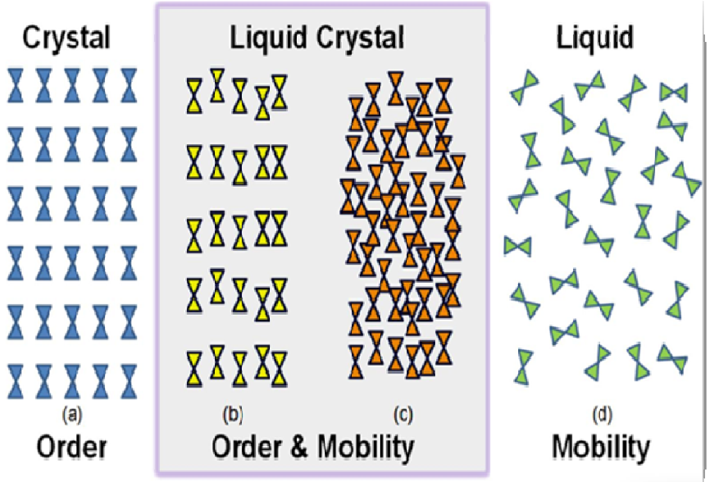
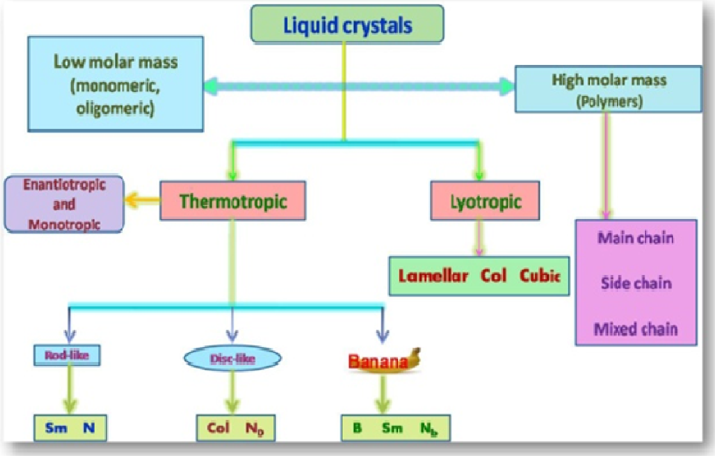
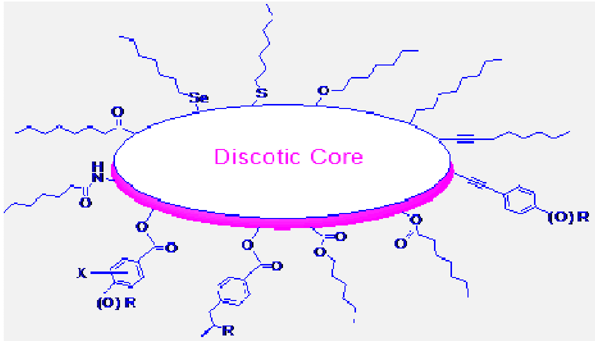
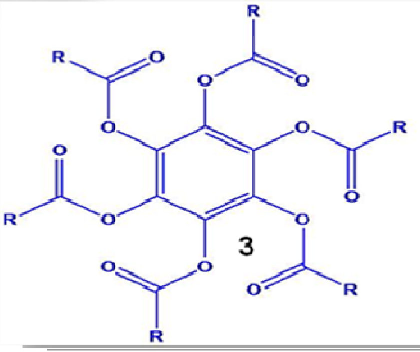
Chapter 1: Introduction









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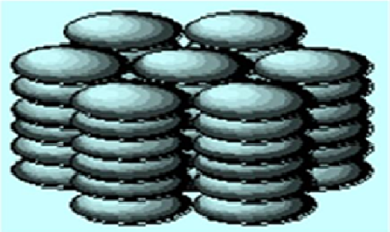

