

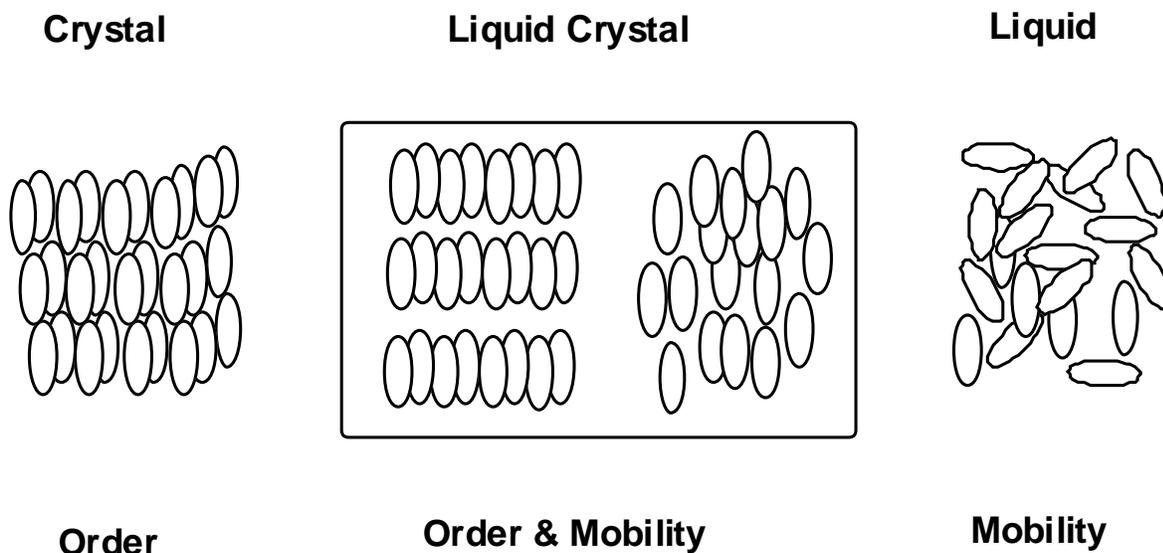
# CHAPTER 1

## Introduction

### 1.1 Liquid crystals

Liquid crystalline state is an intermediate state of matter in between the solid and the liquid. For this reason, they are referred to as intermediate phases or mesophases. Crystals have long-range order, with the molecules being rigid and located in precise, regular, repeating patterns. In the crystal phase the molecules exhibit almost no mobility. Conversely, in the isotropic liquid phase only a short-range order dominates, the molecules are mobile and have no orientation with respect to each other. Liquids usually have very rapid molecular motion (rotation times of *ca.*  $10^{-11}$  s) and are disordered.

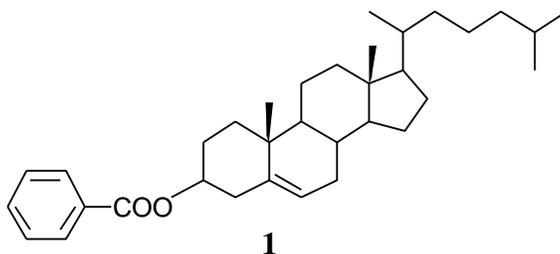
When molecular crystals are heated to their melting point, they usually change directly into the liquid state. The periodic structures of the lattice as well as the orientational ordering of the molecules are destroyed simultaneously. However, if the constituent molecules have a pronounced anisotropy of shape, such as rod or disc, the melting of the lattice may precede the disappearance of the orientational ordering leading an intermediate phase composed of molecules which are more or less parallel to each other but at the same time exhibiting a certain degree of fluidity. The molecules can slide over one another while still preserving their parallelism. The fluid is therefore anisotropic; it is turbid and, like a crystal, shows optical birefringence and dielectric anisotropy. At a higher temperature, there is orientational melting and the anisotropic fluid transforms into the ordinary isotropic clear liquid. Such intermediate phases are referred to as liquid crystals (LCs). They combine both, order and mobility (figure 1). The fundamental requirement for any substance to exhibit a liquid crystalline phase is the shape anisotropy of the constituent molecules [1-5].



**Figure 1.** Basic structural difference among crystal, liquid crystal and liquid.

## 1.2 History of liquid crystals

The definite history of LCs goes back to 1888, when a botanist-cum-chemist, Friedrich Reinitzer synthesized several esters of cholesterol, a natural product occurring in plants and animals. He observed a “double melting” behaviour of cholesteryl benzoate (**1**) [6].



The crystals of this material melted at 145.5 °C into a cloudy fluid, which upon further heating to 178.5 °C became clear. Further investigations of this phenomenon were carried out by the German physicist O. Lehmann who observed and confirmed, using the first polarized optical microscope designed by himself, the existence of “fluid crystals” [7].

Over the next decade about 15 LCs became known. All these materials were discovered by chance only as no relationship between the molecular shape and liquid crystalline state was known. During the first half of twentieth century, progress was mostly made by chemists, who discovered ever new types of liquid crystals. Daniel Vorlander, a professor of chemistry at the University of Halle, started systematic synthetic work in order to find structure-mesophase relationship in the beginning of twentieth century and by 1935 about 1100 liquid crystalline compounds were prepared in his laboratory. He remarked that all the compounds exhibiting mesophases had elongated (rod-like) molecules, now called calamitic molecules. In the middle of 1960s, G.H. Heilmeyer gave the first indication for an application of liquid crystals in electro-optical display technology. This report increased the interest in liquid crystal research exponentially. To date more than 95,000 liquid crystalline compounds are known in the literature.

In 1977, Chandrasekhar and his colleagues reported that not only rod-like molecules, but also compounds with disc-like molecular shape are able to form mesophases [8]. Currently more than 3000 discotic liquid crystals are known in the literature.

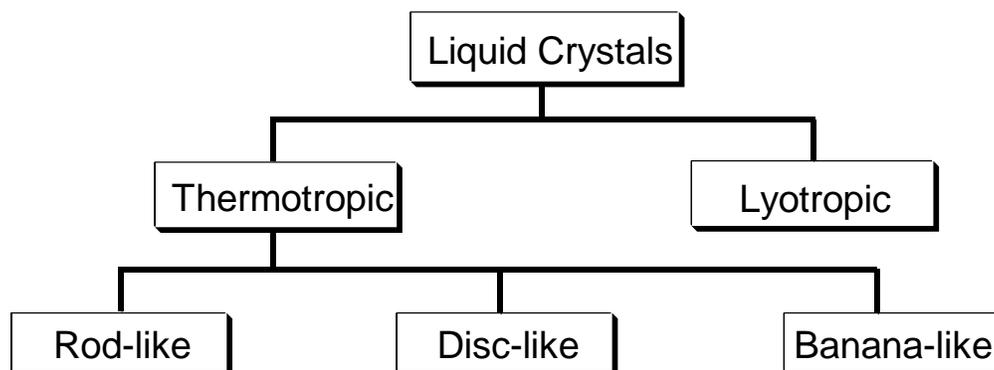
In 1986, liquid crystals formed by board-like (lath-like) were reported [9]. Depending on the relative size of the main axes, these molecules can be derived from rod-like or disc-like molecules. From the Greek word for board, these phases are called “sanidic”.

The latest addition in the liquid crystal family is banana-shaped molecules [10]. Typically, their molecular structure can be regarded as being composed of three units; an angular central unit, two linear rigid cores and the terminal chains [11]. The discovery of ferroelectricity in non-chiral banana-shaped molecules has led to a very intense research activity in the field. Several hundred bent molecular shape compounds have been synthesized so far [10-13].

### 1.3 Classification of liquid crystals

Liquid crystals can be roughly divided into two areas:

1. Thermotropic, whose mesophase formation is temperature dependent, and
2. Lyotropic, whose mesophase formation is solvent and concentration dependent.



**Figure 2.** Classification of liquid crystals.

The classification of liquid crystal mesophases have been shown in figure 2. This thesis is concerned only with thermotropic LCs. They are of interest both from the standpoint of basic research and also for applications in electro-optic displays, temperature and pressure sensors, etc. On the other hand, lyotropic liquid crystals are of great interest biologically and appear to play an important role in living systems.

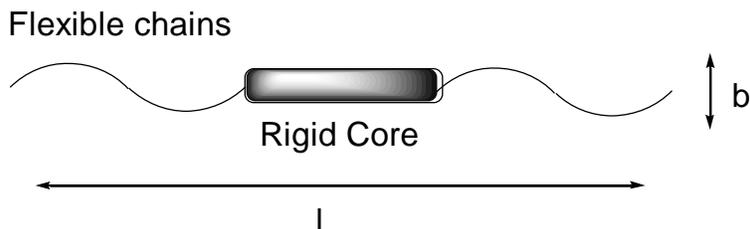
### 1.4 Thermotropic liquid crystals

The term “thermotropic” arises because transitions involving these mesophases are most naturally effected by changing temperature. The essential requirement to be a thermotropic liquid crystal is a structure consisting of a central core (often aromatic) and a flexible peripheral moiety (generally aliphatic chains). Based on the shape of the mesogenic molecules, thermotropic liquid crystals have been classified into three main structural groups.

1. Calamitic (rod-like)
2. Discotic (disc-like)
3. Bent-shape (banana-like)

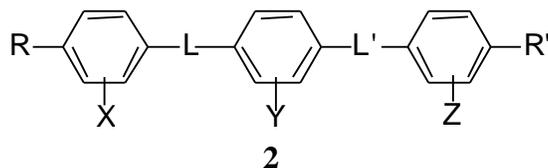
### 1.4.1 Calamitic liquid crystals

The most common type of molecule that forms mesophases is a rod-shaped molecule. These molecules possess an elongated shape (molecular length is significantly greater than the molecular breadth) as depicted in figure 3.



**Figure 3.** Representation of calamitic LCs, where  $l \gg b$

Most of the calamitic liquid crystalline compounds consist of two or more ring structure, bonded together directly or via linking groups. They usually have terminal hydrocarbon chains and some time lateral substitutions as well. The typical chemical structure of these molecules can be represented by the general formula (2) where R and R' are flexible moieties such as alkyl groups, X, Y and Z are generally small units such as halogens, methyl groups. L and L' are covalent bonds or linking units such as, -N=N-, -CH=CH-, -CH=N-, -COO-.

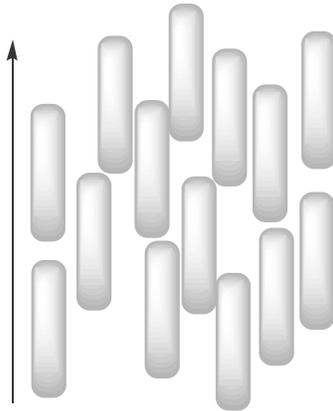


Calamitic liquid crystals can be classified mainly into two types.

