.
10. Weygand C, Gabler R, Hoffmann J. Chemical morphology of liquids. III. Liquid-crystal aliphatic monocarboxylic acids. *Z Phys Chem Abt B*. 1941;50:124-127.
11. Palffy-Muhoray P. *Orientationally Ordered Soft Matter: The Diverse World of Liquid Crystals*. *Electronic-Liquid Crystal Communications (e-LC)*. 2007.
12. Goodby JW, Collings PJ, Kato T, Tschierske C, Gleeson H, Raynes P, et al. *Handbook of liquid crystals*, 8 volume set: John Wiley & Sons; 2014.
13. Lyu X, Xiao A, Shi D, Li Y, Shen Z, Chen E-Q, et al. Liquid crystalline polymers: Discovery, development, and the future. *Polymer*. 2020;202:122740.
14. Khokhlov AR, Emelyanenko AV. *Nanostructured liquid crystal systems and applications*. Beilstein-Institut; 2018. p. 2644-2645.
15. Chrzumnicka E, Bauman D, Jadzyn J. Optical order parameter of dichroic azo-dyes in liquid crystalline side-chain polysiloxanes. *Acta Phys Pol, A*. 2002;102(6):767-780.
16. Jain AK, Deshmukh RR. An overview of polymer-dispersed liquid crystals composite films and their applications. *Liq Cryst Disp Technol*. 2020:1-68.

17. Neto AMF, Salinas SR. The physics of lyotropic liquid crystals: phase transitions and structural properties: OUP Oxford; 2005.
18. Dierking I, Martins Figueiredo Neto A. Novel trends in lyotropic liquid crystals. *Crystals*. 2020;10(7):604.
19. Mo J, Milleret G, Nagaraj M. Liquid crystal nanoparticles for commercial drug delivery. *Liquid crystals reviews*. 2017;5(2):69-85.
20. Lagerwall JP, Scalia G. A new era for liquid crystal research: Applications of liquid crystals in soft matter nano-, bio-and microtechnology. *Current Applied Physics*. 2012;12(6):1387-1412.
21. Jamain Z, Omar NF, Khairuddean M. Synthesis and determination of thermotropic liquid crystalline behavior of cinnamaldehyde-based molecules with two Schiff base linking units. *Molecules*. 2020;25(17):3780.
22. Crystals TL. *Recent Advances*, ed. A. Ramamoorthy. Springer, Dordrecht, The Netherlands; 2007.
23. ashrajbhai Nakum K. Synthesis & Characterization of Some Novel Schiff Base Derivatives, Their Metal Complexes and Study of Their Mesomorphic Behavior: Maharaja Sayajirao University of Baroda (India); 2021.
24. Kiliç M, Cinar Z. Structures and mesomorphic properties of cyano-containing calamitic liquid crystal molecules. *Journal of Molecular Structure: THEOCHEM*. 2007;808(1-3):53-61.
25. Friedel G, editor *Les états mésomorphes de la matière*. Annales de physique; 1922.
26. Andrienko D. Introduction to liquid crystals. *J Mol Liq*. 2018;267:520-541.
27. Nafee SS, Hagar M, Ahmed HA, El-Shishtawy RM, Raffah BM. The synthesis of new thermal stable schiff base/ester liquid crystals: A computational, mesomorphic, and optical study. *Molecules*. 2019;24(17):3032.
28. Kirsch P, Bremer M, Huber F, Lannert H, Ruhl A, Lieb M, et al. Nematic liquid crystals with a tetrafluoroethylene bridge in the mesogenic core structure. *Journal of the American Chemical Society*. 2001;123(23):5414-5417.
29. Mandle RJ. A Ten-Year Perspective on Twist-Bend Nematic Materials. *Molecules*. 2022;27(9):2689.
30. Collings PJ, Hird M. *Introduction to liquid crystals chemistry and physics*: Crc Press; 2017.
31. Nafee SS, Ahmed H, Hagar M. Theoretical, experimental and optical study of new thiophene-based liquid crystals and their positional isomers. *Liq Cryst*. 2020;47(9):1291-1302.
32. Josse J. *Nematic Liquid Crystal Carbon Nanotube Composite Materials for Designing RF Switching Devices*: Marquette University; 2022.
33. Oswald P, Pieranski P. *Nematic and cholesteric liquid crystals: concepts and physical properties illustrated by experiments*: CRC press; 2005.
34. Bisoyi HK, Kumar S. Carbon-based liquid crystals: art and science. *Liq Cryst*. 2011;38(11-12):1427-1449.
35. Senyuk B. *Liquid crystals: a simple view on a complex matter*. Liquid Crystal Institute, Kent State University. 2010.