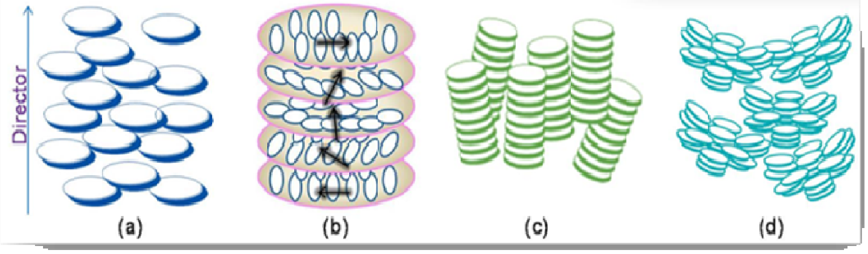

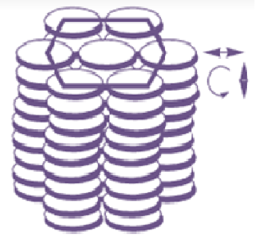

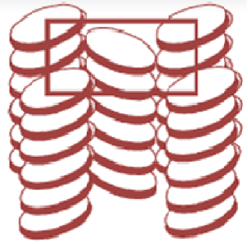

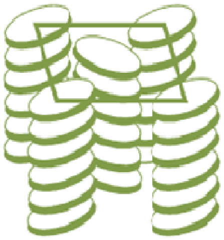

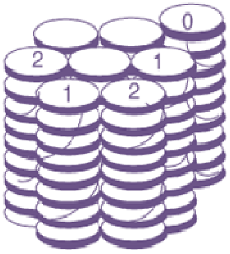

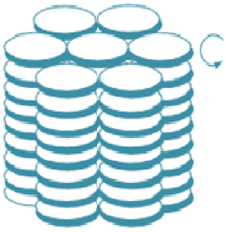

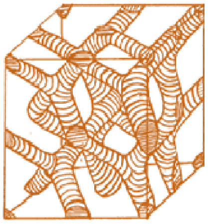

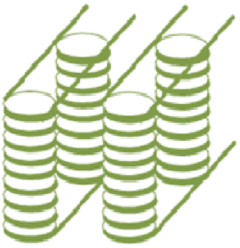

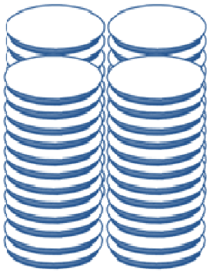

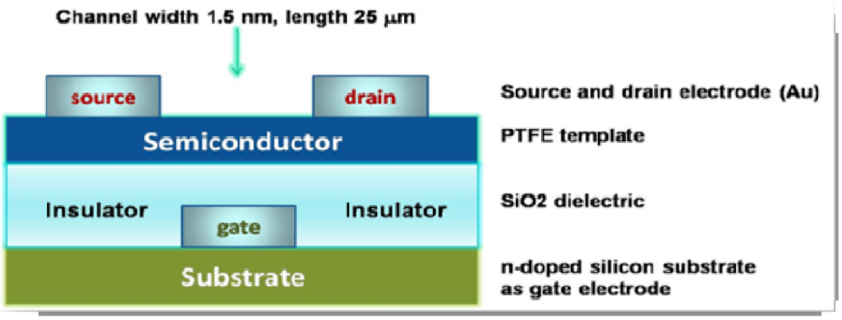

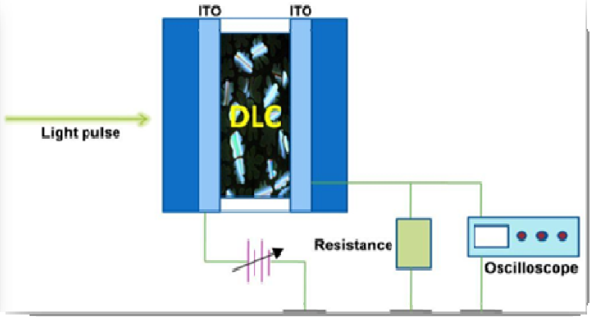

1.1. Liquid crystals

Molecules in the solid phase have practically no chance to move and reorient themselves with respect to one another. They have a certain degree of positional and orientational order that cannot be altered in this phase. However, if the same solid melts to a liquid, both types of order are lost completely. The molecules can now move and tumble randomly. The situation is different when a solid melts to a liquid crystal phase. The positional order is then vanished since the single molecules are free to move in the same fashion as in a liquid, but at least some of the orientational order remains or even increases. Figure 1 shows how both orientational and positional order in liquid crystals may be improved since the molecules are free to move and to orient themselves.

Liquid crystals form a distinctive state of matter. Between the crystalline solid and isotropic liquid phases, some compounds demonstrate a distinctly different, intermediate state, also referred to as the fourth state of matter, or the mesophase. This is a true thermodynamic stable state of matter. The constituent responsible for liquid crystal phase is called mesogen. The mesogens can be organic (forming thermotropic and lyotropic phases), inorganic (metal oxides forming lyotropic phases)[1] or organometallic (metallomesogens).[2] Due to anisotropic weak intermolecular interactions, the molecules or mesogens, in such a liquid crystalline assembly possess some kind of either positional or orientational order, but with a much lower degree of organization than in a crystalline solid. Therefore, the mesophase still shows a liquid-like flowing behavior, although as a result of the higher degree of organization compared to ordinary liquids these materials are much more viscous, and often turbid. Because of this combination of dynamic behavior and high degree of organization, liquid crystals tend to be sensitive to various stimuli, such as temperature, electric and magnetic fields. Combined with their self-assembling behavior, this makes them extremely attractive for both chemistry and physics. Due to their unique properties these materials have found widespread applications in liquid crystal displays (LCDs).

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[1] A. S. Sonin, *J. Mater. Chem.*, 8, 2557, **1998.**

[2] J. L. Serrano, *Metallomesogens-Synthesis, Properties and Application*, VCH Weinheim, **1996.**

Liquid crystals are important in materials science as well as in the life science. Thermotropic LCs are useful in materials science, whereas lyotropic LCs have been proven to be useful in both material and biological fields. Important applications of thermotropic LCs are electrooptic displays, temperature sensors and selective reflecting pigments. Lyotropic systems are incorporated in cleaning process, and are important in cosmetic industries. They are used as model for the preparation of mesoporous materials and serve as representative systems for biomembranes. Lyotropic LCs are important in living matter. Most important are the biological membranes, DNA can form lyotropic mesophases etc. Anisotropic fluid states of rigid polymers are used for processing of high strength fibers like Kevlar. LCs can potentially be used as new functional materials for electron, ion, molecular transporting, sensory, catalytic, optical and bio-active materials. LCs are extremely diverse since they range from DNA to high strength synthetic polymers like Kevlar (used for bullet-proof vests, protective clothing, high performance composites for aircraft and automotive industries) and from small organic molecules like alkyl and alkoxycyanobiphenyls used in liquid crystal displays (LCDs) to self-assembling amphiphilic soap molecules. Recently their biomedical applications such as in controlled drug delivery, protein binding, phospholipid labeling, and in microbe detection have been demonstrated. Apart from material science and bio-science, LCs are now playing significant role in nanoscience and nanotechnology such as synthesis of nanomaterials using LCs as template, the design of LC nanomaterials, alignment and self assembly of nanomaterials using LC phases and so on. Because of their dynamic nature, photochemically, thermally or mechanically induced structure changes of liquid crystals can be used for the construction of stimuli-responsive materials. Although LCs have diverse applications such as temperature sensing, solvents in chemical reactions, in chromatography, in spectroscopy, in holography, etc., they are primarily known for their extensive exploitation in electrooptical display devices such as watches, calculators, telephones, personal organizers, laptop computers, flat panel television etc.

1.2. Liquid crystals as an intermediate phase (mesophase) of matter

Three classical phases of matter includes crystal (solid), liquid and gas. In crystalline phase, the constituent molecules are ordered in an expected pattern all through the entire three-dimensional structure. These patterns are located upon the points of a lattice, which is a collection of points repeating periodically in three dimensions. Contrary to crystal, the molecules in a liquid state do not have much of restrictions to travel. The forces that bind the molecules together in a solid are weak in a liquid permitting them to flow. In liquid, molecules are bound due to cohesive force but not rigidly. They are able to move around one another liberally, resulting in a partial degree of molecular mobility. In gaseous state, molecules are widely separated from one another, and as such do not influence nearby molecules to the same degree as liquids or solids.

In other way we can say that, in crystals, molecules usually have both positional and orientational order *i.e.* the centre of mass of the molecules occupy specific locations and the molecular axes point in certain directions (Figure 1). As a result, various physical properties are dissimilar, when observed in different directions. Both the positional and orientational order of solid fades away on melting to liquid. There is no favored location for the centre of mass or preferred direction of orientation for the molecular axes in liquid state. The center of mass moves in random directions and molecules diffuse freely throughout the sample in all dimensions. Physical properties are not dependent on direction *i.e.* the state is called isotropic phase.

