

Chemistry of Triazene-Liquid Crystals: A Review

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Abstract

This review focuses on star-shaped liquid crystals that possess a highly organized and elongated molecular design, which enables them to exhibit favorable ferroelectric and ionic conductivity functions due to the electron delocalization resulting from π - π stacking conjugation and the electrostatic attraction of ions. The motivation for creating an ionic liquid crystal with a nematic phase is due to its potential engineering uses. The nematic phase is recognized for having the highest fluidity among all liquid crystalline phases. This makes it possible to position the nematic phase by applying an external electric or magnetic field widely utilized in electro-optical electronics. The chemistry of liquid crystals, specifically the state chemistry of matter, involves compounds of chemicals containing features of liquid crystals. Biological sensors made from liquid crystal materials enable monitoring biological phenomena without labels. Liquid crystalline polymers are employed to replicate color-generating structures. Liquid crystal compounds are commonly known as a distinct state; however, their impact on contemporary procedures has been significant. Derived from cholesterol, liquid crystals are molecules often studied and handled by biologists and biomedical engineers.

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1. Introduction

Liquid crystals (LC) in the chemistry of states of matter are substances that have the appearance of a liquid, but their molecules are arranged in certain levels like crystals, which is the occurrence of a transformation in matter and the rearrangement of the molecules in the same state as shown in Figure 1. Liquid crystals are defined as the intermediate state whose composition is confined to a regular crystalline solid state, in which the particles are restricted in movement and have a three-dimensional geometric system, and the regular, irregular liquid state, in which the particles of a substance move randomly [1]. Their study and development is multidisciplinary, integrating fundamental chemistry of liquid crystal. Liquid

crystals are formed by anisotropic organic molecules and are characterized by their fields and outer surfaces, significantly impacting their structure and behaviour. However, the significant scientific and technological revolution caused by this intriguing set of materials primarily occurred in information display rather than in the biological sciences [2]. Liquid crystals are intriguing materials which exhibit characteristics of both liquids and solid crystals. They exhibit fluidic behavior, although their molecular arrangement remains fixed, like to that of a crystal. The mesophase is the term used to describe this unique state. During this phase, the molecules of the liquid crystals exhibit a specific arrangement [1].

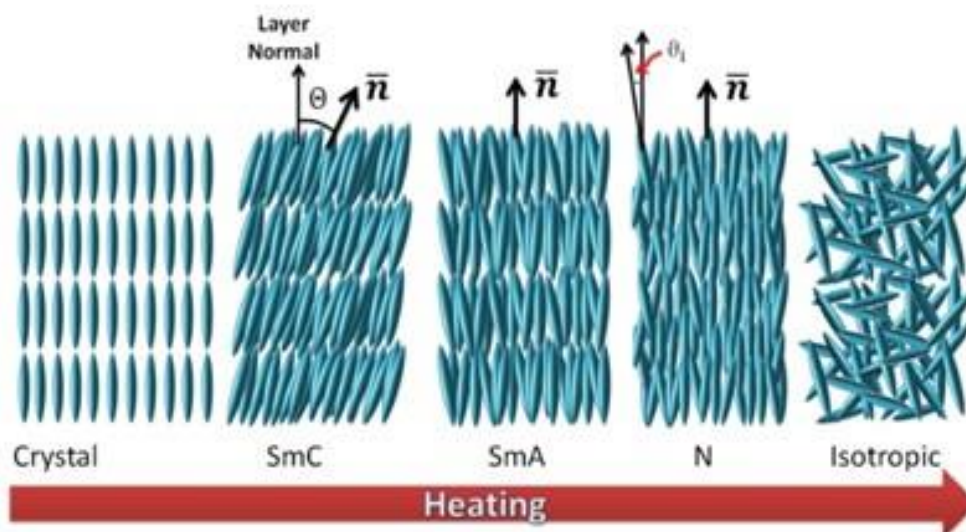


Figure 1. Schematic illustration of different liquid crystal phases observed on heating from the crystalline state [1].

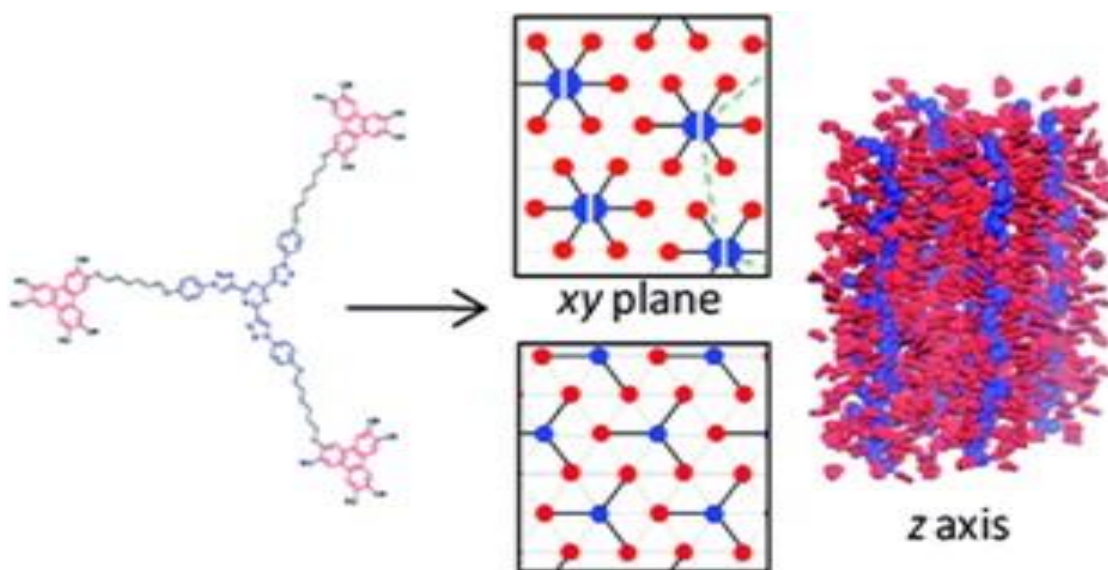


Figure 2. Chemical structure of star-shaped liquid crystal.