1. Nematic (from the Greek word nematos meaning “thread”) &
2. Smectic (from the Greek word smectos meaning “soap”).

#### 1.4.1.1 Nematic Phase

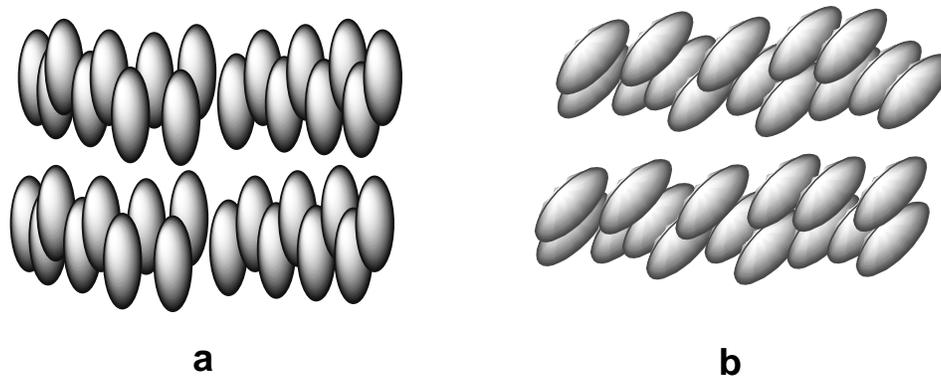
The nematic phase has a high degree of long-range orientational order of the molecules, but no long-range positional order. This is the least ordered mesophase (the closest to the isotropic liquid state). It differs from the isotropic liquid in that the molecules are spontaneously oriented with their long axes approximately parallel. The preferred axis of orientation of the molecules, depicted as a long arrow, is called the director (figure 4).



**Figure 4.** Structural representational of nematic phase formed by calamitic liquid crystal.

#### 1.4.1.2 Smectic Phase

Rod-like molecules are able to form liquid crystalline phases where in addition to the orientational order, the molecules possess positional order as well. The molecules are arranged in layers with a well-defined layer spacing or periodicity. The smectic phase is denoted by the symbol Sm.



**Figure 5.** Schematic representation of the (a) SmA and (b) SmC phase.

There are several types of smectic mesophases, characterized by a variety of molecular arrangements within the layers. Although the total number of smectic mesophases cannot be specified, the following types have been defined: SmA, SmB, SmC, SmF, and SmI. The SmA and SmC phases (figure 5) are the less-ordered and more common phases. In SmA phase the molecules form layers with their main axes parallel to the director. The SmC phase has the same layer structure of the SmA, but the molecules are tilted with respect to the layer plane. In both the phases, there is no positional order between molecules within the layers. SmB, SmF and SmI are more ordered smectic phases in which the molecules possess hexagonal order within the layers. They are called hexatic smectic liquid crystals. Disordered crystals having layer-like structures are often referred to as SmE, SmH, SmK, SmG and SmJ phases but they are more properly defined as lamellar plastic crystals. Tilted smectic mesophases formed by chiral compounds or containing chiral mixtures are designated by the superindex \* (SmC\*, SmF\*, etc.).

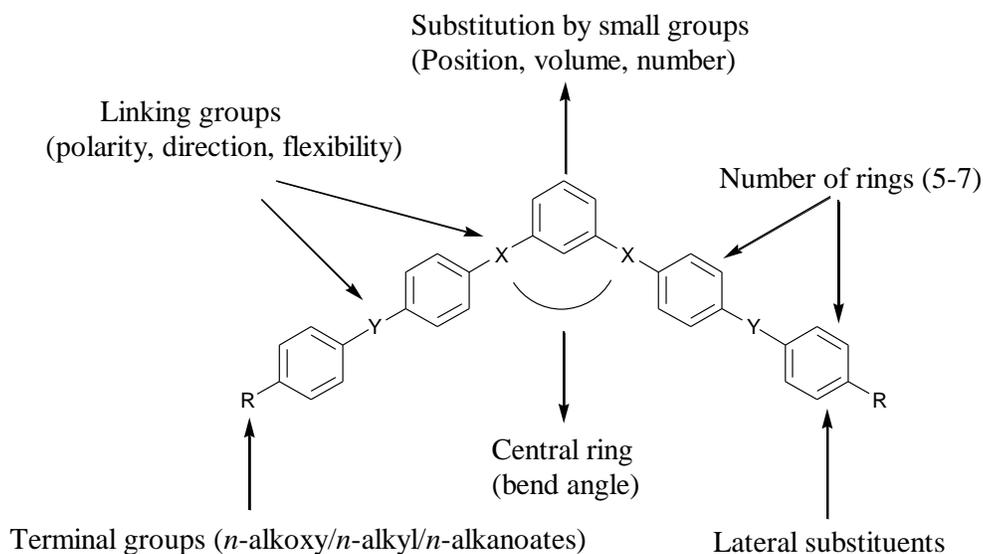
#### **1.4.2 Discotic liquid crystals**

As this thesis is mainly concerned with discotic liquid crystals, it will be discussed in detail (section 1.5) after a very brief discussion on banana-like liquid crystals.

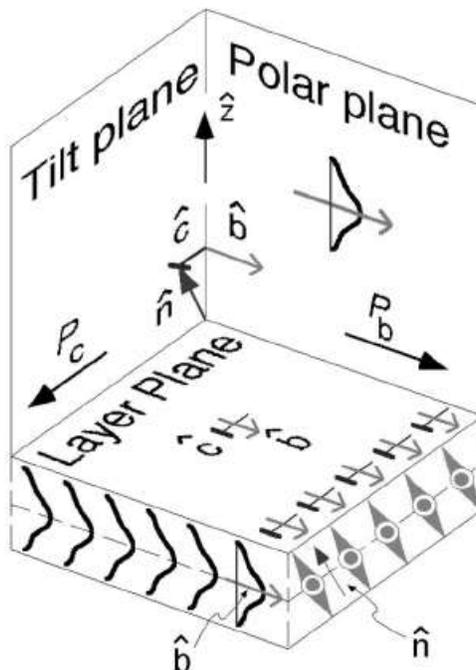
### 1.4.3 Banana liquid crystals

Bent molecular structures represent (figure 6) a new sub-class of thermotropic liquid crystals, which can display, not only classical nematic and/or smectic phases, but also novel types of smectic-like phases called “B” phases [12] and are numbered according to their chronological discovery, from B<sub>1</sub> to the most recent B<sub>8</sub>. The symbol B stands for Banana- or Bent- or Bow-shaped mesogens.

The most important thing in Banana liquid crystals is that the molecules pack along a bent direction, to constitute a polar plane which is perpendicular to the tilt plane. In addition, the tilted molecules exist in layers and produce a layer plane. Thus three different planes exist for a given layer which can be assumed to be three co-ordinates. If these three co-ordinates form a particular handedness (depending on tilt direction with respect to other two-coordinates), the mirror image of this shows the opposite handedness as shown in figure 7. These are non-superimposable mirror images and that’s why the layer becomes chiral though the individual molecules are achiral.



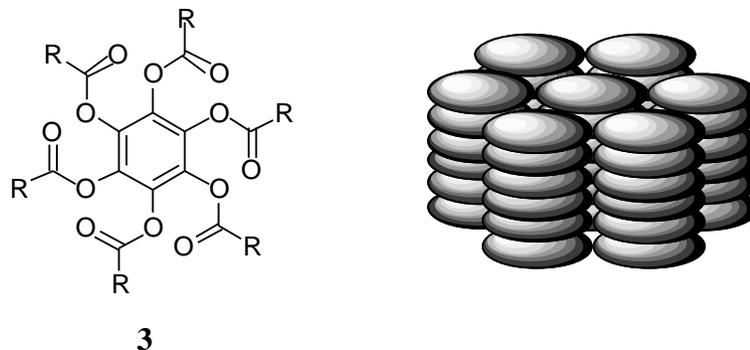
**Figure 6.** A general template of banana liquid crystals.



**Figure 7.** A schematic representation of the arrangement of the bent core molecules showing the origin of layer chirality from achiral molecules.

### 1.5 Discotic liquid crystals: the discovery

In September 1977, when the rod-like thermotropic liquid crystals started revolutionize commercial display technologies, Sivaramakrishna Chandrasekhar and his colleagues reported “...what is probably the first observation of thermotropic mesomorphism in pure, single component systems of relatively simple plate like, or more appropriately disc-like molecules” [8]. They prepared a number of benzene hexa-*n*-alkanoates (**3**) and from thermodynamic, optical and X-ray studies, it was established that these materials form a new class of liquid crystals in which molecules are stacked one on the top of other in columns that constitute a hexagonal arrangement (figure 8). This opened a whole new field of fascinating liquid crystal research.



**Figure 8.** Structure of benzene-hexa-*n*-alkanoates and their columnar arrangement.

It is interesting to mention that Vorlander in 1924 supposed the possibility of the existence of mesophases in leaf-shaped molecules [14] but his attempts to realize any example with this behaviour had been unsuccessful probably because the molecules, he looked at were devoid of flexible chains. He mentioned in his article that leaf-shaped molecules do not form any liquid crystals at all. Of course, the same molecules surrounded by long aliphatic chains are now well-known for forming columnar mesophases.

In the early 1960s, anisotropic mesophases with nematic texture had been observed during the pyrolysis of graphitizable substances (Carbonaceous mesophase) [15]. These mesophases were considered to be built up of flat polyaromatic molecules, however, and not by well-defined organic molecules. They were not stable and homogeneous in nature. Therefore, it was not possible to fully characterize these mesophases.

Self-organization of disc-like molecules to form discotic liquid crystals by Chandrasekhar *et al.* were an entirely new class of liquid crystal, quite different from the classical liquid crystals formed by rod-like molecules that had been known since they were observed by Friedrich Reinitzer in 1888. The disc-like molecules spontaneously form one-dimensional stacks, which in

turn, order themselves on two-dimensional lattices; the third dimension has no translational order-that liquid like characteristic.

## **1.6 Structures of discotic liquid crystalline phases**

Most of the discotics exhibit only one type of mesophase but a few examples with polymorphism are also known. Mesophases formed by disc shaped molecules are primarily three types:

1. Nematic
2. Columnar and
3. Lamellar

### **1.6.1 Nematic Phases (N) of discotic mesogens**

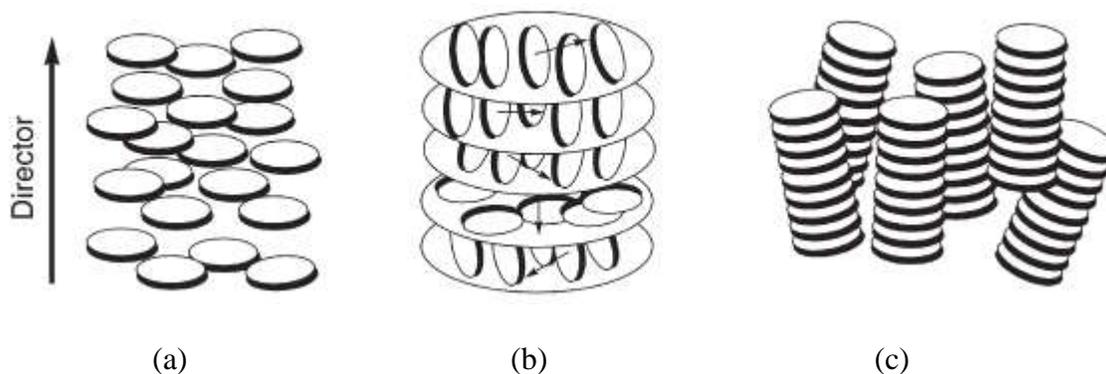
The nematic phases of disc-shaped molecules can be subdivided into three types:

1. Nematic discotic or discotic nematic
2. Chiral nematic and
3. Nematic columnar

In the nematic discotic phase, the molecules stay more or less in parallel position having only orientational order but no long range positional order (figure 9a). Nematic discotic is the least ordered mesophase. In the discotic nematic mesophase, the flat molecules possess full translational and rotational freedom around their short axes, whereas their long axes (spanning the plane of the discotic mesogen) orient, on average, parallel to a general plane.