36. Percec V, Sahoo D. Discotic liquid crystals 45 years later. Dendronized discs and crowns increase liquid crystal complexity to columnar from spheres, cubic Frank-Kasper, liquid quasicrystals and memory-effect induced columnar-bundles. *Giant*. 2022;12:100127.
37. Al Hadeethi AHD. *Synthesis, Characterization and Study the Liquid Crystalline Properties of New Discotic Compounds*: Ministry of Higher Education; 2015.
38. Fazio D, Mongin C, Donnio B, Galerne Y, Guillon D, Bruce DW. Bending and shaping: cubics, calamitics and columnars Basis of a presentation given at Materials Discussion No. 4, 11-14 September 2001, Grasmere, UK. *J Mater Chem*. 2001;11(11):2852-2863.
39. Imrie CT, Henderson PA. Liquid crystal dimers and oligomers. *Current opinion in colloid & interface science*. 2002;7(5-6):298-311.
40. Imrie CT, Henderson PA. Liquid crystal dimers and higher oligomers: between monomers and polymers. *Chem Soc Rev*. 2007;36(12):2096-2124.
41. Imrie CT, Henderson PA, Yeap G-Y. Liquid crystal oligomers: going beyond dimers. *Liq Cryst*. 2009;36(6-7):755-777.
42. Griffin AC, Britt TR. Effect of molecular structure on mesomorphism. 12. Flexible-center Siamese-twin liquid crystalline diesters-a" prepolymer" model. *Journal of the American Chemical Society*. 1981;103(16):4957-4959.
43. Vorländer D. Über die Natur der Kohlenstoffketten in kristallin-flüssigen Substanzen. *Z Phys Chem*. 1927;126(1):449-472.
44. Date R, Imrie C, Luckhurst G, Seddon J. Smectogenic dimeric liquid crystals. The preparation and properties of the α , ω -bis (4-n-alkylanilinebenzylidene-4'-oxy) alkanes. *Liq Cryst*. 1992;12(2):203-238.
45. Imrie CT, Walker R, Storey JM, Gorecka E, Pocięcha D. Liquid Crystal Dimers and Smectic Phases from the Intercalated to the Twist-Bend. *Crystals*. 2022;12(9):1245.
46. Strachan GJ, Harrison WT, Storey JM, Imrie CT. Understanding the remarkable difference in liquid crystal behaviour between secondary and tertiary amides: the synthesis and characterisation of new benzanilide-based liquid crystal dimers. *Physical Chemistry Chemical Physics*. 2021;23(22):12600-12611.
47. Walker R, Majewska M, Pocięcha D, Makal A, Storey JM, Gorecka E, et al. Twist-bend nematic glasses: the synthesis and characterisation of pyrene-based nonsymmetric dimers. *Chemphyschem*. 2021;22(5):461-470.
48. Arakawa Y, Komatsu K, Ishida Y, Tsuji H. Thioether-linked azobenzene-based liquid crystal dimers exhibiting the twist-bend nematic phase over a wide temperature range. *Liq Cryst*. 2021;48(5):641-652.
49. Arakawa Y, Komatsu K, Inui S, Tsuji H. Thioether-linked liquid crystal dimers and trimers: The twist-bend nematic phase. *J Mol Struct*. 2020;1199:126913.
50. Hogan J, Imrie C, Luckhurst G. Asymmetric dimeric liquid crystals The preparation and properties of the α -(4-cyanobiphenyl-4'-oxy)- ω -(4-n-alkylanilinebenzylidene-4'-oxy) hexanes. *Liq Cryst*. 1988;3(5):645-650.
51. Attard G, Date R, Imrie CT, Luckhurst G, Roskilly S, Seddon J, et al. Non-symmetric dimeric liquid crystals the preparation and properties of the α -(4-cyanobiphenyl-4'-yloxy)- ω -(4-n-alkylanilinebenzylidene-4'-oxy) alkanes. *Liq Cryst*. 1994;16(4):529-581.
52. Blatch A, Fletcher I, Luckhurst G. The intercalated smectic A phase. The liquid crystal properties of the α -(4-cyanobiphenyl-4'-yloxy)- ω -(4-alkyloxycinnamoate) alkanes. *Liq Cryst*. 1995;18(5):801-809.
53. Walker R, Pocięcha D, Faidutti C, Perkovic E, Storey JM, Gorecka E, et al. Remarkable stabilisation of the intercalated smectic phases of nonsymmetric dimers by tert-butyl groups. *Liq Cryst*. 2022;49(7-9):969-981.