Heterocyclic compounds are an essential group of organic chemicals that have numerous applications in different scientific domains. Five-membered heterocyclic compounds exhibiting liquid crystalline characteristics have been effectively assessed. Typically, the molecule consists of interconnected units, end groups, and elongated, pliable chains with flat, rigid centres. The capacity of mesogenic compounds to organize themselves and undergo self-assembly is determined by their molecular geometry [2]. Over a long time, researchers have developed numerous thermotropic liquid crystals containing

heterocyclic units while studying heterocyclic liquid crystal derivatives. As part of our study on variants of liquid crystals that contain heterocyclic units, we have developed a range of thermotropic liquid crystals with heterocyclic units over an extended period. The structural arrangement of rigid-cored calamitic molecules has been considered to be the most favorable for exhibiting mesogenic properties. Hence, comprehending the connection between the arrangement and characteristics is vital in the process of creating novel liquid crystal substances [2]. A wide range of mesogens have been synthesized and examined

due to the application of innovative thermotropic liquid crystals. Real-world applications of liquid crystal (LC) technology in science and technology include devices such as display devices, photoconductors, organic light-emitting diodes (OLEDs), and semiconductor materials [3]. Utilizing a triazine core, along with substituted

1,3,5-triazines and benzoic acid mesogenic arms, as shown in Figure 2, has resulted in the discovery of a novel liquid crystal structure. The presence of different nucleophilic substituents in cyanuric chloride results in the formation of discotic or calamitic morphologies based on their specific components, Figure 3 [4].

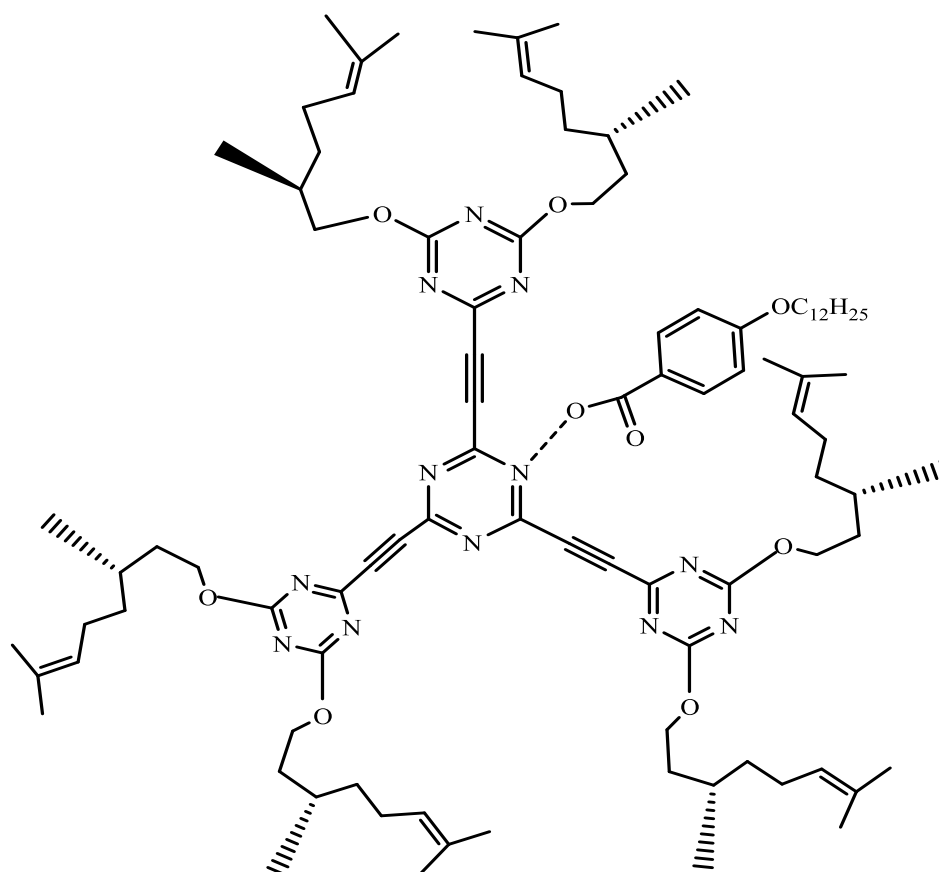


Figure 3. 1,3,5-triazines and benzoic acid mesogenic arms.

In ionic liquids, substances that combine the features of both liquid crystals and ionic liquids are called ionic liquid crystals Figure 4 [5].

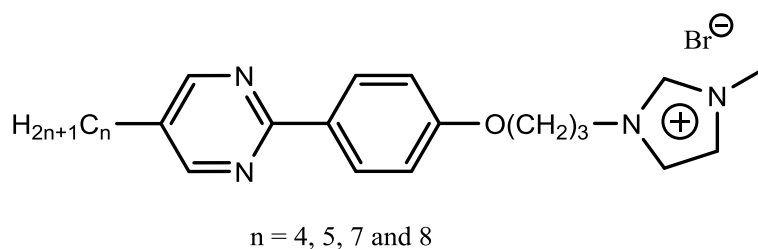


Figure 4. Example of ionic liquid crystal

These materials have garnered increasing attention in recent decades. Ionic liquid crystals have various applications, including their use as

solvents and batteries in extraction processes, in solar cells for dye sensitization, and as electrolytes in fuel cells [6].

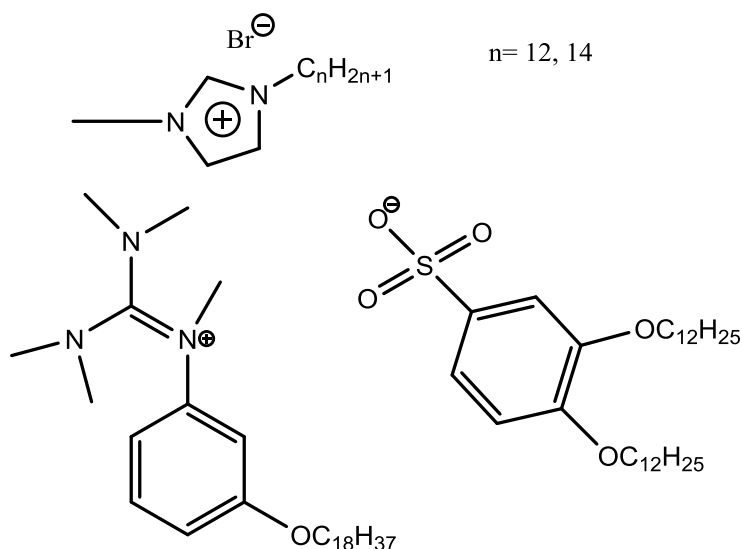


Figure 5. Example of solvent ionic liquid crystal

Despite the present circumstance, heteroatomic polycyclic aromatic sub-units have been extensively employed in creating novel stimuli-responsive compounds because of their distinct electronic characteristics and coordination capabilities of the heteroatoms. Out of the several types of molecular units that can be combined, the cyclic 1,3,5-homotriazine structure is especially suitable since it allows for the easy expansion of the conjugated system [7], resulting in luminous qualities. The combination of the N atom's strong electronegativity and their outstanding electron-accepting capacity makes them appealing for creating intramolecular charge-transfer donor-acceptor (D-A) molecules that also have fluorescence versatility such as 1,3,5-triethynylbenzene as a core and 2,5-

diphenyloxadiazole. The nitrogen lone electron pair of the triazine ring is capable of accepting hydrogen bonds and can also be quaternized; supramolecular LC has gradually developed into a mature and widely applied discipline for lots of aspects such as nanowire, templates, LC physical gel and electro-optic materials as shown in Figure 6 [7]. The above distances are even shorter than those estimated in the experimental data, and are very short compared to the typical C–H ... N separation shown in Figure 5. When considering to what extent the interactions can be characterised as C–H ... N hydrogen bonds, it is significant that all three calculations indicate a substantial electron-withdrawing influence from the nitrogen atoms upon the carbon atoms [7].