The nematic phase of disc-shaped molecules is usually not miscible with the nematic phase of rod-shaped molecules, though they exhibit similar fluid schlieren textures [16]. However, unlike the usual calamitic nematic, discotic nematic phase is optically negative, the director

being the preferred axis of orientation of the disc normals (or the short molecular axis). The symbol “ $N_D$ ” is often used to denote discotic nematic phase. However, as the symmetry of a nematic phase formed by disc-shaped molecules is identical to that formed by rod-shaped molecules, it has been recommended [16] to remove the subscript “D” from the symbol “ $N_D$ ”.



**Figure 9.** Schematic representations of (a) discotic nematic (b) helical structures of chiral nematic phase and (c) nematic columnar phase.

Like chiral calamitic nematic or cholesteric phase, chiral discotic nematic mesophases,  $N_D^*$  also exist. The mesophase occurs in mixtures of discotic nematic and mesomorphic or nonmesomorphic chiral dopants, as well as in pure chiral discotic molecules [17, 18]. The helical structure of chiral discotic nematic phase is schematically shown in figure 9b.

The nematic columnar ( $N_{Col}$ ) phase is characterized by a columnar stacking of the molecules. However, these columns do not form two-dimensional lattice structures. They display a positional short-range order and an orientational long-range order (figure 9c).

### 1.6.2 Columnar phases of discotic mesogens

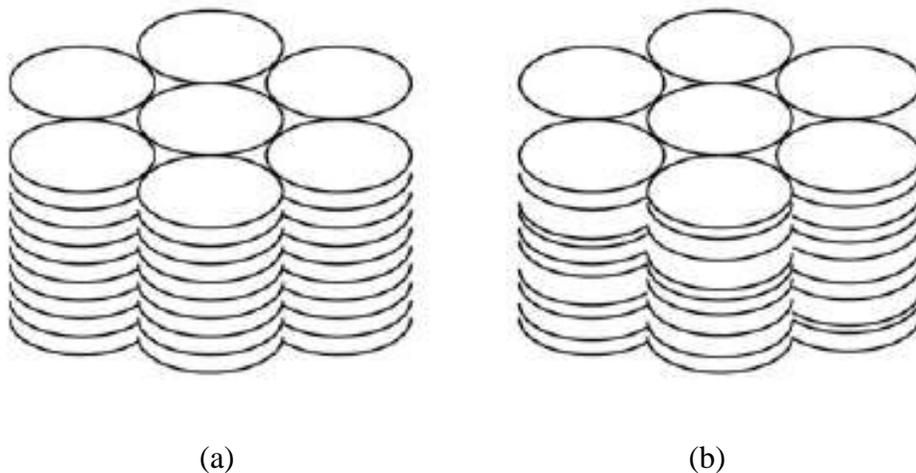
In columnar mesophases, molecules assemble themselves one on the top of the other in columns packed parallel on a two-dimensional lattice. The molecules may be arranged in a regular

ordered manner or aperiodically (disordered). Depending on the order in the molecular stacking in the columns and the two-dimensional lattice symmetry of the column packing, the columnar mesophases may be classified in five classes.

1. Columnar hexagonal mesophase
2. Columnar rectangular mesophase
3. Columnar oblique phase
4. Columnar plastic phase and
5. Columnar helical phase

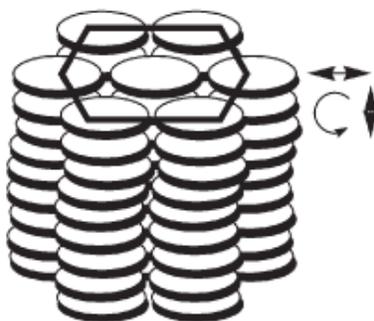
#### 1.6.2.1 The hexagonal columnar mesophase ( $\text{Col}_h$ )

Columnar hexagonal mesophase is characterized by a hexagonal packing of the molecular columns. Hexagonal mesophases are often denoted as  $\text{Col}_{ho}$  (figure 10a) or  $\text{Col}_{hd}$  (figure 10b) where h stands for hexagonal and o and d for ordered or disordered stacking of the molecules.



**Figure 10.** The stacking of the mesogen in the columns: (a) ordered stacking ( $\text{Col}_{ho}$ ) (b) disordered stacking ( $\text{Col}_{hd}$ ).

In both the cases, fluidity exists; only the correlation lengths are different and, therefore, it is recommended to discontinue o and d subscripts. The recommended abbreviation for columnar hexagonal phase is “Col<sub>h</sub>”. Figure 11 illustrates the molecular packing in a Col<sub>h</sub> mesophase.



**Figure 11.** Schematic representation of hexagonal columnar mesophase.

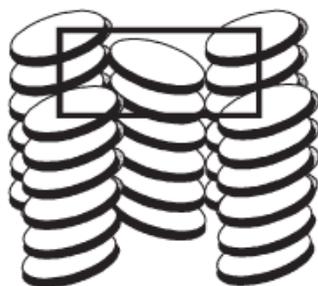
The planar space group of a hexagonal columnar mesophase is  $p6/mmm$ , which is equivalent to  $p6/m2/m$  in the International System (figure 12a) and belongs to the point group  $D_{6h}$  in Schoenflies notation. The symmetry elements are shown in figure 12b.



**Figure 12.** (a) Plan views of the 2D lattices in hexagonal (b) symmetry elements of a Col<sub>h</sub> mesophase: the point group  $D_{6h}$  has one  $C_6$  axis and perpendicular to this axis, six  $C_2$  and a mirror plane  $\sigma_h$ .

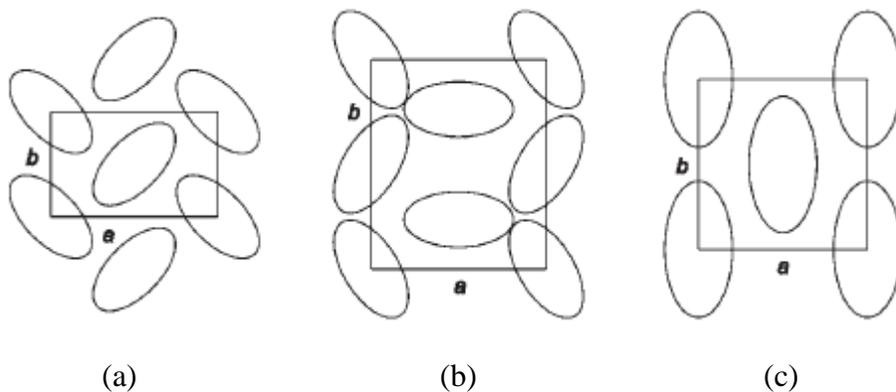
### 1.6.2.2 The rectangular columnar mesophase ( $Col_r$ )

The columnar rectangular mesophase consist of the stacking of the aromatic cores of the molecules in columns surrounded by disordered aliphatic chains and packed in a rectangular fashion (figure 13).



**Figure 13.** Schematic representation of a rectangular columnar mesophase.

Three different types of rectangular mesophase  $Col_r$  have been identified (figure 14a-c) [19]. In general, the molecules are tilted with respect to the column axis [20], whereby the cross section, orthogonal to the axis of a column, is elliptic.



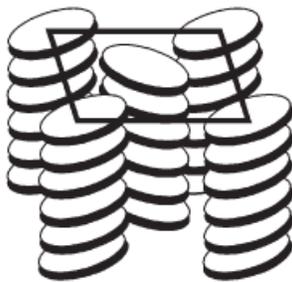
**Figure 14.** Plan views of the two-dimensional lattices of  $Col_r$  (a-c) mesophases.

The symmetries of the 2D lattices are specified by three different planar space groups  $P2_1/a$ ,  $P2/a$ , and  $C2/m$  [21, 19], belonging to the subset of space groups without any transitional

periods in the direction of the principle symmetry axis, that is direction of columns. As a result of the elliptical projection of the molecules in the plane, the symmetry of the  $\text{Col}_r$  phases deviates from a proper hexagonal arrangement. However, stronger core-core interactions are needed for the formation of the rectangular phases because the cores of one column have to know how they must be tilted with respect to the cores of the neighboring columns. Therefore, crossover from columnar rectangular to hexagonal mesophases with increasing side-chain lengths has often been observed.

### 1.6.2.3 The columnar oblique mesophase ( $\text{Col}_{ob}$ )

Figure 15 shows the arrangement of the columns in a columnar oblique mesophase, in which the tilted columns are represented by elliptic cross sections. The symmetry of this 2D lattice corresponds to the space group  $P_1$ . Examples for columnar oblique mesophases are rare because of strong core-core interactions.

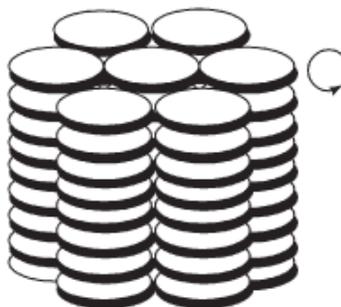


**Figure 15.** Schematic representations of columnar oblique phase.

### 1.6.2.4 The columnar plastic mesophase ( $\text{Col}_p$ )

Columnar plastic phase, denoted as  $\text{Col}_p$ , has been identified recently in discotic liquid crystals [22]. This phase is characterized by three-dimensional crystal-like order in a hexagonal lattice, while the discs within the columns are able to rotate about the column axis (figure 16). In the

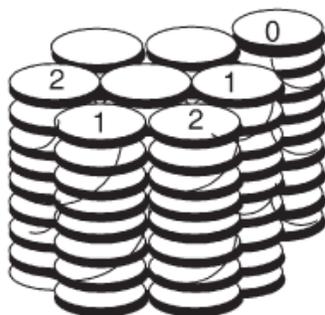
case of Col<sub>h</sub> phase structural disorders such as non-parallel arrangement of the discs, longitudinal and lateral displacements and rotation around the columnar axis occur, while the motional freedom of discs in the Col<sub>p</sub> phase is restricted.



**Figure 16.** Schematic representation of columnar plastic phase.

#### 1.6.2.5 The columnar helical (H) phase

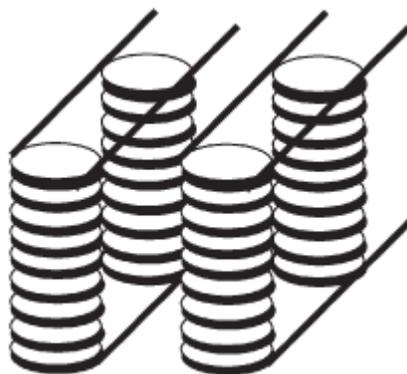
An exceptional mesophase structure with helical order has been demonstrated for a triphenylene derivative namely hexahexylthiotriphenylene (HHTT) [23, 24]. In this so-called H phase helical columns develop with interdigitate in groups of three columnar stacks. From extensive X-ray studies it has been found that the helical H phase is unique to HHTT and certain mixtures of compounds with an average chain length close to 6 carbons [25]. The H phase found in HHTT is illustrated in figure 17.