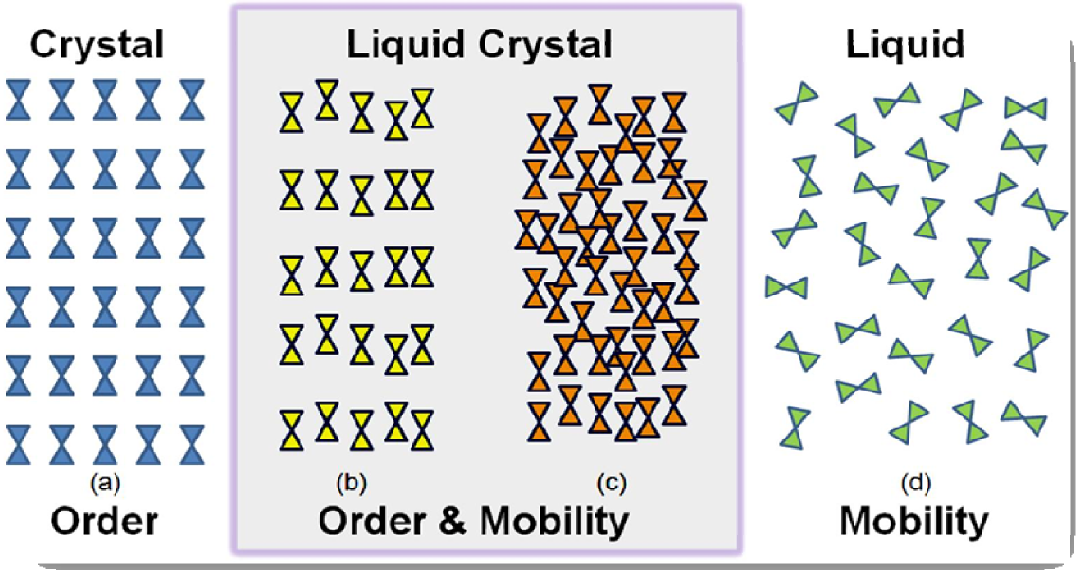
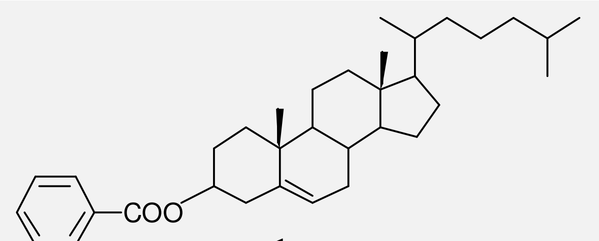


Figure 1. Basic structural difference among crystalline solid, liquid crystal and isotropic liquid.

In addition to isotropic liquid and anisotropic solid phases there are some phases that have order which is intermediate between these two edges. In one example the molecules are usually permanent at lattice points but they are able to vibrate and rotate at their positions. These types of phases are called as plastic crystal phase. In some anisotropic shaped molecules *i.e.* one axis of the molecule is much longer or shorter than the other two axes, there is possibility of occurrence of additional phases in which there is some positional and orientational order, but much less than the same found in solids and plastic crystals. These type of phases are referred to as liquid crystalline phases or mesophases. In liquid crystalline phase molecules diffuse all through the sample but maintain some short-ranged *positional and orientational order*. If we think about a particular molecule, the extent of interaction of this molecule with nearby molecules is not identical in all directions. The mobility of molecules is not similar in all dimensions. Hence we can say that the system is anisotropic rather than isotropic liquids. For this reason liquid crystals combine some properties (anisotropy and order) which are common with crystalline solid and some other property (mobility) which is actual property of liquids. Since these anisotropic ordered fluids lie in between solids and liquids and hold properties of both, they are described as intermediate phases or *mesophases*.

1.3. Discovery and History of liquid crystals

The fascinating world of liquid crystal started in 1888, when a botanist-cum-chemist, F. Reinitzer, for the first time observed the existence of liquid crystalline phase.[3] He noticed "double melting" behavior of cholesteryl benzoate **1**.



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He synthesized cholesteryl derivative of benzoic acid. This compound had two melting points, 145 °C where it melted to a cloudy liquid and 179 °C where it went to a

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[3] (a) F. Reinitzer, *Wiener Monatsh. Chem.*, 9, 421, **1888**; (b) F. Reinitzer, *Liq. Cryst.*, 5, 7, **1989.**

transparent liquid. In beginning, Reinitzer attributed this phenomenon to the presence of impurities in the material, but he observed same behavior after further purification. This behavior was further examined by the German physicist, Otto Lehmann, who was an expert in polarizing optical microscopy.[4] It was concluded that the cloudy liquid was a new state of matter and coined the terms '*fluid crystal'* or '*liquid crystal'* to indicate that it was something between a liquid and solid, sharing imperative properties of both. The discovery of liquid crystals itself was a multidisciplinary task and so also the present day science and technology of liquid crystals. It is notable that researchers as early as 1850s actually dealt with liquid crystals but did not realize the uniqueness of the phenomena.[5]

Over the next decade about 15 liquid crystals became known. All these materials were discovered unintentionally only as no relationship between the molecular shape and liquid crystalline state was known. During the first half of twentieth century, progress was mostly achieved 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 alone.[6] He remarked that all the compounds exhibiting mesophases had elongated (rod-like) molecules, now called calamitic molecules. In 1965 at the International Liquid Crystal Conference (ILCC), the application of cholesteric liquid crystals in thermography was presented, but in 1968 ILCC, Heilmeier's group gave the first indication for an application of liquid crystals in electrooptical display technology. This report increased the interest in liquid crystal research exponentially which continues even today. By 1992 the number of liquid crystalline materials increased to about 50,000. To date more than hundred thousand liquid crystalline compounds are known in the literature.

In 1977, Chandrasekhar and his colleagues accounted that not only rod-like *i.e.* calamitic molecules, but also compounds with disc-like molecular shape are capable to form mesophases.[7] Currently more than 3000 discotic liquid crystals are known in the literature. In

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[4] O. Lehmann, *Z. Phys. Chem.*, 4, 462, **1889.**
[5] W. Heintz, *J. Prakt. Chem.*, 66, 1, **1855.**
[6] D. Vorlander, *Kristallinisch-flussige Substanzen*, Enke, Stuttgart, **1905.**
[7] S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana,* 9, 471, **1977.**

1986, liquid crystals formed by board-like (lath-like) were reported.[8] 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 in 1996.[9] Typically, their molecular structure can be regarded as being composed of three units; an angular central unit, two linear rigid cores and terminal chains. 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. Bent shaped molecules provide access to mesophases with polar order and supramolecular chirality.