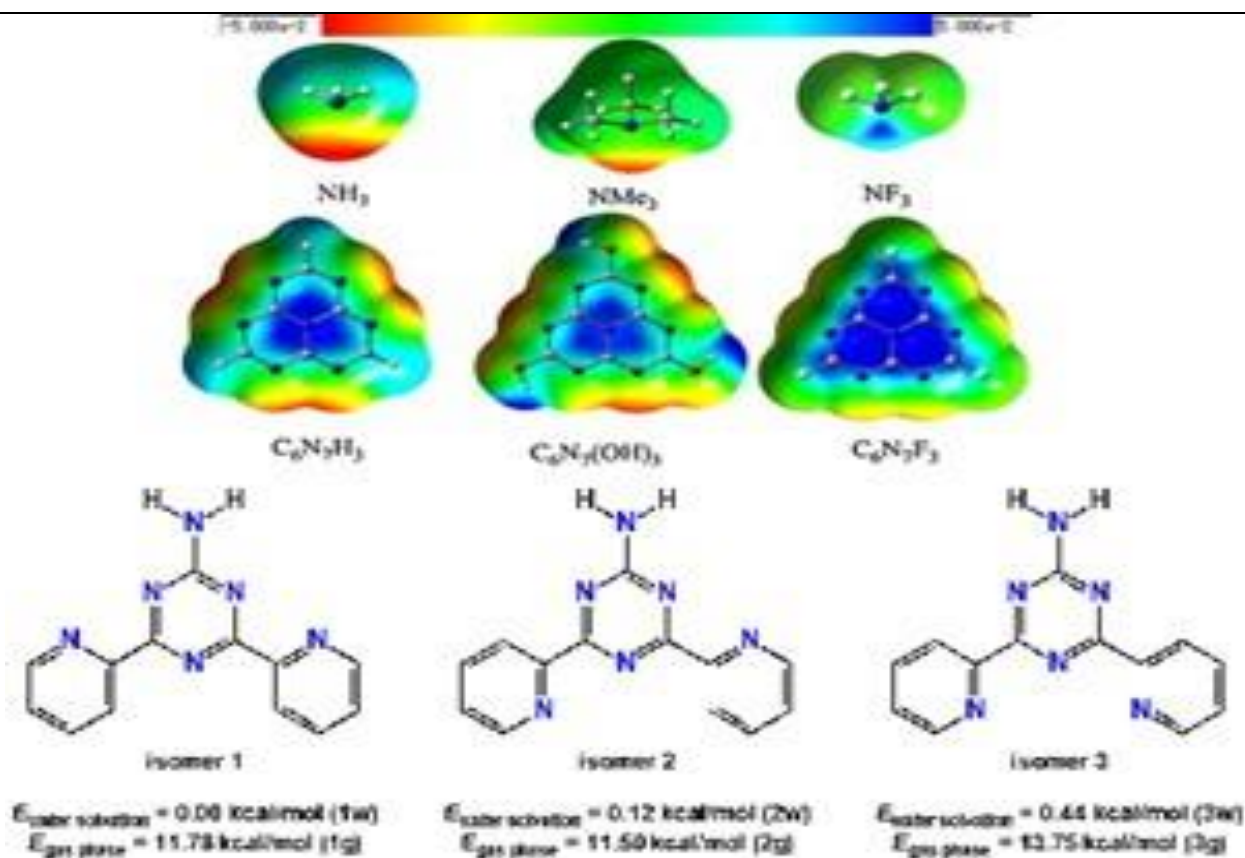


Figure 6. H-bonding with nitrogen lone pair.

Despite some research in the areas of optics (such as two-photon absorption and OLEDs), pharmacology, and supramolecular materials, there is a scarcity of reports on luminescent liquid-crystal semiconductor materials that can respond to multiple stimuli [8].

1.2. Star shape of Liquid Crystal

The distinctive star-shaped structure such as tris(2,6-dimethyl-1,4-dihydro pyridine-3,5-dicarbonitrile), Figure 7 can serve as a component for creating macromolecular liquid crystal materials in addition to its luminous features [9].

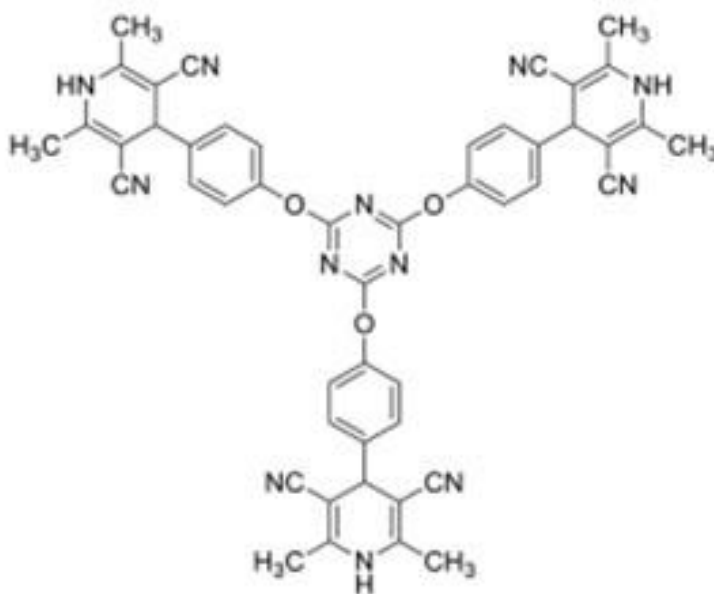
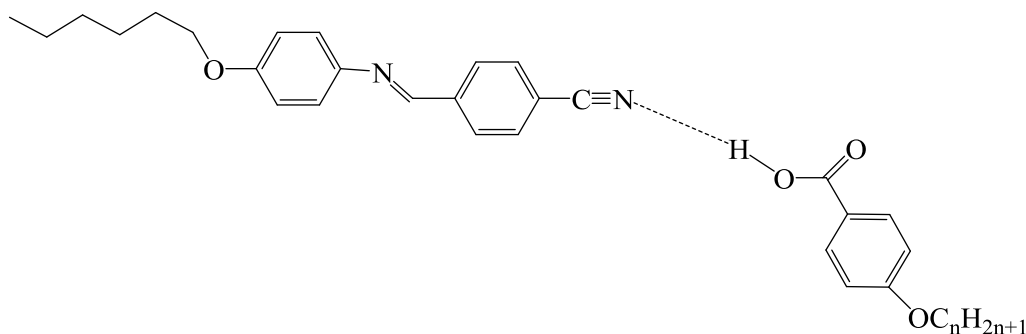


Figure 7. Structure of tris(2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile).