**Figure 17.** Structure of the helical H phase.

### 1.6.2.6 The columnar lamellar mesophase

A layered structure is known to exist for mesophases of certain discotic compounds e.g. bis(p-n-decylbenzoyl)methanato copper(II), some perylene derivatives, etc. [26-30]. Such a columnar lamellar mesophase which is denoted by the symbol  $Col_L$  is shown in figure 18.



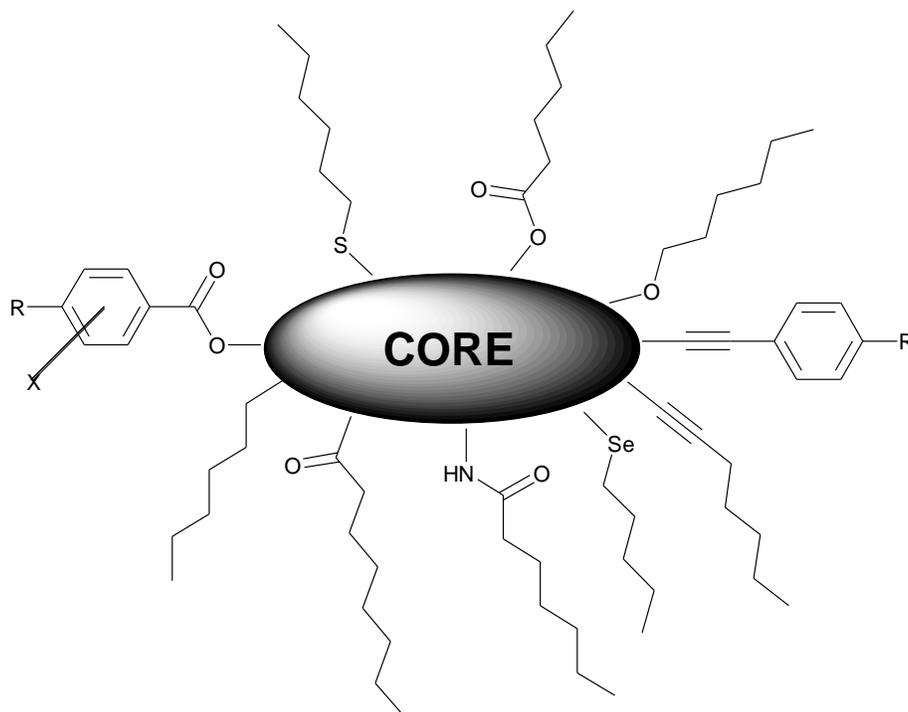
**Figure 18.** Schematic representation of columnar layered ( $Col_L$ ) mesophase.

## 1.7 Chemistry of discotic liquid crystals

Discotic liquid crystals (DLCs) generally consist of flat, rigid aromatic cores surrounded by flexible chains. These materials often have two, three, four or six-fold rotational symmetry and three or more peripheral chains of three or more carbon atoms. However, there are many exceptions and materials with low symmetry, a non-planar, non-aromatic core having shorter number of chains are also documented. Flexible chains are connected to core via different linking groups such as ether, ester, benzoate, etc. Figure 19 represents a general molecular architecture for discotic mesogens.

From the synthetic chemistry point of view, strategies to prepare discotic mesogens are fairly straightforward. Assembling an aromatic core followed by nucleophilic or electrophilic aromatic substitutions is most common in the synthesis of discotic liquid crystalline materials. General methods for their synthesis have recently been described in the Handbook of Liquid

Crystals [3]. While preparation of these materials is often but not always simple, their purification is usually difficult and tedious. This is primarily because of incomplete substitution of all the functional groups. Partial substitution of polyfunctional groups gives a mixture of structurally similar products having almost identical  $R_f$  values on a chromatographic plate and their separation is often difficult even by HPLC. It is advisable to push the reaction towards completion by taking excess of the reagent and/or longer reaction time. However, in many cases, excess of the reagent or longer reaction time cause side reactions and thus a complex mixture of the products. Finding optimum reaction conditions is the crucial part of the synthesis. The chemistry of some of the discotic liquid crystals has been improved significantly in last few years. Highly regio-selective and high yielding methods are now available particularly for the synthesis of triphenylene based discotic liquid crystals.



**Figure 19.** A general structural template for discotic mesogens.

More than 50 different cores are known which on appropriate substitutions afford DLCs. These cores are mainly (a) aromatic hydrocarbons such as, benzene, naphthalene, anthraquinone, phenanthrene, pyrene, perylene, triphenylene, truxene, dibenzochrysene, decacyclene, dibenzopyrene, tetrabenzoanthracene, hexabenzocoronene; (b) macrocyclic cores such as, metacyclophane, tribenzocyclononatriene, tetrabenzocyclododecatetraene, phenylacetylene; (c) heterocyclic cores such as, benzopyrone, oxatruxene, thiatruxene, benzotrisfuran, tricycloquinazoline, bispyran, hexaazotriphenylene, pyrrillium salt, coroneneimide, triazine, tetrathiofulvalene; (d) metallomesogens such as,  $\beta$ -diketone complexes, triketone complexes, dioxime complexes, tetraketone complexes, dithiolene complexes, benzalimine complexes, tetrabenzo-tetraazacyclohexadecine, dibenzaldimine complexes, pyrazolatogold complexes, porphyrin, tetraazoporphyrin, tetrapyrazinoporphyrazine, phthalocyanine; (e) saturated cores such as, cyclohexane, pyranose sugars, azamacrocycles and hexacyclans. Additionally, a number of discotic cores generated through non-covalent H-bonding are also known to display columnar mesophases.

Various options of synthesis pursued to prepare different DLCs are as follows. The simplest route is the attachment of chains to commercially available polyfunctional cores, e.g. esterification of naturally occurring *scyllo*-inositol. However, this option is limited as only a few polyfunctional cores, suitable to prepare DLCs, are commercially available. The direct electrophilic aromatic substitution of polycyclic aromatic hydrocarbons has been used in some cases to generate polyfunctionalized core or directly liquid crystalline materials but because of regioselectivity problem, such examples are also not common. The third option is the preparation of polyfunctional cores directly starting from unprotected functionalized precursor molecules, e.g. one step preparation of hexahydroxy anthraquinone from gallic acid. However, this option is

also limited as many functional groups are sensitive towards the drastic reaction conditions used to build the core. The most common method used to prepare DLCs involves construction of the core with protected functional groups, cleavage of the protecting groups and finally grafting pendant chains. Recently, particularly to prepare discotics with ether linkages, efforts have been made to avoid the protection and deprotection steps and thus, long aliphatic chains required to induce mesogeneity were attached in the starting molecules and these then transformed directly to liquid crystalline materials using classical or modern synthetic methods. This methodology has also been applied to prepare a number of alkyl substituted DLCs.

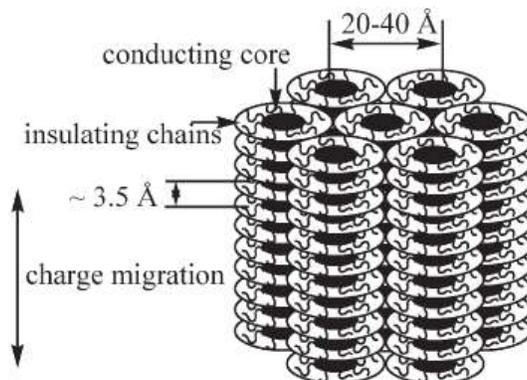
### **1.8 DLCs as materials for a new generation of organic electronics**

In recent years, the organic electronics, *i.e.* the use of conjugated molecules as active components in electronic devices, is a field of immense scientific research areas because of the prospect of creation of new industry, electronic devices such as, light-emitting diodes (LED), field effect transistors (FET), memory elements, sensors, photovoltaic solar cells, etc. The interest in devices is not only because of potential applications but also formidable tools to probe the basic structure-property relationships that govern by the physics and chemistry of organic materials. This challenge creates the need of new organic materials with innovative design and semiconducting behaviour that deviate from conventional conjugated materials [31, 32]. Molecules with hierarchical self-assembly into supramolecular systems, like liquid crystals which bring order (governs the performance of semiconductor) as well as dynamics (ability to self-healing of structural defects) are currently viewed a new generation of organic semiconductors in devices. Simple thermal annealing treatment of liquid crystals leads to formation of large domains from  $\mu\text{m}$  to mm thickness [33, 34]. The orientation of molecules

within these large domains can be manipulated by changing temperature, irradiation with polarized light or surface alignment layers [35-40]. The low molecular weight of conjugated liquid crystals associated with discrete mass allows the synthesis of defect-free chemical structures that are amenable to a higher purity level than most conjugated polymers [41].

## 1.9 Why discotics?

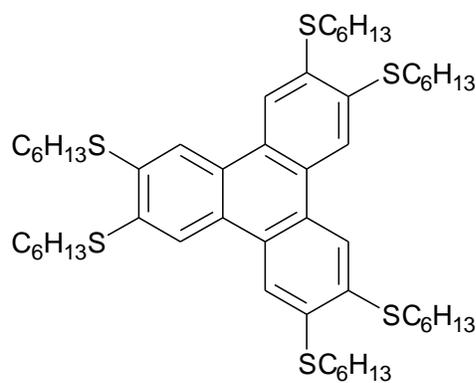
The two-dimensional chemical structure of discotics creates a new situation that results in a set of unusual features. A majority of discotic liquid crystals form columnar mesophase probably due to intense  $\pi$ - $\pi$  interactions of polyaromatic cores. Columns of discotic mesogens exhibit one-dimensional charge transport that is rather sensitive to the structural defects. The core-core separation in a columnar mesophase is usually of the order of 0.35 nm so that there is considerable overlap of  $\pi$ -orbitals. As flexible long aliphatic chains surround the core, the intercolumnar distance is usually 2-4 nm, depending on the lateral chain length. Therefore, interaction between neighboring molecules within the same column would be much stronger than interactions between neighboring columns. Consequently, charge migration in these materials is expected to be quasi-one-dimensional. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than in perpendicular direction [41, 42]. Thus columns may be described as molecular wires (figure 20). Charge carrier mobility as high as  $0.71 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  along the columns has recently been observed [43]. The two dimensional structures associated with the disc shape allows one to tailor the emissive properties by the control of the mutual orientation of transition dipoles upon rotation of the discs [44]. This paves the way to columnar mesophases that combine high charge carrier mobility with intense fluorescence [45, 46].



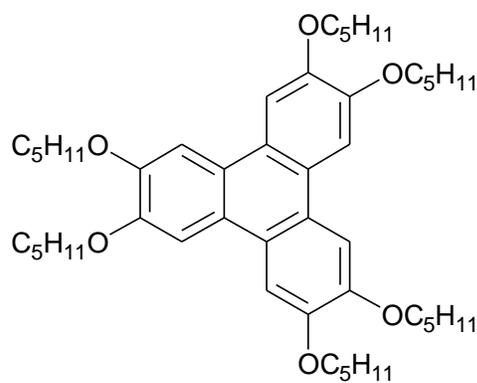
**Figure 20.** Schematic view of charge migration in columnar mesophase.