1.4. Classification of liquid crystals

Liquid crystals can be classified in various ways. On the basis of molar mass of the constituent molecules one can categorize these materials in to low molar mass (monomeric, dimeric and oligomeric) and high molar mass (polymeric) liquid crystals; depending on how the liquid crystalline phase has been obtained whether by adding solvent (*lyotropic*) or by varying the temperature (*thermotropic*); depending the nature of the constituent molecules (organic, inorganic and organometallic); depending on the geometrical shape of the molecules (rod-like , disc-like, bent core); depending on the arrangement of the molecules in the liquid crystalline phase (nematic, smectic, columnar, helical, B phases etc). The classification of liquid crystals is shown in Figure 2.

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[8] O. H. Schönherr, J. H. Wendorff, H. Ringsdorf, Peter Tschirner, *Makromol. Chem. Rap. Commu.,* 7, 791, **1986**.

[9] (a) T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takazoe, *J. Mater. Chem*., 6, 1231, **1996**; (b) G. Pelzi, S. Diele, W. Weissflog, *Adv. Mater*., 11, 707, **1999**; (c) C. Tschierske, G. Dantlgraber, *Pramana*, 61, 455, **2003**; (d) M. B. Ros, J. L. Serrano, M. R. de la Fuente, C. L. Folcia, *J. Mater. Chem.,* 15, 5093, **2005**; (e) R. A. Reddy, C. Tschierske, *J. Mater. Chem.,* 16, 907, **2006**; (f) H. Takezoe, Y. Takanishi, *Jpn. J. Appl. Phys*., 45, 597, **2006**; (g) J. Etxebarria, M. B. Ros, *J. Mater. Chem*., 18, 2919, **2008**.

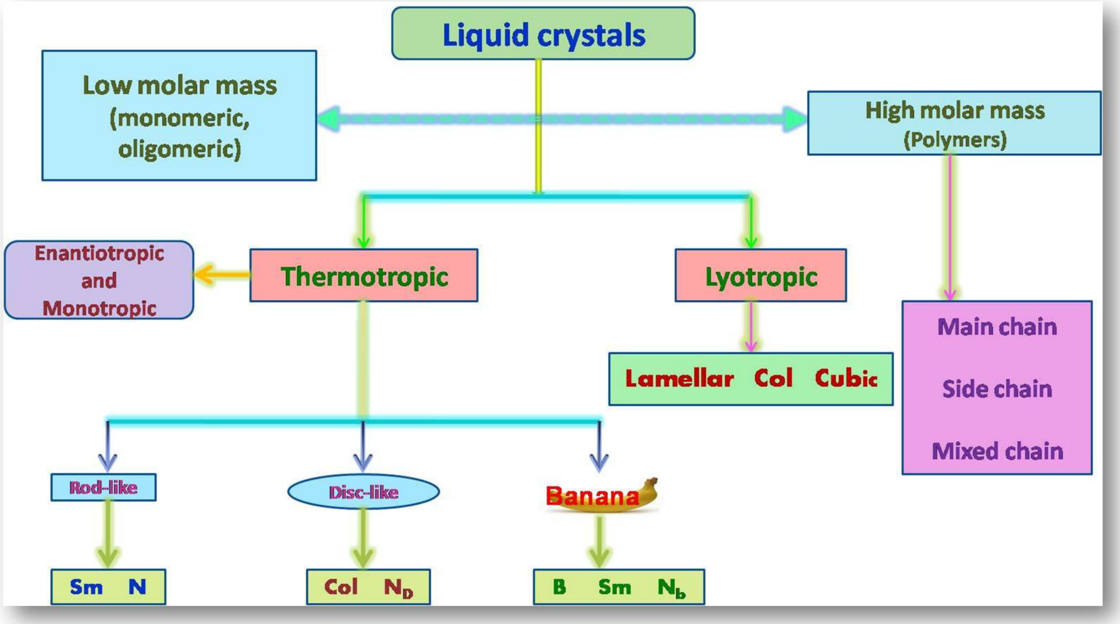

Figure 2. Classification of liquid crystals.

However, the most widely used classification of liquid crystals is into two major categories; (a) thermotropic liquid crystals (mesophase formation is temperature dependent), and (b) lyotropic liquid crystals (mesophase formation is solvent and concentration dependent). If a compound displays both thermotropic and lyotropic liquid crystalline phases then it is called *amphotropic* liquid crystal. Since this thesis deals with **thermotropic liquid crystals**, a very brief introduction of the lyotropic liquid crystals has been given below owing to their biological significance and they play an important role in living systems.[10]

1.4.1. Lyotropic liquid crystals

Some molecules contain both water-loving *i.e.* hydrophilic part (which may be ionic or non-ionic) and water-hating *i.e.* hydrophobic part in it. Standard hydrophobic groups are saturated or unsaturated hydrocarbon chains. These type of molecules having two distinct parts of complementary behavior, a hydrophilic polar “head” and a hydrophobic nonpolar “tail” are called amphiphilic molecules. For these amphiphilic molecules mesomorphism is

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[10] I. Koltover, T. Salditt, J. O. Radler and C. R. Safinya, *Science*, 281, 78, **1998**.

the consequence of addition of a solvent. These materials are called lyotropic liquid crystals *i.e.* lyotropic liquid crystals are multi-component systems. Mesophase formation in lyotropic liquid crystals is governed by concentration as well as temperature.[11] Typical examples of lyotropic liquid crystals are the salts of fatty acids; phospholipids. On being added to water, these amphiphilic molecules form self collection through a self assembly process as a result of hydrophobic effect. This self collection or self assembly is distinguished by anisotropic structures (anisotropic aggregates) having hydrophobic non-polar chains inside, shielded from outside by hydrophilic head groups. In this way water-disliking hydrophobic chains are protected from contact with water. These anisotropic aggregates are called micelles. These micelles are the basic structural units of lyotropic liquid crystals.[12] Similar to thermotropic mesogens, depending on amphiphilic concentration, these micelles self assemble in different manner to construct different types of lyotropic liquid crystalline phase patterns. Three different classes of lyotropic liquid crystal phase structures are widely recognized. These are cubic, hexagonal columnar and lamellar phases (Figure 3).