54. Knežević A, Dokli I, Novak J, Kontrec D, Lesac A. Fluorinated twist-bend nematogens: the role of intermolecular

- interaction. *Liq Cryst.* 2021;48(5):756-766.
55. Abberley JP, Walker R, Storey JM, Imrie CT. Molecular structure and the twist-bend nematic phase: the role of terminal chains. *Liq Cryst.* 2020;47(8):1232-1245.
 56. Forsyth E, Paterson DA, Cruickshank E, Strachan GJ, Gorecka E, Walker R, et al. Liquid crystal dimers and the twist-bend nematic phase: On the role of spacers and terminal alkyl chains. *J Mol Liq.* 2020;320:114391.
 57. Chaudhari R, Chauhan M, Doshi A. Synthesis and mesogenic behavior of novel liquid crystals with a-CH⁺ CH-CO-central bridge. *Mol Cryst Liq Cryst.* 2013;575(1):88-95.
 58. Soman SS, Jain P. DESIGN, SYNTHESIS AND STUDY OF CALAMITIC LIQUID CRYSTALS CONTAINING CHALCONE AND SCHIFF BASE LINKAGES ALONG WITH TERMINAL ALKOXY CHAIN. *Journal of Advanced Scientific Research.* 2022;13(04):59-68.
 59. ONAR HÇ. OVERVIEW ON COUMARIN CHALCONE COMPOUNDS AND PROPERTIES SYNTHESIZED IN 2020. *ACADEMIC RESEARCH AND REVIEWS IN SCIENCE AND MATHEMATICS.*35.
 60. Nakum KJ, Katariya KD, Hagar M, Jadeja RN. The influence of lateral hydroxyl group and molecular flexibility on the mesogenic behaviour of a new homologous series based on thiophene-chalcone: Synthesis, characterization, crystal structure and DFT study. *J Mol Struct.* 2022;1261:132891.
 61. Dwivedi DJ, Sharma VS, Rathod SL, Mali HA, Shrivastav PS, Shah RR. Synthesis and characterization of chalcone-linked bis-cinnamate-based liquid crystals: structure-property relationship. *Mol Cryst Liq Cryst.* 2022:1-16.
 62. Souza GB, Santos TA, Silva AP, Barreiros ALS, Nardelli VB, Siqueira IB, et al. Synthesis of chalcone derivatives by Claisen-Schmidt condensation and in vitro analyses of their antiprotozoal activities. *Natural Product Research.* 2022:1-8.
 63. Kaundal V, Singh D, Devi A, Jindal S, Ankalgi AD, Goyal K. A Laconic Review on Chalcones: Synthesis, Antimicrobial and Antioxidant activities. 2022.
 64. Jber NR, Shukur MM, Najaf AA. Schiff Base liquid Crystals with Terminal Alkoxy Group Synthesis and Thermotropic Properties. *Al-Nahrain Journal of Science.* 2014;17(2):64-72.
 65. Hagar M, Ahmed H, Saad G. Mesophase stability of new Schiff base ester liquid crystals with different polar substituents. *Liq Cryst.* 2018;45(9):1324-1332.
 66. Rananavare SB, Pispipati V. An overview of liquid crystals based on Schiff base compounds. *Liquid crystalline organic compounds and polymers as materials of the XXI century: from synthesis to applications.* 2011:19-52.
 67. Hagar M, Ahmed H, Alhaddad O. New azobenzene-based natural fatty acid liquid crystals with low melting point: Synthesis, DFT calculations and binary mixtures. *Liq Cryst.* 2019;46(15):2223-2234.
 68. Sharma VS, Patel R. Design and investigation of calamitic liquid crystals: Schiff base (-CH⁺ N), chalcone (-CO-CH⁺ CH-), and ester (-COO-) linkage group contain rigid rod shape with various terminal parts. *Mol Cryst Liq Cryst.* 2017;643(1):141-158.
 69. Dubey R, Mishra A, Singh K, Alapati P, Dhar R. Electric behaviour of a Schiff's base liquid crystal compound doped with a low concentration of BaTiO₃ nanoparticles. *J Mol Liq.* 2017;225:496-501.
 70. Nafee SS, Hagar M, Ahmed HA, Alhaddad O, El-Shishtawy RM, Raffah BM. New two rings Schiff base liquid crystals; ball mill synthesis, mesomorphic, Hammett and DFT studies. *J Mol Liq.* 2020;299:112161.