### 1.10 Discotics as semiconductor: molecular concepts, one-dimensional electrical & photoconductivity

As described already, columns in discotic liquid crystals would form molecular wires with conductive channels surrounded by insulating peripheral chains and that's why the columnar liquid crystal may display photoconductivity. Model systems for conductivity studies were based on triphenylene derivatives, which do not usually possess intrinsic charges [47]. To investigate the charge transport along the columns, charges were created by doping or through photogeneration. Vaughan *et al.* [48] doped hexahexylthiotriphenylene (HHTT) **4** with iodine, which increased the conductivity by several orders of magnitude. Boden *et al.* used hexapentyloxytriphenylene **5** with  $\text{AlCl}_3$ , which transformed the insulating hexaalkoxytriphenylene **5** into a p-doped semiconductor, in which the conduction along the columns was three orders of magnitude greater than in perpendicular direction. This result clearly indicates the high anisotropy of conduction in the columnar phase and the columnar phase can be considered as a practical one-dimensional conductor along the columnar axis.



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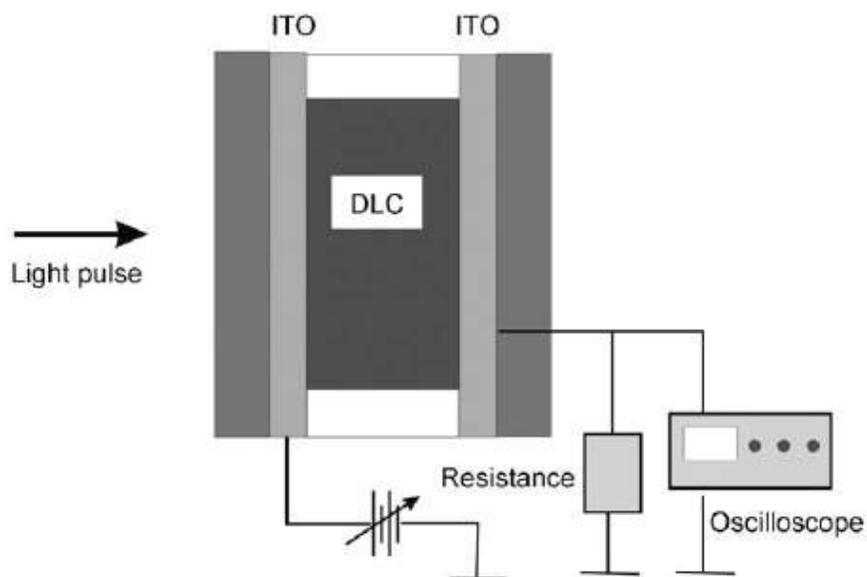
For studying charge transport (CT) in discotic liquid crystals the time-of-flight (TOF) technique, which relies on charge photoregeneration, is most widely used. Charges are generated by light irradiation of discotic films in a typical sandwich-cell configuration as shown in figure 21. A light pulse with a definite wavelength and a short duration is sent, so that the absorption and the following charge generation occurs in a very thin layer at only the first interface. An electric field is applied to induce a drift of the charges. Depending on the polarity of the applied field, holes or electrons will move across the sample, thus inducing a transient current, which is recorded in an external circuit, and allowing the deduction of the type of the charge carriers involved.

The time that these charges take to travel between the electrodes allows the mobility  $\mu$  to be recorded. In fact,  $\mu$  depends on the applied voltage  $V$  and the transit time  $t_t$  according to the following equation, where  $v$  is the drift velocity,  $d$  is the film thickness, and  $E$  is the applied electric field.

$$\mu = v/E = d^2/Vt_t$$

The disadvantage of the TOF method is that monodomains with the columns aligned perpendicular to the electrodes (homeotropic alignment) are required. Any defect in the path has a strong effect on the mobility, so the values can underestimate the true transport potential of the

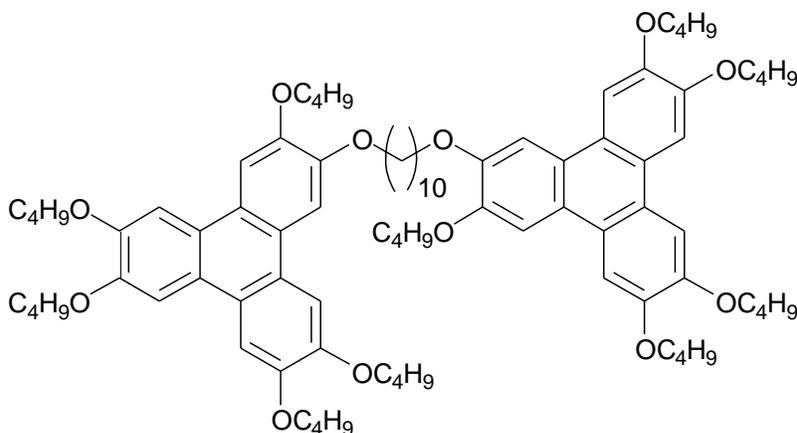
material. Discotics that do not align accordingly might be impossible to investigate with the TOF method.



**Figure 21.** Set up of the TOF experiments

Transport in triphenylenes was modeled by Haarer and co-workers [49]. Despite the remarkable results in terms of mobility because of the high degree of order in the columns, the transport seems not to be described by a bandlike model but rather by a hopping process, in which the charges stay in one site until they jump to the next. A 1D hopping model was used that was based on a Gaussian distribution in the energy levels involved in the conduction (for example, the HOMOs, the highest-occupied molecular orbitals) and dependent on the disorder and on a jump rate between adjacent sites. This rate is a function of the hopping distance (taken as the intermolecular distance) and temperature. By using a Monte Carlo simulation, the photocurrent was predicted. The dependence of the electric field on the field and the temperature were derived from this model, and this dependence agrees with the measured temperature dependence of the mobility in the triphenylene dimer **6** in its glassy phase. For higher

temperatures, however, other factors, such as the variation of the order parameter with the temperature and the thermal activation effects, should be taken into account in the model.



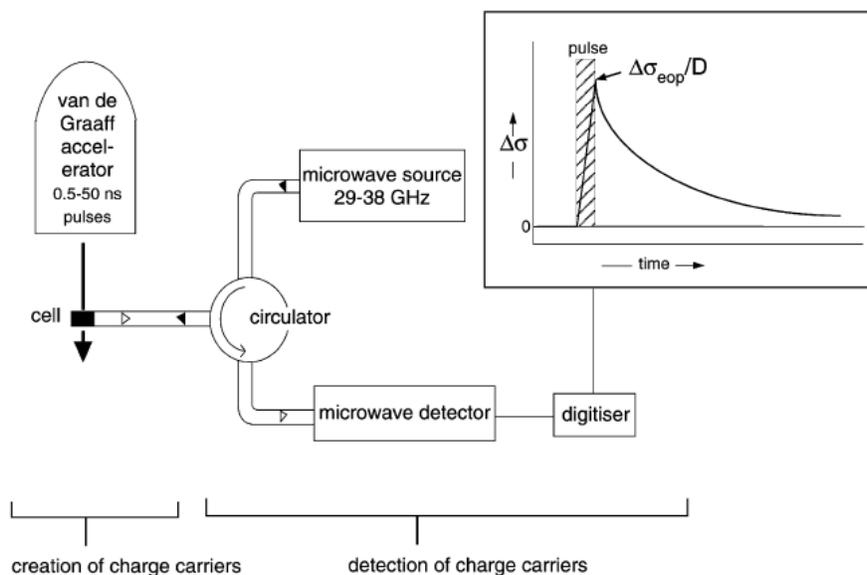
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When samples cannot be properly aligned, the pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC) has been used [50]. In this technique the material of interest is ionized by a nanosecond pulse of high-energy electrons from a Van de Graaff accelerator. This results in the creation of charge carriers with a uniform and known concentration of the order of micromolar. If the charge carriers formed are mobile this results in an increase in the conductivity of the sample which is monitored with nanosecond time-resolution as a transient decrease in the power of microwaves which propagates through the irradiated medium. A simple schematic representation of the technique is shown in the figure 22.

A PR-TRMC conductivity transient has two characteristics; the magnitude at the end of the pulse, which is proportional to the product of the concentration of carriers formed, and their mobility, and the decay after the pulse, which provides information on the subsequent recombination and/or trapping of the charge carriers. This has been related by the following equation

$$\Delta\sigma(t) = e \sum [N_i(t) \mu_i]$$

where  $\mu_i$  is the charge mobility and the  $N_i$  is the induced charge-carrier concentration in the sample. The charge carrier mobility in triphenylene discotics, measured by Adam *et al* using time of flight photoconductivity (TOF) method [51, 52] was confirmed by van de Craats *et al.* using electrode-less pulse-radiolysis time resolved microwave conductivity method [53].



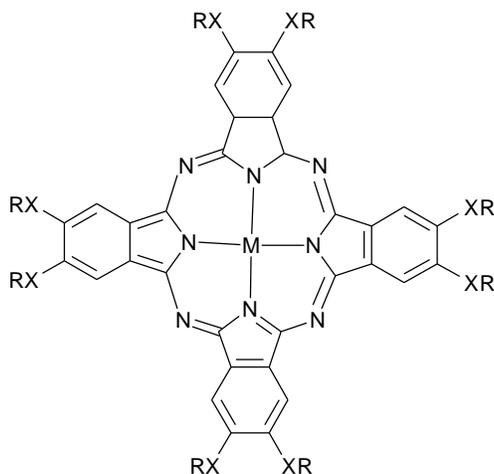
**Figure 22.** Schematic diagram of the PR-TRMC equipment.

Many theories have been suggested to confirm the experimental observations of charge transport in a discotic liquid crystal. According to the theory, the transfer integral which is a function of the overlap of HOMO (LUMO) orbitals of adjacent molecules for hole and the internal reorganization energy associated with the energy difference between charged and neutral species play an important role in charge transport and electron hopping rate in adjacent discs. Discotic liquid crystals besides their efficient charge transport have the ability to carry excitons over large distances. Detailed theoretical studies have been reported [54] by Markovisti *et al.* in 2001.

The chemical structure, symmetry and size of the conjugated core, the shape of the wave function, the nature of the connecting groups between the conjugated core and the flexible alkyl chains, the phase and transition temperatures all play significant role to have a good discotic semiconductor.

### 1.10.1 Size of the discotic core

Due to efficient  $\pi$ -stacking in larger cores rather than in small aromatic core like benzene, variation of size of the conjugated core to design and explore novel discotic mesogens is one of the main research themes in science. The relatively larger discotic molecules like triphenylenes **4** and **5** have been extensively studied [55]. It has been proposed that increasing the size of conjugated core would reduce the core-core separation and thus enhance the charge mobility [56]. Extraordinary thermal and photochemical stability of phthalocyanines **7-10** (M = Metal) and porphyrin discotics in the field of dyes and pigments have also been reported [57, 58].