Nevertheless, the intricate arrangement of their propeller structure typically poses challenges for these molecules to demonstrate a significant level of columnar stacking. Typical methods to address this limitation involve elongating the flexible chains to produce nematic liquid crystals such as cyanobiphenyls and another with rigid and mantle

group in the system, augmenting the number of flexible chains and expanding the π -conjugated system, stabilizing the twisted triazine ring while decreasing the rotational freedom through hydrogen bonding, and achieving stable hexagonal columnar phases through microphase separation of fluoroalkyl chains, Figure 8 [10].



$$n = 6, 8, 10, 12 \text{ and } 16$$

Figure 8. The intermolecular H-bonding between the electron rich terminals CN and –COOH moieties.

Discotic liquid crystals, such as triphenylene, have been extensively studied in organic semiconductor materials and displays due to their well-structured, self-assembled intermediate phases.

The creation of liquid-crystalline phases is made easier by connecting triazine units to triphenylene structures using flexible chains, Figure 9 [11].

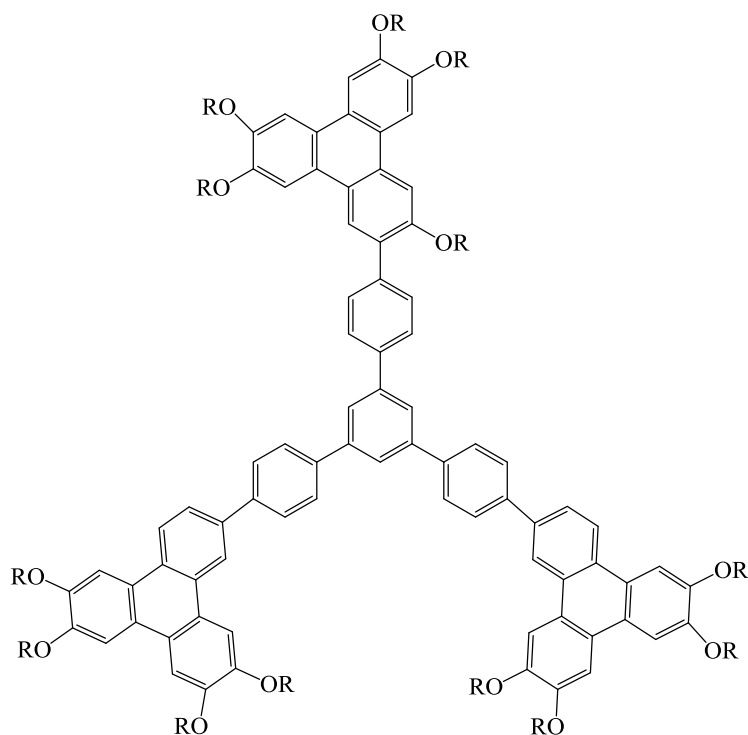


Figure 9. Star-shaped compounds triphenylene-phenyl-triazine.

This study examines the properties of new triphenylene-triazine derivatives, specifically their ability to respond to stimuli and form self-assembled liquid crystals. The study also investigates their optical and luminescent properties. The research is conducted to gain knowledge in the field and explore their possible applications [11]. Discotic liquid crystals usually display intense fluorescence in a diluted solution because of the flat structure of the aromatic core. However, when they are in an aggregated state, the strong intermolecular π - π stacking absorbs the energy absorbed by the stack, resulting in a decrease in fluorescence known as aggregation-caused fluorescence quenching (ACQ) [12]. Liquid crystal displays do not emit light directly, and the

requirement for additional light sources to be added results in increased energy consumption, which restricts the use of liquid crystal materials. The identification of aggregation-induced luminescence (AIE) and its hypothesized mechanism offer a promising solution to successfully counter the aggregation-caused quenching (ACQ) effect, a long-standing challenge. Aggregation of deformed molecules can result in intense fluorescence emission. Hence, the creation and production of AIE discotic liquid crystals hold great significance, as these substances can be utilized in OLEDs, which are light-emitting diodes. Triphenylene derivatives have been documented as OLED materials that emit red and blue light, primarily emphasizing blue light, Figure 10 [12].

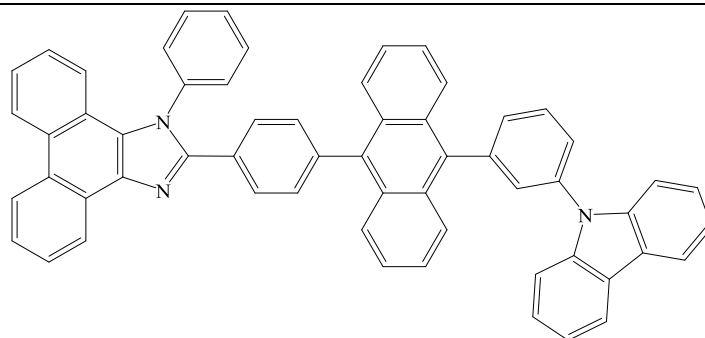


Figure 10. Example of Triphenylene derivatives have been documented as OLED materials.

However, green triphenylene materials are uncommon and exhibit a high turn-on voltage and low luminous efficacy. The star-shaped mesogens, or Hekates, consist of three extended branches attached to a tiny disc-like core group. They are believed to be one of the simplest multiarm mesogens, but more complex star-shaped liquid crystals with up to three mesogenic arms have been documented. The benzene ring and 1,3,5-triazine group are the core units most frequently employed

in synthesizing the simplest three-armed star-shaped mesogens. Several star-shaped molecules have been created, with a central core consisting of symmetrical and non-symmetrical phenyl rings such as 4-[4'-n-alkoxybenzoyloxy] benzoyl chloride, as shown in Figure 11. These molecules include mesogens and have varying lengths of alkyl spacer groups. The mesomorphic and photophysical properties of these molecules have been analyzed [13].