 71. Banoon ZR, Al-Lami AKA, Abbas AM. Synthesis and Studying the Optical Properties of Novel Zinc Oxide/a symmetric dimer Liquid Crystal Nanohybrid. *Journal of Nanostructures.* 2023;13(1):159-172.
 72. Maier W, Saupe A. Eine einfache molekular-statistische Theorie der nematischen kristallinflüssigen Phase. Teil II. *Zeitschrift für Naturforschung A.* 1960;15(4):287-292.
 73. Al-Hamdani UJ, Abdulwahhab HA, Hussein KA. Effects of terminal substituents on mesomorphic properties of Schiff base-ester mesogens and DFT calculations. *Liq Cryst.* 2022;49(14):1998-2007.
 74. Ha ST, Foo KL, Lin HC, Ito MM, Abe K, Kunbo K, et al. Mesomorphic behavior of new benzothiazole liquid crystals having Schiff base linker and terminal methyl group. *Chin Chem Lett.* 2012;23(7):761-764.
 75. Al-Taifi EA, Yeap G-Y, Ibrahim OF, Marae IS, Al-Waleedy SA, Bakhite E. Synthesis and mesomorphic properties of non-symmetric liquid crystal dimers stabilized by benzothiazole and substituted aromatic imines. *Egyptian Journal of Chemistry.* 2023;66(1):419-429.
 76. Gray GW, Winsor PA. *Liquid crystals & plastic crystals.* Editors1974.
 77. Pathak G, Hegde G, Prasad V. Octadecylamine-capped CdSe/ZnS quantum dot dispersed cholesteric liquid crystal for potential display application: Investigation on photoluminescence and UV absorbance. *Liq Cryst.* 2021;48(4):579-587.
 78. Lakowicz JR. *Principles of fluorescence spectroscopy:* Springer; 2006.
 79. Schweizer T, Kubach H, Koch T. Investigations to characterize the interactions of light radiation, engine operating media and fluorescence tracers for the use of qualitative light-induced fluorescence in engine systems. *Automotive and Engine Technology.* 2021;6:275-287.
 80. Willeford K. *The Luminescence Hypothesis of Olfaction.* *Sensors.* 2023;23(3):1333.
 81. Valeur B, Berberan-Santos MN. *Molecular fluorescence: principles and applications:* John Wiley & Sons; 2012.
 82. Lawson-Wood K, Upstone S, Evans K. Determination of Relative Fluorescence Quantum Yields using the FL6500 Fluorescence Spectrometer. *Fluoresc Spectrosc.* 2018;4:1-5.
 83. Mohammad A-T, Mustafa HK. Unsymmetrical Coumarin based dimeric liquid crystals: Synthesis, Characterization, Mesomorphic investigation, Photoluminescence and Thermal conductivity. *Liq Cryst.* 2022;49(3):354-365.
 84. Buchs J, Geßner A, Heyne B, Janietz D, Sawade H. Fluorescent liquid crystals with rod-shaped π -conjugated hydrocarbon core. *Liq Cryst.* 2019;46(2):281-298.
 85. Banoon SR, Ghasemian A. The characters of graphene oxide nanoparticles and doxorubicin against HCT-116 colorectal cancer cells in vitro. *J Gastrointest Cancer.* 2021:1-5.
 86. Ali ZH, Al-Saady MAAJ, Aldujaili NH, Rabeea Banoon S, Abboodi A. Evaluation of the Antibacterial Inhibitory Activity of Chitosan Nanoparticles Biosynthesized by *Streptococcus thermophilus*. *Journal of Nanostructures.* 2022;12(3):675-685.
 87. Erhardt CS, Guaglianoni W, Garcia AP, Basegio TM, Bergmann CP. Ultra-rapid microwave-assisted synthesis of gallium doped zinc oxide for enhanced photocurrent generation. *Ceram Int.* 2023;49(8):12231-12239.

88. Happy A, Soumya M, Kumar SV, Rajeshkumar S, Sheba RD, Lakshmi T, et al. Phyto-assisted synthesis of zinc oxide nanoparticles using *Cassia alata* and its antibacterial activity against *Escherichia coli*. *Biochemistry and Biophysics Reports*. 2019;17:208-211.
89. Saliba S, Coppel Y, Davidson P, Mingotaud C, Chaudret B, Kahn ML, et al. Liquid crystal based on hybrid zinc oxide nanoparticles. *J Mater Chem*. 2011;21(19):6821-6823.
90. He M, Yang L, Lin W, Chen J, Mao X, Ma Z. Preparation, thermal characterization and examination of phase change materials (PCMs) enhanced by carbon-based nanoparticles for solar thermal energy storage. *Journal of Energy Storage*. 2019;25:100874.