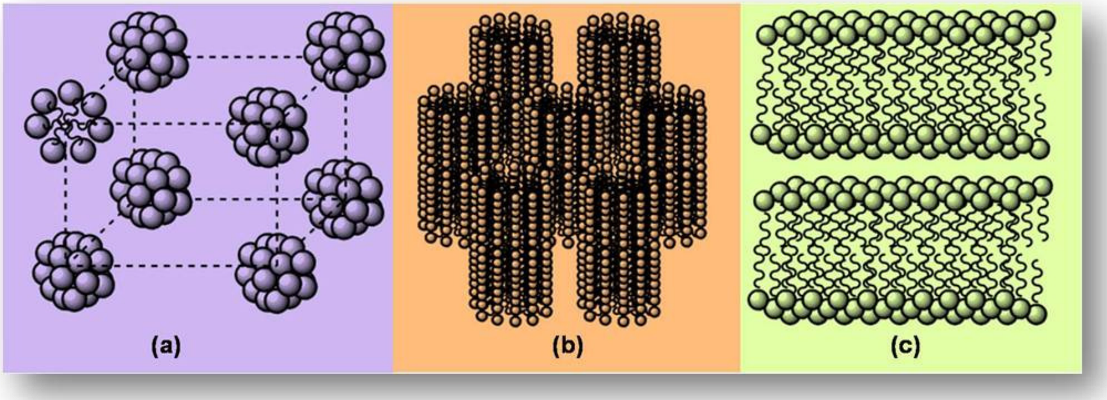

Figure 3. Lyotropic liquid crystalline phase structures; (a) cubic (low concentration), (b) hexagonal columnar (medium concentration), (c) lamellar phase (high concentration).

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[11] P. G. de Gennes and J. Prost, *The physics of Liquid Crystals, 2nd ed.* (Oxford: Clarendon Press), **1993**.

[12] Y. Hendrikx, J. Charvolin, M. Rawiso and M. C. Holmes, *J. Phys. Chem.*, 87, 3991, **1993**.

1.4.2. Thermotropic liquid crystals

Thermotropic liquid crystals are those that occur in a certain range of temperature. If the temperature rise is too high, thermal motion will destroy the delicate and balanced ordering of molecules, forcing the material to go into a usual isotropic liquid phase. At too low temperature, most mesomorphic materials will form a conventional crystal.[11,13] Many thermotropic LCs exhibit a range of phases as temperature is varied. The mesophase can be achieved either by heating a crystalline solid or by cooling an isotropic liquid. The transition temperature, at which the material goes from the crystal to the mesophase is called the *melting point*, while the transition temperature related to disappearance of mesophase *i.e.* transformation from the mesophase to the isotropic liquid is named as *clearing point* or *isotropization point*. However there are some molecules which are liquid crystalline at room temperature. For these type of materials only clearing point is observed. Some molecules have more than one type of crystalline or liquid crystalline arrangements. Crystal-to-crystal, crystal-to-mesophase and/or mesophase-to-mesophase transitions can be noticed in these systems depending on various interactions. When thermodynamically stable mesophases are detect both on heating and on cooling then the phases are termed as *enantiotropic*. If the mesophase is noticed only while cooling the isotropic liquid then it is called *monotropic* phase and is a metastable mesophase, as the mesophase transition occurs below the melting point.

The fundamental prerequisite for a molecule to exhibit a thermotropic mesophase is a structure consisting of a central core (often aromatic) and a flexible peripheral moiety (generally aliphatic chains). Moreover, along with the geometric anisotropy, anisotropy in interaction and microsegregation are the motivating parameters for liquid crystal phase formation. On the basis of molecular shape of mesogens, thermotropic liquid crystals are classified into three main groups:

(a) Calamitic (rod-like)
(b) Bent core (banana-like)
(c) Discotic (disc-like).

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[13] S. Chandrasekhar, *Liquid Crystals*, 2nd ed. (Cambridge: Cambridge University Press). ISBN 0-521-41747-3, **1992**. http://books.google.com/?id=TxvUxFlQsEsC&printsec=frontcover.

1.4.2.1. Calamitic liquid crystals

The most general type of molecules that form mesophase is rod-like or calamitic molecules. These molecules have an elongated shape *i.e.* the molecular length (l) is notably greater than the molecular breadth (b) as depicted in Figure 4.

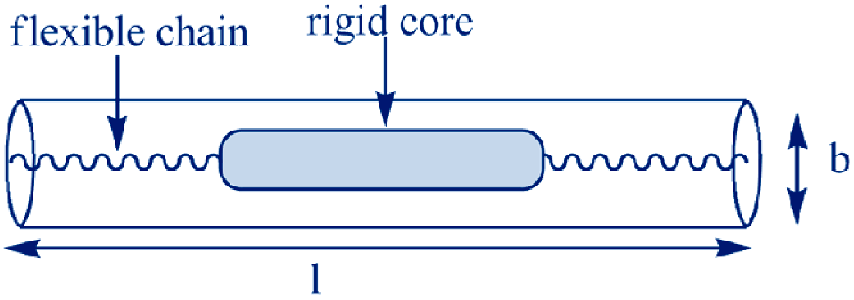

Figure 4. Representation of calamitic LCs, where l >> b.

The shape anisotropy in combination with interaction anisotropy and microsegregation of incompatible parts in calamitic liquid crystals results in a number of mesophase structures. Most of the rod-shaped meosgenic compounds contain two or more ring structures, linked together directly or through connecting groups. They frequently have terminal hydrocarbon chains and for a while contain lateral substituents as well. The representative chemical structure of these molecules can be demonstrated by the general template as shown in Figure 5, where A and B are rigid core units (benzene, naphthalene, biphenyl etc.), R and R' are flexible moieties such as normal and/or branched alkyl groups, M and N are generally small lateral substituents (-X, $-NO_2$, $-CH_3$, $-OCH_3$, -CN etc.). Y is a linking group to the core units and X & Z are linking groups (-O-, -OCO- etc.) of terminal chains and core units.

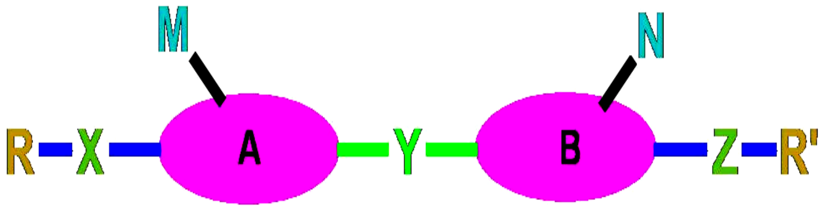

Figure 5. General template of calamitic liquid crystals.

Lateral substituents M and N are responsible to modify the mesophase morphology and physical properties of calamitic liquid crystals. Depending on the arrangement of the mesogens, calamitic liquid crystals can be further classified into two types.

(a) Nematic (from Greek word *nematos* meaning “thread”), and

(b) Smectic (from the Greek word *smectos* meaning “soap”).

1.4.2.1.1. 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 and hence the most fluid and the least viscous mesophase (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 (Figure 6). The preferred direction of orientation of the molecules, depicted as a long arrow, is called the *director*.