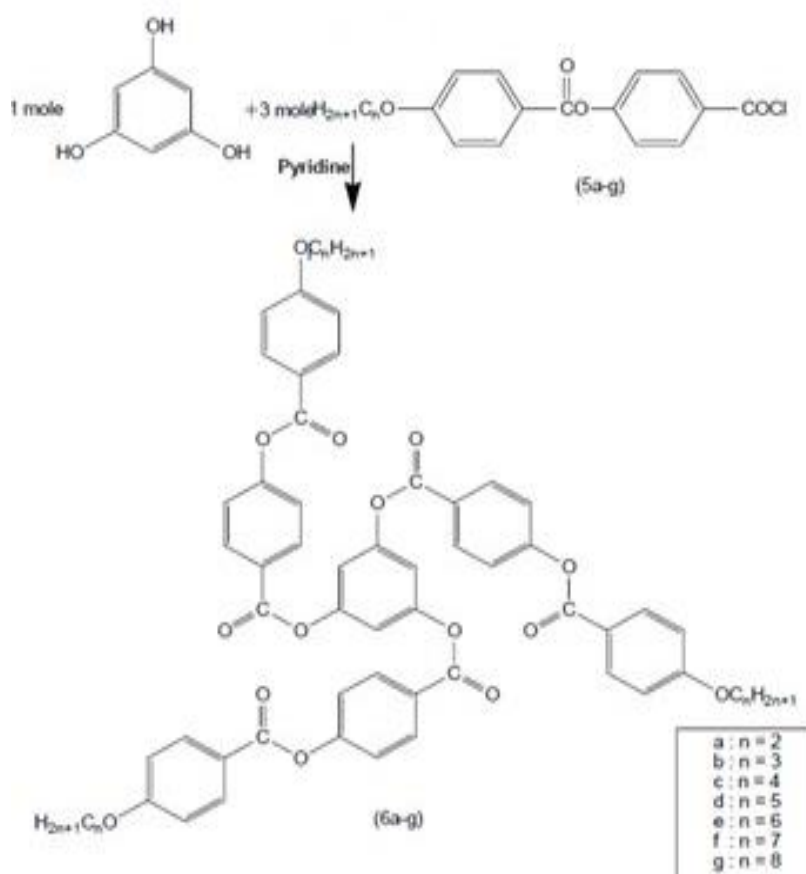


Figure 11. Structure of Triazine derivatives.

Star-shaped molecules possess a unique structural structure that allows for flexibility in their creation, incorporating different functional groups to achieve specific physical and chemical properties [13]. Their adaptability allows them to be used as important building blocks for the formation of mesophases, such as nematic, smectic, and columnar liquid crystalline phases. The star-shaped compounds, namely the three-armed star mesogens, have attracted significant attention as essential building blocks for mesogenic chemicals that induce nematic phases. The reason for pursuing the development of ILC with a nematic phase is its potential for technological applications, as the nematic phase is well acknowledged for its exceptional fluidity in comparison to other LC phases [14].

1.3. Heterocycles

Heterocycles play a critical role in creating and producing new useful organic materials, particularly in advancing thermotropic liquid crystals. Various molecular properties such as phase structure, polarity, geometry, and luminescence can be modified by incorporating heteroatoms. LC are compounds that exhibit the physical properties of a liquid while maintaining a distinct molecular order [15]. However, the molecules are organized in certain patterns similar to crystals, indicating a substance transition and the molecules' reconfiguration while remaining in the same state. Liquid crystals are defined as the intermediate state whose composition is confined to a regular crystalline solid state, in which the particles are restricted in movement and have a three-dimensional geometric system, and the regular, irregular liquid state, in which the particles of a substance move randomly [2]. Their study and development are multidisciplinary, integrating the fundamental chemistry of liquid crystal. Liquid crystals are formed by anisotropic organic molecules and are characterized by their fields and outer surfaces, significantly impacting their structure and behaviour. Nevertheless, the notable scientific and technical revolution brought about by this fascinating group of materials mostly took place in the field of data display rather than in biological research [16].

1.4. Cyanuric acid

Cyanuric acid serves as a chlorine stabilizer in swimming pools [17]. The term commonly used to describe it is stabilizer. It is important to note that

chloric acid, used to alter the pH, should not be mistaken for this, and the chemical structure is shown in Figure 12.

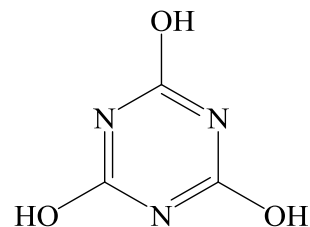


Figure 12. Chemical structure of Cyanuric acid.

Cyanuric acid establishes a feeble link with unbound chlorine in the pool water, safeguarding it against the sun's UV rays to diminish chlorine depletion [17]. When cyanuric acid is effectively controlled, it has been proven to decrease the quantity of chlorine required to maintain the minimal chlorine level in an outdoor swimming pool. Cyanuric acid can greatly decrease the expense of chemical disinfection in a small pool with a reasonable number of swimmers [17]. Cyanuric acid reacts with available chlorine in pool water, shielding against the sun's UV radiation and minimizing chlorine depletion. When effectively controlled, cyanuric acid can decrease the chlorine required to maintain the minimum chlorine level in an outdoor pool. Chemical suppliers often advise maintaining cyanuric acid levels between 30-50 ppm. However, a study by the University of California at Davis suggests that even lower levels of 2 or 3 ppm can still result in substantial savings in chemical expenses [18]. Cyanuric acid diminishes the overall efficacy of chlorine by establishing transient bonds with the free chlorine. As the concentration of cyanuric acid increases, the duration required to eliminate germs becomes longer. Therefore, we advise that all outdoor pools that utilize cyanuric acid as a stabilizer should uphold a minimum free chlorine residual of at least 2 parts per million (ppm) [19]. Other experts suggest a concentration of approximately 20 parts per million (ppm) to achieve a favorable cost-to-benefit ratio. When the concentration of chlorine in pools exceeds 50 ppm, it reaches a threshold where the advantages of using cyanuric acid are outweighed by the decrease in chlorine's efficacy and the cost of purchasing the acid. Dichloro consists of 57% cyanuric acid by weight. Trichloro is composed of 54% cyanuric acid [20].