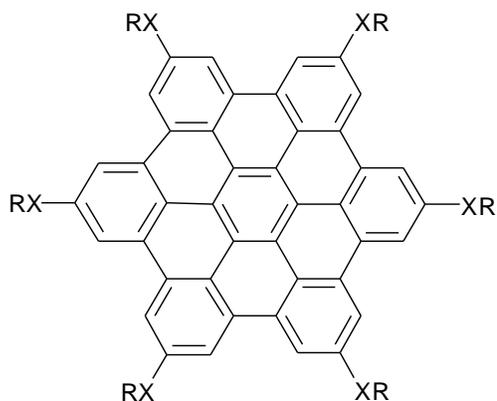
**7:** X = O, R =alkyl

**8:** X = CH<sub>2</sub>, R = alkyl

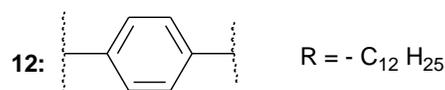
**9:** X = CH<sub>2</sub>O, R = alkyl

**10:** X = COO, R = alkyl

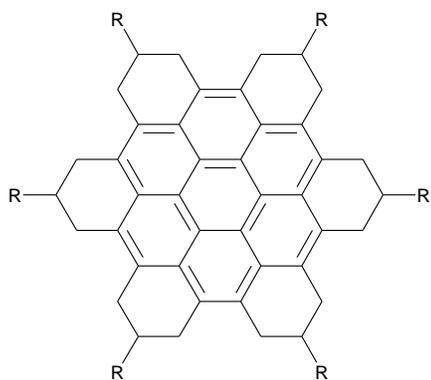
The syntheses of hexa-peri-haxabenzocoronene (HBC) derivatives **11** and **12** [59a] have shown an important achievement not only because of highest charge carrier mobility but also to passivate a way to have very large polycyclic aromatic hydrocarbons (PAH). They have an excellent opportunity in charge transport and mobility on the basis of core diameter.



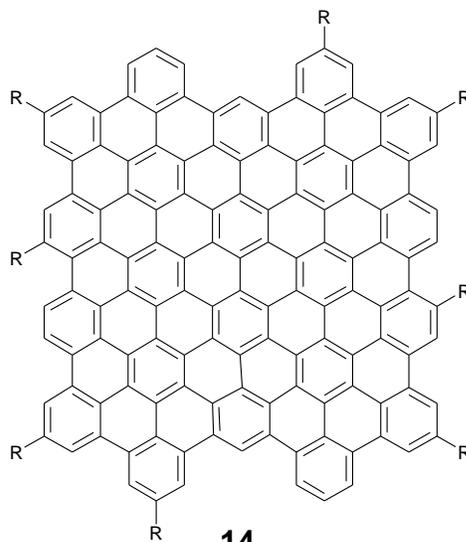
**11:** X = CH<sub>2</sub>, R = - C<sub>11</sub> H<sub>23</sub>



R = - C<sub>12</sub> H<sub>25</sub>



**13**

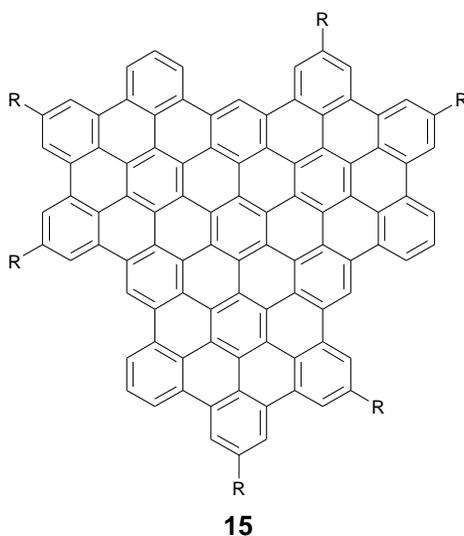


**14**

The empirical relationship on the basis of charge mobility value in discotics suggested by van de Craats and Warman is

$$\Sigma\mu_{1D} = 3\exp(-83/n) \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$$

Where  $\Sigma\mu_{1D}$  is a mobility sum for holes ( $\mu_+$ ) and electrons ( $\mu_-$ ) along the axis of the columnar stacks and n is the number of atoms in the aromatic core.

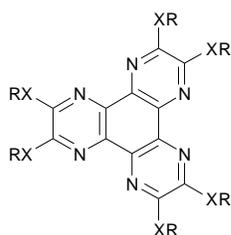


The experimentally found and calculated values for HBC **9** and PAH (**13-15**) are reported by Mullen *et al.* [59b]. For relatively small cores like **9** and **13**, the results of PR-TRMC measurements are in good agreement with calculations. For the aromatic cores with 60 and more carbon atoms the measured values are not convenient by the calculation results and interestingly remain insensitive to the core size. This can be the influence of fluctuations on the charge transfer integral, as reported [60-62].

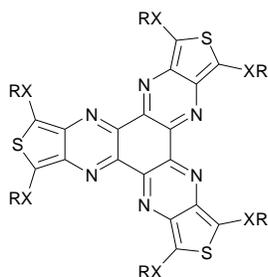
### 1.10.2 Shape of the wave functions

Although size of the conjugated core influences charge transport, the connecting groups of the side chains in the light of the shape of the wave functions play an important role. For example, the following compounds **16**, **17**, **18** that share six nitrogen atoms in the centre of the molecule and six sulphur atoms at the periphery of the conjugated core has been specifically designed of donor and acceptor groups. The idea is that to have a better orbital overlap and finally improving the hole transport and also would have little variation of orbital splitting upon rotation of disc-like molecules around their director axis [63, 64]. The largest LCAO (linear combination of atomic orbitals) coefficients are calculated on the nitrogen atoms in the centre of the molecules.

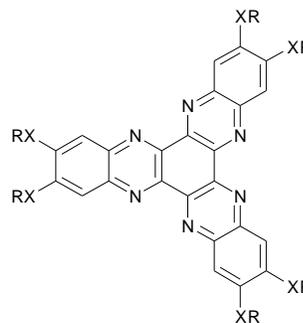
The splitting of the LUMO varies (due to the shape of the wave function) from 0.4 to 1.5 electron volt for rotation angles of adjacent molecules from 0° to 60°, respectively. So nitrogens atoms must be advantageous for improving charge transport.



**16a - f**



**17d**



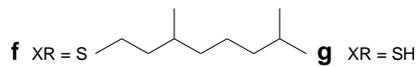
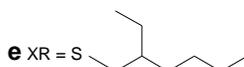
**18a - f**

**a** XR = SC<sub>6</sub>H<sub>13</sub>

**c** XR = SC<sub>10</sub>H<sub>21</sub>

**b** XR = SC<sub>8</sub>H<sub>17</sub>

**d** XR = SC<sub>12</sub>H<sub>25</sub>



**g** XR = SH

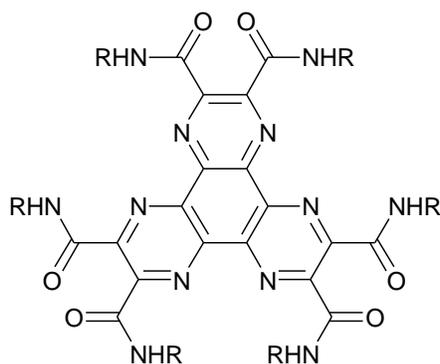
**h** XR = OH

On the other hand a partial negative charge (maximum 0.54 | e | ) on the nitrogens causes electronic repulsion which is detrimental for the columnar mesophase. As a result **16a-f** [65] and **17d** [66] does not show any LC phase but **18a-e** form columnar mesophase over a wide temperature range where electrostatic repulsion is compensated by more efficient  $\pi$ -stacking. However,  $\mu$  values measured by the PR-TRMC technique [67] for **18** range from 0.02 to 0.2 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>.

### 1.10.3 Connecting groups

The connecting groups between the aromatic core and the flexible alkyl chains play an important role on charge transport properties. The connecting groups and also flexible peripheral substituents together change the thermotropic behaviour of octa-substituted phthalocyanines [68-70]. When connecting groups are involved in some specific non-covalent intermolecular

interactions, such as intermolecular hydrogen bonding for example in case of hexamide derivative of hexaazatriphenylene **19**, a inter-disc distance as short as 0.318 nm *i.e.* smaller than the Van der Waals radii of carbon atoms in PAH [71]. Also connecting groups dramatically influences the reorganization energy for positive and negative polarons of selected conjugated cores with or without substituent, which is modulated by an additional element, the orbital coefficient on the carbon atoms of the  $\pi$ -system directly connected to the heteroatom [72].



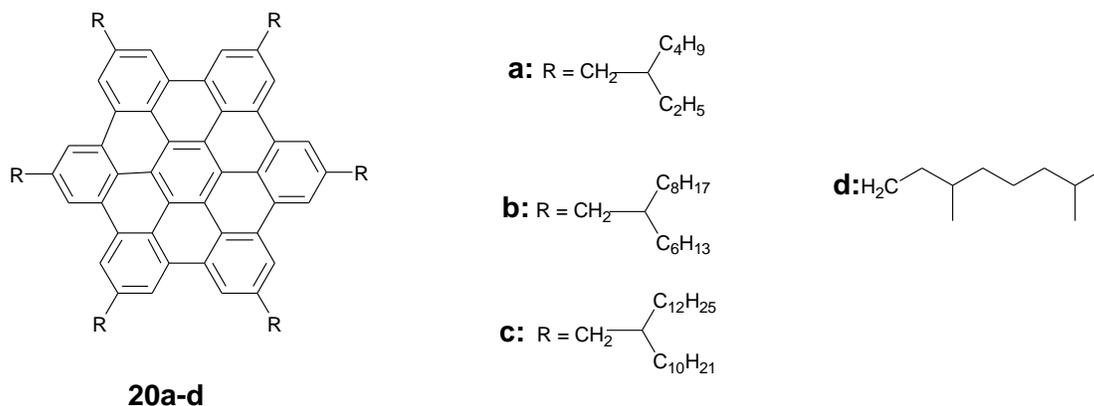
**19**

#### 1.10.4 Phase behaviour and transition temperatures

Supramolecular order in mesophases is the most important parameter for efficient charge transport. The primary criteria of the material to be most suitable in charge transport, is to be liquid crystalline at ambient temperature and mesophase should be stable over a sufficiently broad temperature range.

The increase of alkyl chain length and branching of the side chains of discotic molecules decreases the transition temperatures. For example the replacement of normal alkyl chains by branched alkyl chains in hexaalkynylbenzene [73] and tricycloquinazoline [74] produces room temperature discotic nematic and columnar phases, respectively. In hexaalkyl-HBC series of discotic mesogens (**20**), the compound **20a** forms mesophases only above 100 °C with a very

high clearing point [75]. On the other hand compound **20b** with longer and more sterically substituted is liquid crystalline at room temperature. Octa-alkoxycarbonyl phthalocyanines with branched chains are reported to be room-temperature liquid crystals in literature [76]. It is clear that introduction of branching produce steric hindrance within the chains and thus has an important influence on the phase behaviour of the discotic molecules. Similar behaviour was observed for the family of tetra-alkoxy phthalocyanines [72].