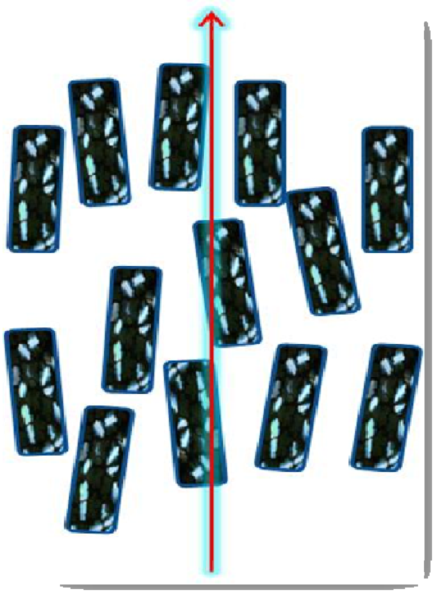

Figure 6. Structural representational of nematic phase formed by calamitic liquid crystal.

It is the nematic phase that is utilized in the huge majority of liquid crystal display formats developed over the past few decades.

1.4.2.1.2. The chiral nematic phase

The chiral nematic phase (N*) is the phase which was present in the first thermotropic mesomorphic material discovered in 1888 by Austrian botanist Reinitzer. By tradition, the chiral nematic phase was named as the *cholesteric phase* for the reason that the first materials displaying this phase were derivatives of cholesterol. These days this is not the case and there are various types of chiral materials that exhibit the chiral nematic (cholesteric) phase and these have no similarity with cholesterol. Indeed, a chiral nematic phase can be caused by adding a small quantity of chiral material (not essentially mesomorphic) to a nematic material. It is thought that this is achieved by the chiral dopant creating a chiral environment for all of the other achiral molecules and hence a helical macrostructure is generated.

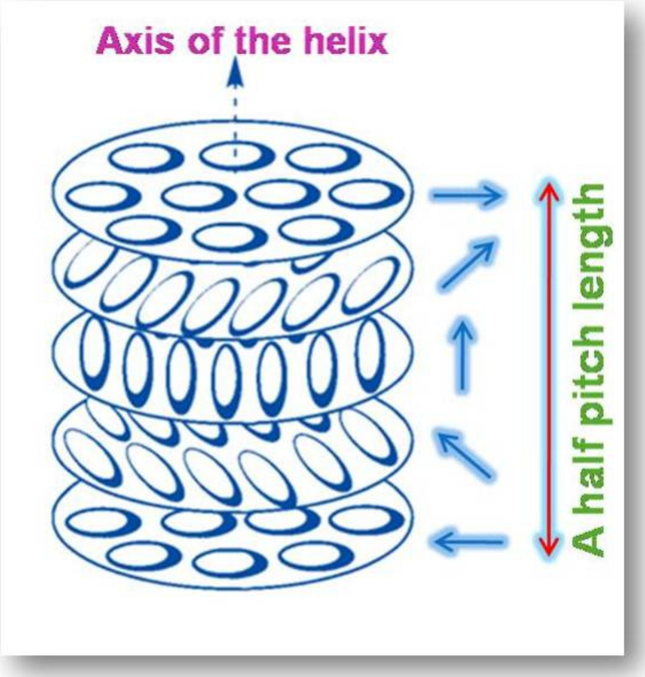

Figure 7. Representation of cholesteric phase.

The asymmetry of the ingredient molecules of the chiral nematic phase results in a slight and gradual rotation of the director. This gradual change describes a helix which has a specific, temperature-dependent pitch (Figure 7). The helical structure has the ability to selectively reflect light of a wavelength equal to that of the helical pitch length. If the pitch length is of the order of the wavelength of visible light, then colours are selectively reflected. The pitch length is temperature dependent and hence so is the color of the reflected light. This is the basis behind the commercially successful use of chiral nematic materials in thermochromic thermometer devices and other devices that change colour with temperature.

1.4.2.1.3. Smectic Phase

Calamitic or Rod-like molecules are proficient to construct mesophases where in addition to the orientational order, the molecules possess short range positional order as well. The molecules are arranged in layers with precise layer spacing or periodicity. The smectic phase is denoted by the symbol Sm. There are several types of smectic mesophases, characterized by a variety of molecular arrangements within and between the layers. Possible different organization of the molecules within the layers as well as between the layers gives rise to several different smectic liquid crystal phase structures.

Although the total number of smectic phases cannot be specified, the following types have been defined: SmA, SmB, SmC, SmF, SmI etc. However, SmA and SmC mesophase are more commonly encountered (Figure 8). In SmA phase the molecules form layers with their long molecular axes and hence the director parallel to the layer normal.

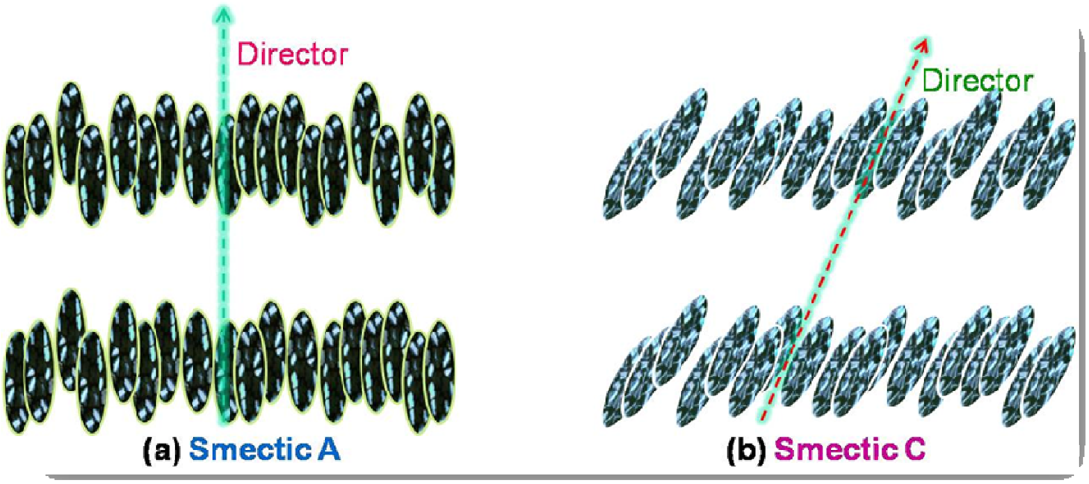

Figure 8. Smectic A and Smectic C liquid crystal phases.