1.5. Triazines

Triazines are cyclic compounds consisting of six atoms, with three carbon and three nitrogen atoms, arranged in an aromatic structure. The 1,3,5-

triazines are the most ancient and intensively researched among the isomeric forms. S-triazine is a widely employed name for 1,3,5-triazine due to its symmetrical characteristics [21]. For the purpose of this article, the term "triazine" will specifically denote the 1,3,5-derivatives products. In 1895, Nef first synthesized the chemical 1,3,5-triazine by reacting hydrogen cyanide with ethanol in an ether solution that was saturated with hydrogen chloride. Nevertheless, this discovery was made inadvertently [22]. Afterwards, the salt that was acquired underwent base treatment and distillation, resulting in the production of 1,3,5-triazine, which resulted in only 10%. Nef mistakenly categorized what was produced as a dimeric entity [23]. However, in 1954, Grundmann and Kreutzberger provided evidence that the substance is composed of three molecules of

hydrogen cyanide called s-triazine. Triazine exhibits high thermal stability, remaining intact unless exposed to temperatures exceeding 600 °C [24]. At this point, it undergoes decomposition, resulting in the formation of hydrogen cyanide. The triazine ring exhibits notable resistance to electrophilic substitution [25]. However, it is prone to ring cleavage when confronted with nucleophiles and is very vulnerable to hydrolysis by water and other hydroxyl compounds, but to a lesser degree [26]. The molecule 1,3,5-triazine can undergo chemical reactions with bifunctional amines or related chemicals to produce various heterocycles [27]. Moreover, it can function as a replacement for HCN in some procedures. Figure 13, illustrates the three commonly used triazine derivatives: cyanuric acid, melamine, and cyanuric chloride [17].

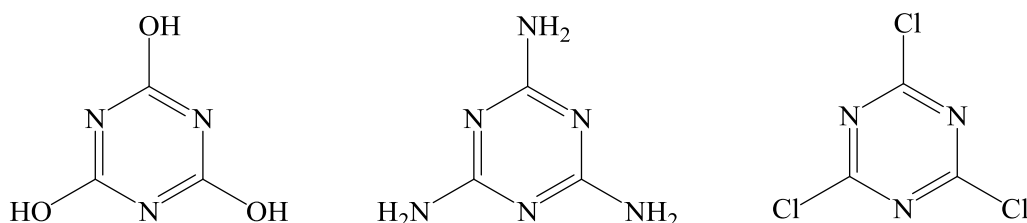


Figure 13. Common triazine compounds.

The synthesis of triazines was initially achieved by creating cyanuric acid [28]. In 1776, Scheele synthesized cyanuric acid by subjecting uric acid to pyrolysis. The term "cyanuric acid" was coined due to the belief that the substance consisted of cyanide groups and was derived from uric acid. In 1820, Serullas replicated Scheele's experiment to produce

cyanuric acid by dissolving cyanogens in water. In 1830, it was determined that the two products were identical, and Liebig and Wohler clarified their structure. Cyanuric acid exhibits limited solubility in water and is susceptible to heat instability, as shown in Figure 14 [29].

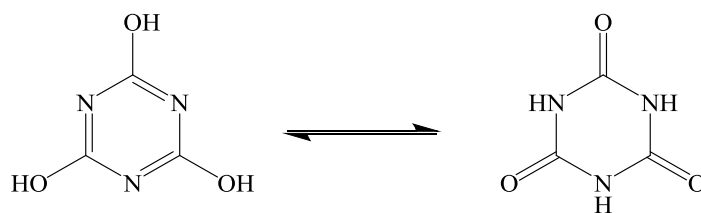


Figure 14. Cyanuric acid tautomerism.

Cyanuric acid is synthesized through pyrolysis of urea [30], Figure 15.

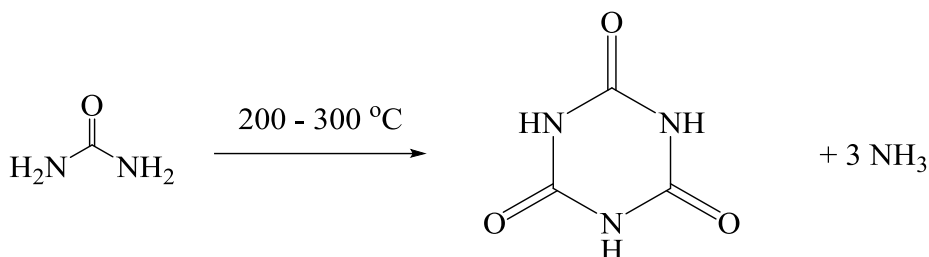


Figure 15. Industrial synthesis of cyanuric acid.

The documentation in 1996 recorded the fabrication of triazine-based dendritic structures using cyanuric chloride as Gd chelating ligands for MRI applications. Other research groups have also recorded the existence of triazine dendrimers, and Steffensen and his team have extensively investigated this subject [31]. The primary focus of the Simanek group has been to improve the synthesis techniques used for melamine dendrimers. This has been accomplished by exploiting the diverse reactivity of cyanuric chloride to incorporate different

reactive molecules for further changes while utilizing orthogonal protecting categories or diamines with specific sensitivity [32].

1.6. Applications of Star Shape Liquid Crystals

Star Shape Liquid Crystal, as shown in Figure 16 [33], technology has significantly impacted various science, engineering, and gadget technology fields. The applications of this unique material are still being explored, and efficient answers to a wide range of challenges are consistently offered.