It clearly appears that the steric hindrance introduced by branching of the side chains has an important influence on the phase behavior of discotic mesogens. However, role of stereoheterogeneity due to branched chains is not negligible, as demonstrated for the HBC derivative **20d**. The temperature of Cr-LC transition for the stereohomogeneous (all-*S*)-**20d** is 15 °C higher than that of **20d** bearing the racemic side chains and comprising multiple diastereoisomers.

### 1.11 Discotic liquid crystals in display devices

The twisted nematic and supertwisted nematic display devices have dominated commercial displays since their innovation. The liquid crystal layer in these devices is exclusively the calamitic liquid crystal (composed of rod-shaped molecules). The major disadvantage of current

LCDs is the narrow and non-uniform viewing cone. The growing emphasis towards higher quality wide viewing angle LCDs has fostered numerous development efforts such as, the multidomain technique [77], the introduction of an optical compensator to reduce the amount of light leakage in the dark state [78], the application of an electric field parallel to the plane of the substrates [79], the so-called ‘amorphous’ twisted nematic liquid crystals [80], etc. The viewing angle of LCDs for gray scale and colour has significantly improved over the past few years due to these recent developments. However, some additional complex processes are necessary to be used. Very recently, it has been demonstrated that discotic nematic liquid crystals can be utilized instead of calamitic nematic liquid crystals to overcome this problem [81]. The LCD prepared using hexalkynylbenzene based discotic nematic liquid crystal shows wide and symmetrical viewing angle and no reversal of contrast ratio in any direction [81]. However, because of the very high viscosity of discotic nematic liquid crystal, the device is extremely slow.

The problem of viewing angle, brightness, contrast, sharpness of focus and image inversion associated with classical twisted nematic displays due to positive birefringence of the calamitic nematic liquid crystal layer can be suppressed by the use of compensation films, which should ideally have negative birefringence. The most promising materials for negative birefringence films are discotic liquid crystals. Fuji Photo Films has recently commercialized an optical phase-compensation film using a triphenylene-based cross linked polymer to overcome these problems [82]. These films are usually prepared by aligning the reactive monomer, a triphenylene benzoate ester, with up to six epoxide or acrylate groups homeotropically aligned in the nematic discotic phase followed by photopolymerisation. These compensation films are the most successful commercial application of discotic liquid crystals.

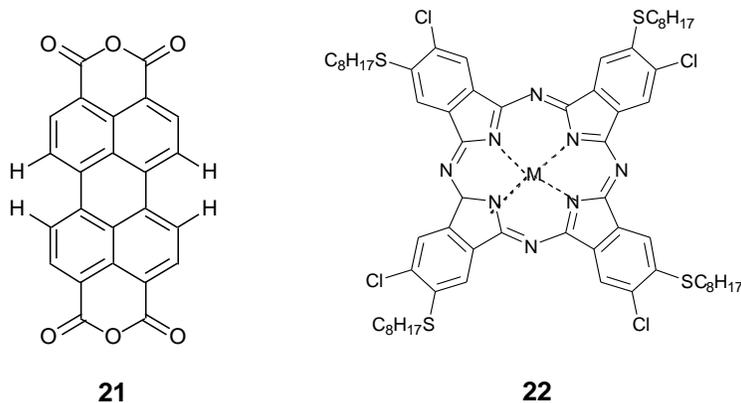
### 1.12 Discotics in Xerographic processes

A commercially available photocopier or laser scanner consists of a rotating cylinder that is covered with a photoconducting surface, which moves over the original document with simultaneous irradiation [83]. The light reflected by the document hits the photoconducting surface thereby leading to charge separation. An electrostatic image is generated on the cylinder surface. In the next step, the cylinder is covered with black toner particles that preferentially adsorb at the positive charges of the cylinder surface. On rotation of the cylinder over black paper, the toner particles are transferred to the paper and the crude hardcopy is generated and submitted to thermal fixation.

There are several requirements for photoconducting materials for them to be useful for applications. To achieve a high contrast potential for image development, the photoreceptor must be an insulator or have low conductivity in the dark and become conductive on exposure to light. A highly sensitive photoconductor not only requires less energy to generate the electrostatic image, but also increases the speed of the xerox process. Thus, photosensitivity and dark conductivity of a certain material must be assessed. In addition, the lifetime and processibility of the material must be considered. While copier applications require that the photoconductor is sensitive in the visible region, the corresponding photoconducting materials of laser printers are sensitive in the IR spectra.

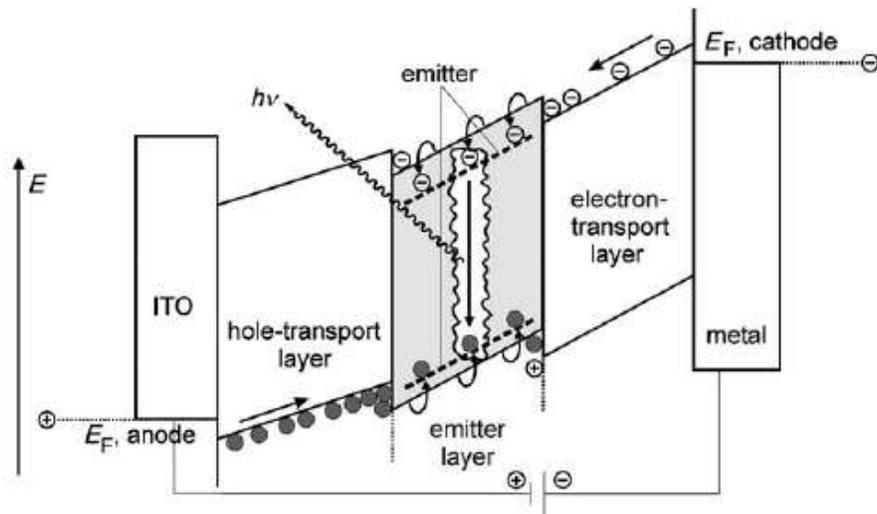
Classes of compounds which are particularly well studied for photoconducting devices that operate in the visible region are the perylene bisimides such as compound **21** [84]. On the other hand phthalocyanines have a strong absorption both in the visible and near infrared region. Eichhorn *et al.* discovered that mixtures, which contained amphitropic phthalocyanines such as **22** with a different substitution pattern, display much higher inter- and intracolumnar order than

the single compounds [85]. In addition, macroscopic homeotropic alignment was simply achieved by mechanical shearing, thus providing an easy way to orient the material for laser printers.



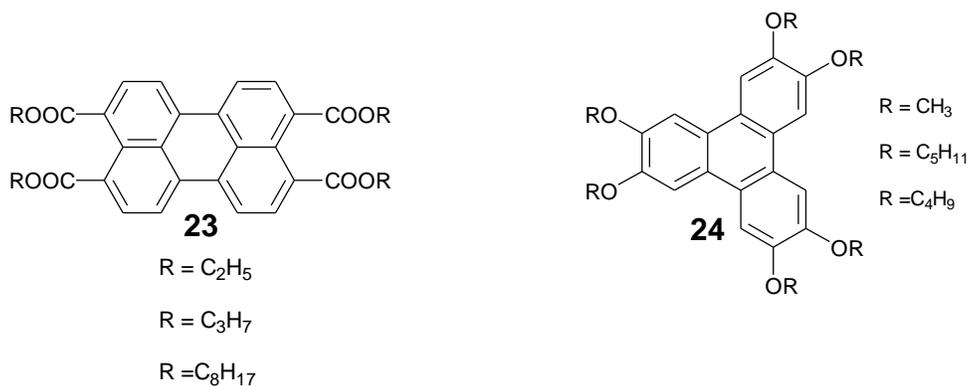
### 1.13 Discotics as organic light-emitting diodes

An OLED is a device, in which light is generated by electrical excitation. In a single-layer OLED, a thin film of an organic emitter is sandwiched between a transparent anode (ITO) and a metallic cathode [86, 87].



**Figure 23.** Energy diagram of a multilayer diode [87].

A multilayer device (figure 23) consists of separate hole-transporting layer, emitter layer and electron transporting layer. Electrons and holes, which are injected into the LUMO and HOMO, respectively, drift through the organic film under the influence of the applied electric field. The coulombic attraction between an electron and hole at the same chromophore site results in the formation of an exciton, a bound electron-hole pair, whose recombination produces luminescence. Efficient devices require the matching of energy levels to minimize the barriers for carrier injection and to trap both electron and holes exclusively in the emitter region. For OLED applications, columnar perylene derivatives have been successfully used. The research groups of Kitzerow and Bock [88] described an all-columnar bilayer OLED that consisted of fluorescent columnar 3,4,9,10-tetra(alkoxycarbonyl)perylene **23** as the luminescent electron transport layer combined with columnar hexaalkoxytriphenylenes **24** as the hole transport layer. A particular advantage of columnar LCs in such devices is their ability to expel defects in an annealing process which leads to increased lifetimes.

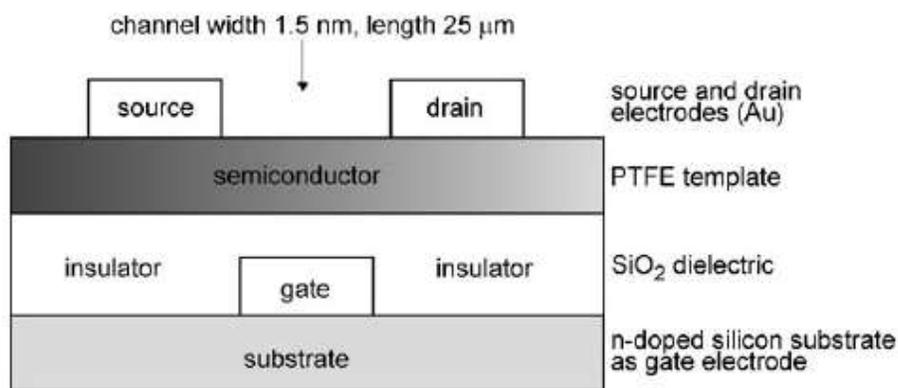


#### 1.14 Discotics as organic field-effect transistors

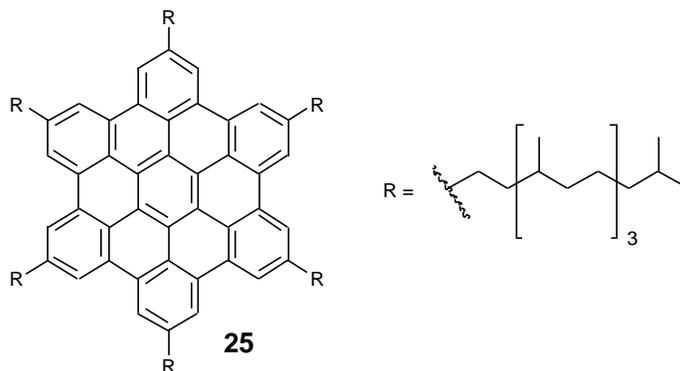
The self-assembly properties of columnar LCs, in combination with their ability to provide anisotropic charge-carrier transport along the channel, makes them viable candidates for OFETs.

A typical OFET device is shown in figure 24.