The SmC phase has the same layer structure of the SmA, but the molecules are tilted with respect to the layer normal. In both the phases, there is no positional order among the molecules within the layers. However, they possess 1D layer periodicity (periodical stacking of 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 suitably defined as lamellar plastic crystals. Tilted smectic mesophases formed by chiral compounds or containing chiral mixtures are designated by the superscript * (SmC*, SmF*, etc.). More recently, a frustrated smectic liquid crystal phase has been discovered that occurs above the temperature of the normal smectic phases in some chiral materials; this phase is called the twist-grain boundary (TGB) phase.

1.4.2.1.4. Smectic C* phase

When the constituent molecules of the smectic C phase are chiral the phase is called smectic C*. The phase structure is defined by the azimuthal rotation of the molecular director from one smectic layer to the next one. The phase structure is basically the same except that the molecular chirality causes a slight and gradual change in the direction of the molecular tilt (there is no change in the tilt angle with respect to the layer normal). This change in tilt direction from layer to layer gradually describes a helix (Figure 9). Since the tilted molecules of the smectic C* phase are chiral the symmetry of the layers is reduced to a two-fold axis of rotation.

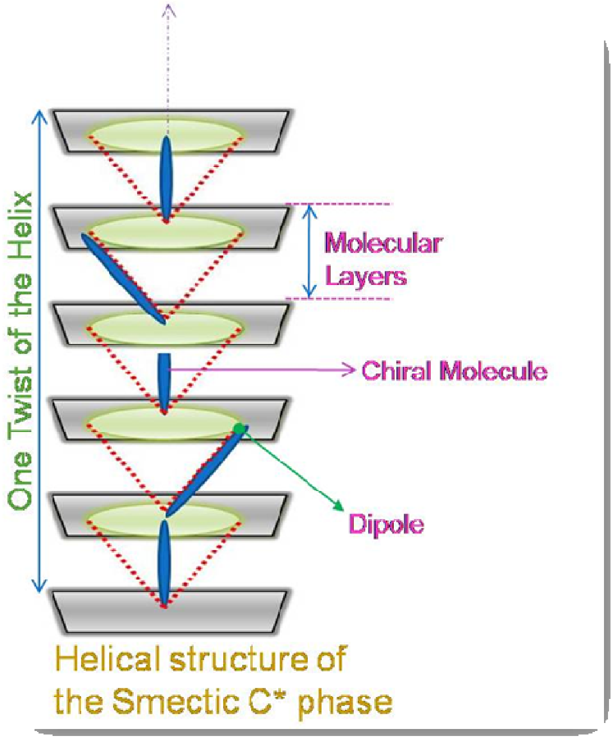

Figure 9. Helielectric structure of smectic C* liquid crystal.

Even though the molecules are undergoing rapid reorintational motion, the overall result of the reduced symmetry is to create an inequivaleance in the dipole moment along the C_2 axis. Such dipole inequivalence generates a spontaneous polarization (P_S) along the C_2 axis, the direction of which changes with the changing tilt direction of the helix. Accordingly, P_S is reduced to zero throughout a bulk sample which is not influenced by external forces, hence the SmC* phase is truly defined as helielectric. However, a single layer of the chiral smectic C phase is ferroelectric and so by unwinding the helix (by external forces such as surface interactions) a true ferroelectric phase is generated.[14]

1.4.2.1.5. Ferro-, antiferro- and ferrielectric chiral smectic C phases

Ferroelectricity results from relaxation of helielectric smectic C* phase. If this unwinding of the helix permits the layer polarizations to point in the same direction then the phase is called ferroelectric. This phase will possess a net bulk polarization. However, the unwinding of the helix can lead to two other phases known as antiferroelectric and ferrielectric phases.

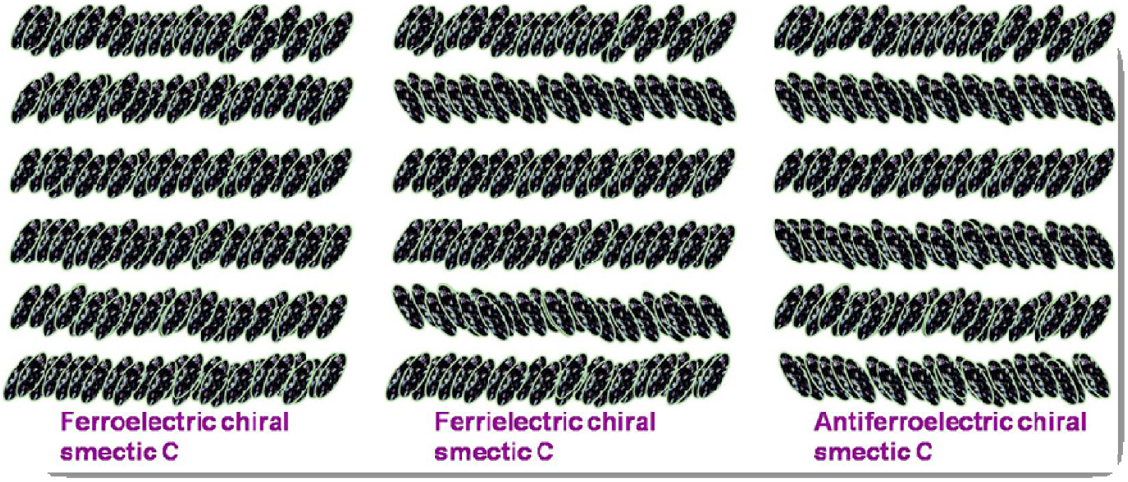

Figure 10. Schematic representation of ferro-, ferri- and antiferroelectric chiral smectic phases.

The suggested structure of the antiferroelectric phase shows that the molecular layers are arranged in such a way that the polarization directions in subsequent layers point in opposite directions which results in an averaging of the spontaneous polarization to zero. Evidence to support this hypothesis comes from the fact that when a strong electric field is applied to this phase the layer ordering is perturbed and the phase returns to a normal

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[14] (a) S. T. Lagerwall, *Ferroelectric and Antiferroelectric Liquid Crystals*, Wiley–VCH, Weinheim, **1999**; (b) J. P. F. Lagerwall and F. Giesselmann, *ChemPhysChem*, 7, 20, **2006.**

ferroelectric phase. Removal of the field will generate the antiferroelectric phase. In the ferrielectric phase, the layers are stacked in such a way that there is a net overall spontaneous polarization. In this phase, the number of layers of opposite polarization is not equal *i.e.* more layers are tilted in one direction than the other. The structures are shown in the Figure 10.