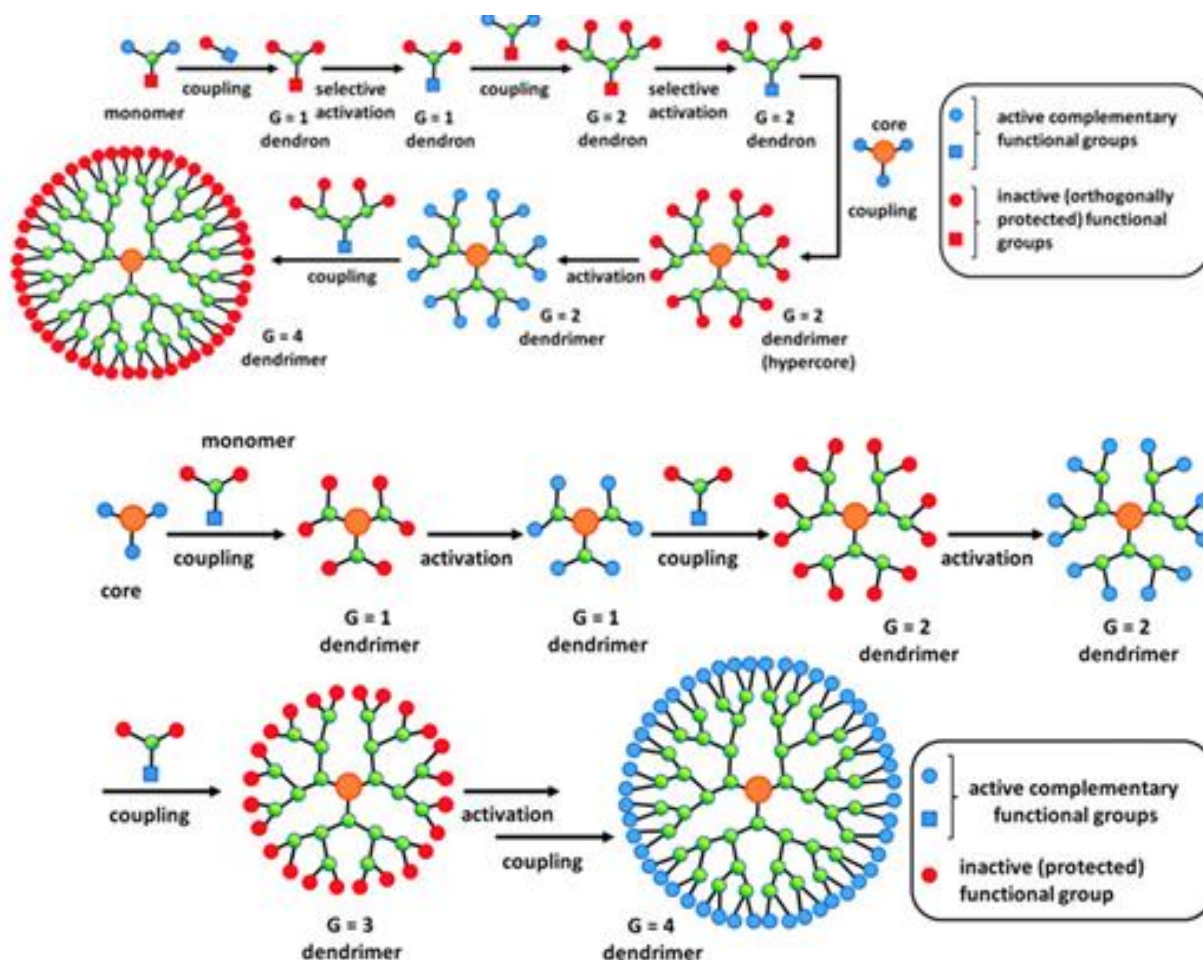


Figure 16. Convergent and Divergent growth method of star shape liquid crystal to dendrimers.

i. **Star Shape Liquid crystal displays**

Star Star-shaped liquid crystal displays (LCDs) are the most prevalent application of liquid crystal technology. This discipline has expanded into a

lucrative sector worth billions of dollars, with numerous notable scientific and engineering breakthroughs, as shown in Figure 17 [34].

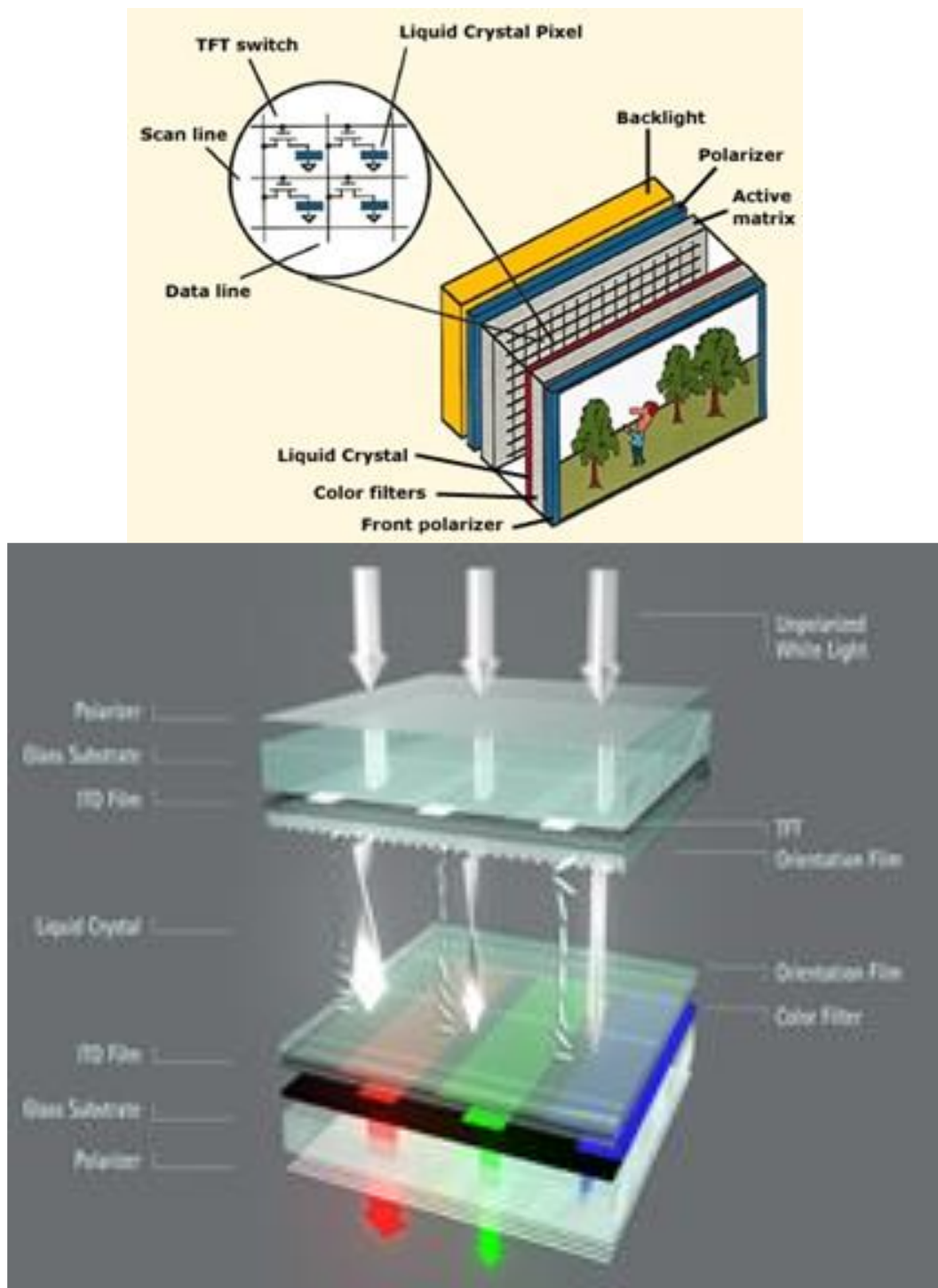


Figure 17. An active-matrix liquid crystal display (LCD).