For a p-type semiconductor, conduction of charge between the source and the drain electrodes is governed by the gate voltage. When the gate is biased negatively, carriers accumulate in the channel between source and drain. The drain current is then proportional to the material mobility [89]. The extraordinary hole mobility for aligned hexaperi-hexabenzocoronene **25** (HBC-C8, 2;  $\mu = 0.5\text{-}1.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ ) films on oriented PTFE has been used by the research group of Mullen [40, 36]. By meso-epitaxial solution-growths of the HBC semiconductor devices were built, which displayed on/off ratios of more than  $10^4$  and a turn-on voltage of -5 to -10 V. The solution processibility, uniaxial parallel orientation and promising material and device stability under ambient conditions pave the way to the industrial production of these OFETs.



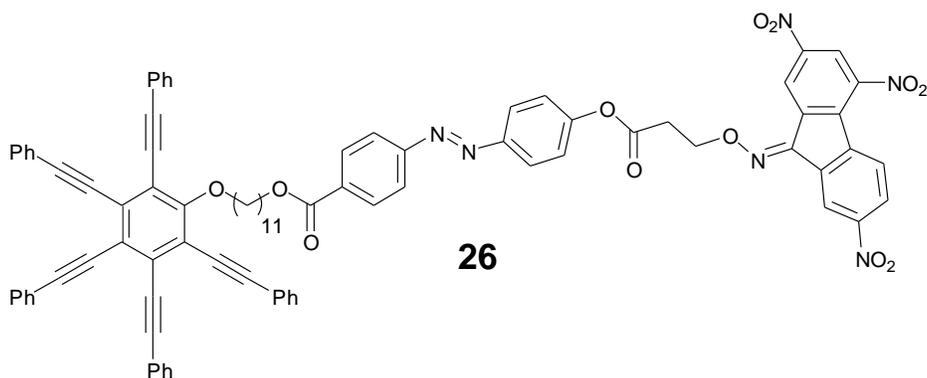
**Figure 24.** Schematic representation of an organic-field effect transistor.



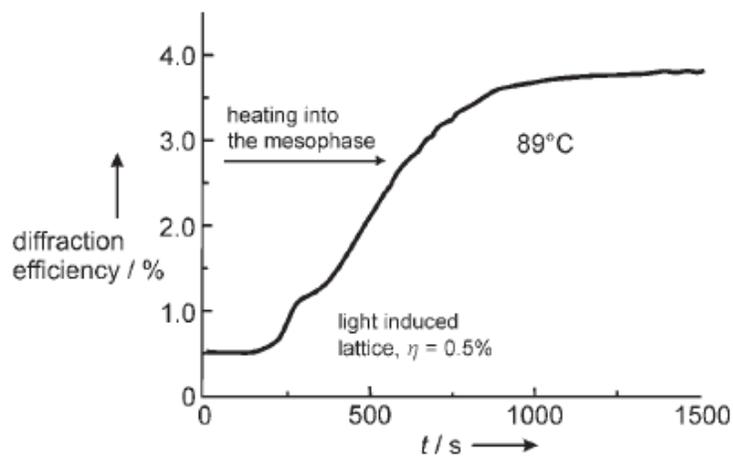
### 1.15 Discotics as holographic optical data storage

The principle of optical data storage relies on the E/Z isomerisation of dyes such as azobenzenes and stilbenes. The imprinting with two linear polarized laser-light beams induces a reorientation of the chromophores, which results in a change of the refractive index at the irradiated areas. The dye molecules are incorporated in a liquid crystalline matrix, which strongly enhances the change in refractive index. The periodic modulation of the refractive index, induced by writing laser beam, can be read out by a reading laser beam.

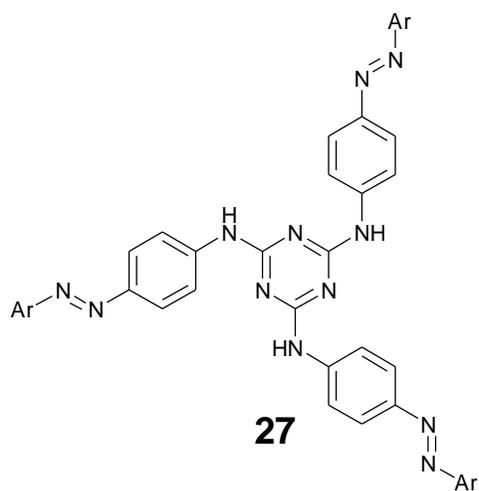
The columnar donor-acceptor triple compound **26** bears an azobenzene moiety as the chromophoric group [90, 87]. The strong electron-acceptor TNF in combination with the electron donor pentakis(phenylalkynyl)benzene resulted in the improved stability of the nematic columnar mesophase. As can be seen in the figure 25, at ambient temperature the refractive index of the photoinduced grating in the material differs by only 0.5%. On heating the sample to the nematic columnar mesophase, the diffraction efficiency increases to 4%.



Wendorff, Janietz, and co-workers found that triazomelamine **27** is not only suitable for the light-induced isomerization of the azobenzene units to give rise to photo-reorientation, but also causes surface modulations [91]. The gain effect of these surface modulations was achieved by thermal treatment.



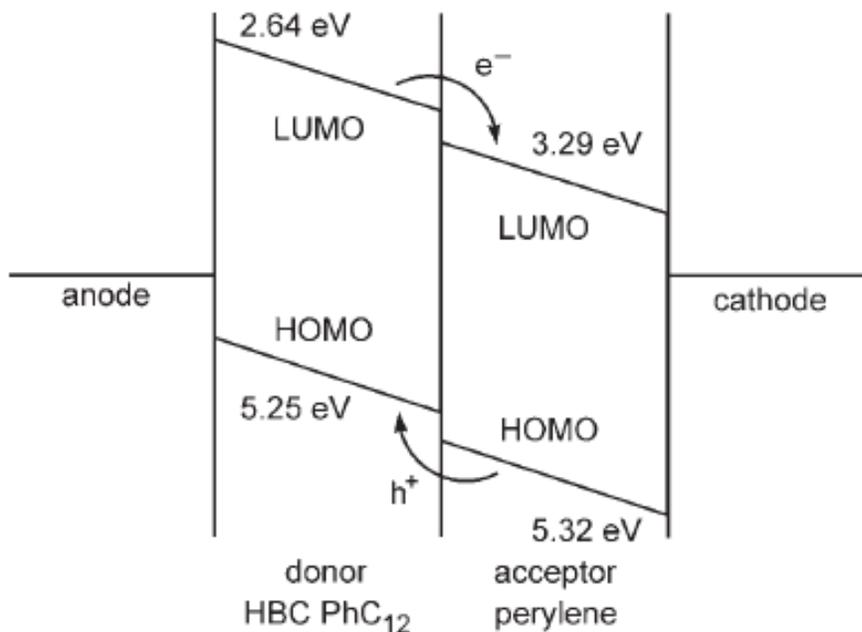
**Figure 25.** Thermal gain effect of the diffraction efficiency.



### 1.16 Discotic liquid crystals as photosynthetic light harvesting

The light-induced electron-hole generation, separation and migration is an important process for the conversion of light to electric or chemical energy (solar cells; photosynthesis), the latter being the basis of life on earth. The photovoltaic effect requires (a) the absorption of solar radiation and the photogeneration of electrons and holes, and (b) the charge separation, and the transport of electrons and holes for collection at the cathode and anode, respectively. For a

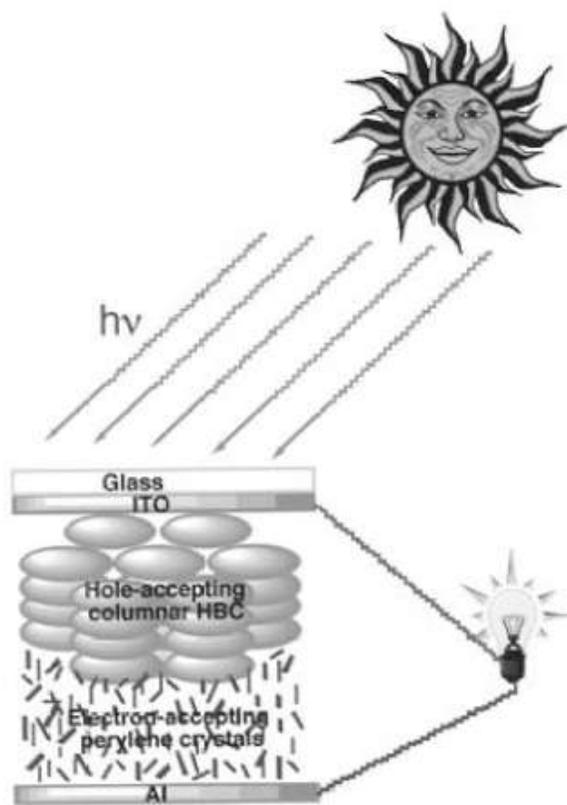
typical blended device under short-circuit conditions, the energy-level diagram is shown in figure 26 [92].



**Figure 26.** Energy level diagram shows the charge separation and transport in a mixture that consists of an electron donor and acceptor placed between a dissimilar anode and cathode to provide a built-in field [92].

Both processes should be highly efficient and charge recombination should be kept as a minimum. Absorption is achieved by exciton formation. Charge separation is achieved by ionization of an exciton over a distributed interface between electron-donating and electron-accepting species. The separated carriers drift to external electrodes in the built in field introduced by dissimilar electrodes. The photosensitivity of semiconducting organic materials can be enhanced by blending donor and acceptor molecules to optimize photoinduced charge

separation. Blends of conjugated polymers and fullerene ( $C_{60}$ ) were utilized to prepare solar cells with external quantum efficiencies (EQEs) of 5-10%. Yu *et al.* [93] achieved EQE of 29% for a blend of a hole-transporting polymer with the electron acceptor  $C_{60}$ . The efficiency was further improved by blending a soluble methanofullerene into the conjugated polymer film. Shaheen *et al.* [94] recently reported photovoltaic devices having EQEs of 50% and power conversion efficiencies of 2.5%. An organic-inorganic heterojunction device based on ZnO and single crystalline pentacene doped with bromide gives solar energy conversion efficiencies up to 4.5%.



**Figure 27.** Schematic diagram of a discotic-based photovoltaic solar cell.

Gregg *et al.* studied photovoltaic effects in symmetrical cells filled with discotic liquid crystalline porphyrin complexes [95]. Photovoltaic effect comparable with that of some of the better organic solar cells was found. However, the authors did not study the charge mobility in

the mesophases itself but utilized the liquid crystalline properties to fill the cells and to promote macroscopic order, which on cooling, forms polycrystalline films. Schmit-Mende *et al.* utilized discotic liquid crystalline hexabenzocoronene as the hole transporting layer and a perylene dye to construct a p/n type photovoltaic solar cell [96]. Mullen and coworkers have shown in a seminal contribution [96, 97] that thin film prepared by self-organization of a mixture of columnar LC and crystalline-conjugated materials directly from a xylene solution showed a photovoltaic response with external quantum efficiencies greater than 34% at 490 nm and power efficiencies up to 2%. The formation of vertically segregated nonmesomorphic electron-accepting perylene bismide and the columnar phase forming hole accepting hexa-peribenzocoronene with a high interfacial surface was shown by AFM, STM, and optical polarizing microscopy (figure 27) [96]. The high efficiencies result from an efficient photoinduced charge transfer between the two molecules and an effective charge transport through the layered structure.

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