The man responsible for this society-changing innovation was George Gray — his innovative liquid crystal molecules (now known as 5CB) made liquid crystal displays (LCDs) practical and kickstarted the multibillion-dollar flat-screen business. The narrative starts in 1967 when John Stonehouse, a Labour MP and Minister for technology under Prime Minister Harold Wilson, formed a committee to advance an innovation that had just emerged in Star Trek — a full-colour flat-screen display [35].

ii. **Star Shape Liquid Crystal Thermometers**

Chiral nematic (cholesteric) liquid crystals reflect light with a wavelength that matches their pitch, as previously shown. The pitch and the colour reflected are both contingent on temperature, Figure 18: thermochromic Liquid Crystals (LCs) may depend on

temperature, shift to numerous hues, and are more costly than leuco dyes. LCs start black below their temperature range, go through the hues of a rainbow, and return to black again above the temperature range. LCs are reversible in that they may be used again and over again. The photo depicts an example of a liquid crystal sheet reacting to warming [36]. Popular liquid crystal uses include medical gadgets, forehead, aquarium and room thermometers, promotional items and advertising applications [37]. Additionally, utilitarian products such as propane tank gas level indicators are obtaining significant renown. Liquid crystal thermometer strips are utilized for thermal mapping and other industrial applications where bespoke affordable temperature monitoring is necessary [38].

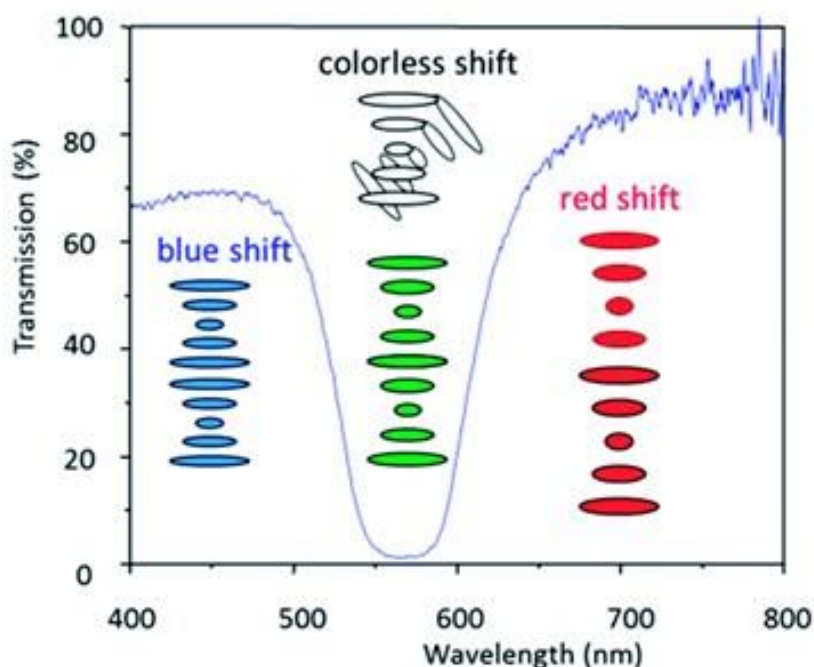


Figure 18. Possible changes of the reflection band of a Cholesteric Liquid Crystals CLC.

iii. **Optical Imaging**

Optic scanning and storage have recently developed uses of liquid crystals. This method entails positioning a liquid crystal cell in between two layers of photoconductor [39]. Photons are focused on the photoconductor, causing an increase in the conductivity of the substrate. This leads to the creation of an electric field within the liquid crystal that is proportional to the brightness of the photon. The electrode can transmit the electrical pattern, enabling the picture to be captured [40].

iv. **Polymer dispersed star shape liquid crystals**

PDLs are composed of liquid crystal particles that are distributed within a solid polymer matrix, as depicted in Figure 19 [41]. The resultant substance is a polymer resembling Swiss cheese, with voids filled by liquid crystal drops. The substance's distinct properties can be attributed to these minuscule droplets, which typically measure a few microns in diameter for practical purposes. By manipulating the alignment of the liquid crystal molecules using an electric field, it is feasible to alter the strength of the light that passes through.

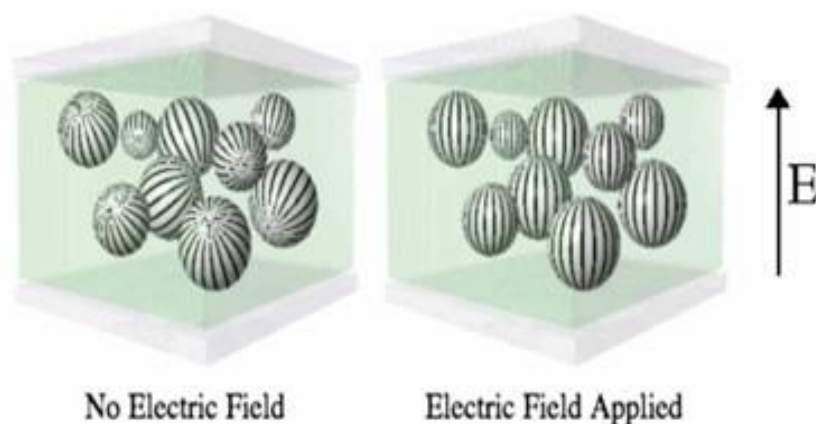


Figure 19. Effect of an external electric field on the director orientation of a PDLC droplet. (a) Electric field off and (b) electric field on.

v. Other Applications of Star Shape Liquid Crystal

Liquid crystals have a multitude of additional uses. These tools do nondestructive mechanical testing on materials under stress [42]. This approach also examines radio frequency (RF) waves within waveguides. These devices are utilized in medical applications to measure transitory pressure, such as the pressure exerted by a walking foot on the ground. Low molar mass (LMM) liquid crystals are utilized in various applications such as erasable optical disks, full color "electronic slides" for computer-aided drawing (CAD), and light modulators for color electronic imaging. As scientists continue to explore and study new features and varieties of liquid crystals, these materials will undoubtedly become increasingly significant in commercial and scientific applications [43].

2. Conclusion

The emergence of the liquid crystal state for some chemical compounds and some materials has sparked more recent developments and important applications in several vital fields as liquid crystal research began to move and merge with many basic aspects of biological sciences to generate new fields of application. This review examines the consequences of artificially created liquid substances for biological and medical uses. The introduction of new liquid crystal technologies will inevitably stimulate further study in both fundamental and practical disciplines. The spectral fingerprint of a particular cell, tissue, or other biological material holds significant importance in clinical the method.

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