1.4.2.2. Banana liquid crystals

Though conventional thermotropic liquid crystals (LCs) are commonly made up of calamitic and disk-like molecules, the liquid crystalline phase is demonstrated by molecules with unconventional molecular structures also. One example of such a molecular architecture is a banana-shaped one, with a bend in the middle of the mesogenic part.[15] Niori *et al.*[9a] first reported the phenomenon of ferroelectricity in a smectic liquid crystalline phase which was created from achiral banana-shaped molecules. Since then, several other research groups have reported banana-shaped molecules that exhibited ferroelectric properties in the mesophase.[16] The ferroelectricity is attributed to the polar packing of molecules with C_{2v} symmetry where the molecules are packed in the same direction.

Banana-shaped mesogens are also called as bent core liquid crystals. Generally, these compounds are composed of a bent central aromatic part (*i.e.* a 1,3-disubstituted benzene) and two flexible tails. The curve in the middle of rigid core of the banana shaped compounds causes a reduction of the rotational disorder of the molecules about their long axes. The reduced symmetry of the rigid segments of such molecules leads to a directed packing of the molecules within layers. The main outcome of the directed packing of such molecules is the occurrence of a polar order parallel to the smectic layers. In order to escape from a macroscopic polarization, the layer structures are modified, and this leads to new mesophase morphologies. Bent core molecules are the first examples which have experimentally shown that antiferroelectric switching with large spontaneous polarization is indeed possible in a liquid crystal phase composed of non-chiral materials. In most of these mesophases the

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[15] (a) T. Niori, T. Sekine, J. Watanabe, T. Frukawa, H. Takezoe, *Mol. Cryst. Liq. Cryst.*, 301, 337, **1997** (b) T. Sekine, Y. Takanishi, T. Niori, J. Watanabe, T. Takezoe, *J. Mater. Chem.*, 7, 1307, **1997**; (c) Y. Matsunaga, S. Miyamoto, *Mol. Cryst. Liq. Cryst.*, 237, 311, **1993**; (d) R. Cai, E. Samulski, *Liq. Cryst.*, 9, 617, **1991**.

[16] W. Weissflog, C.H. Lischka, H. Kruth, *Proceeding of the European Conference on Liquid Crystals, Science and Technology*, Zakopane, Poland, December 10-11, 3-8, 126, **1997**.

molecules are additionally tilted (SmCP) and this leads to a further reduction of the phase symmetry. An inherent handedness of such SmCP phase is observed, and this handedness is *geometrical* in nature and does not result from a molecular chirality. This inherent chirality can lead to mesophases with chiral supramolecular structures even though the molecules themselves are achiral.

The formation of helical super structures to facilitate escaping from a macroscopic polarization is another way to chirality in such supramolecular systems composed of achiral molecules. Moreover, in some cases macroscopic regions of opposite handedness are spontaneously formed. Due to the absence of molecular chirality both enantiomeric structures are equally feasible. These dark conglomerates or dark racemates are optically isotropic phases with local SmCP order. Bent core molecules open the door to novel complex types of molecular self-organization and to the new field of supramolecular stereochemistry. None of the B phases are miscible with any smectic phase of calamitic compounds. Special molecular packing of bent molecules in smectic layers could give rise to ferro-, ferri- or antiferroelectric properties. Bent core mesogens are the first thermotropic liquid crystals for which a biaxial nematic (N_b) phase was unambiguously determined.[17] The happening of superstructural chirality in the mesophase of bent-core compounds without having any chiral auxiliary in the molecules is not only of fundamental scientific interest but also of industrial application as this chirality can be switched in external electric fields. Various new applications of these materials include nonlinear optics, flexoelectricity, photoconductivity, molecular electronics and the design of biaxial nematic phase. Figure 11 shows a general template of banana liquid crystal molecules.

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[17] (a) L. A. Madison, T. J. Dingemans, M. Nakata, E. T. Samulski, *Phys. Rev. Lett.,*92, 145505, **2004**; (b) B. R. Acharya, A. Primak, S. Kumar, *Phys. Rev. Lett.,* 92, 145506, **2004.**

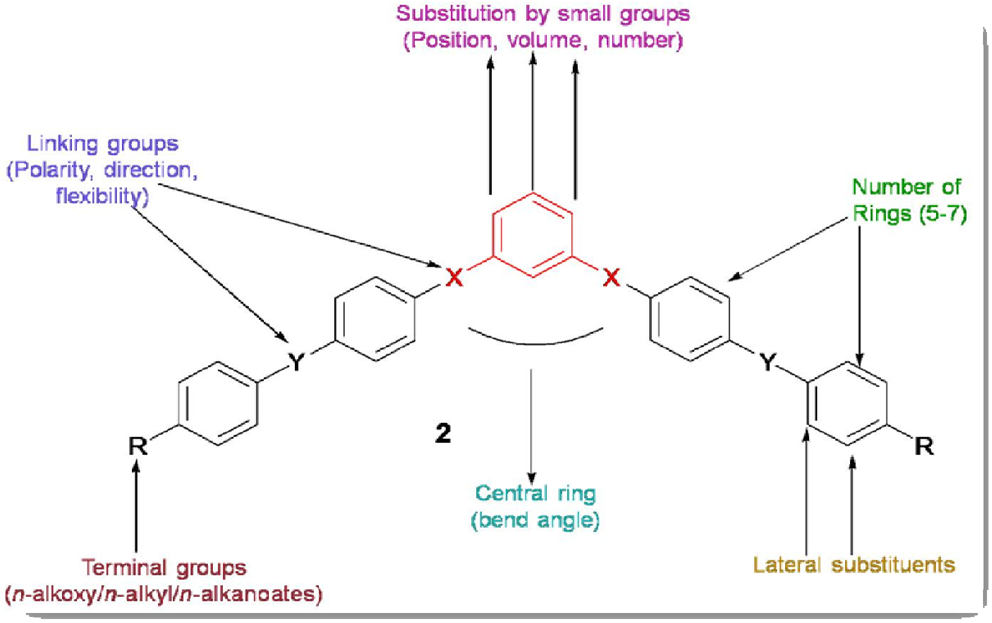

Figure 11. General template for banana liquid crystals.

Bent molecular structures symbolize a new sub-category of thermotropic liquid crystals. In addition to classical nematic and/or smectic phases, they can also display novel types of smectic-like phases called “B” phases and are numbered according to their chronological discovery, from B_1 to the most recent B_8. The symbol B stands for banana- or Bent- or Bow-shaped mesogens. The three vectors (1) layer normal, (2) tilt direction and (3) polar axis (kink direction) make-up an orthogonal system which may be left or right handed. Right and left handed systems are mirror images of one another and hence chiral (Figure 12). If there is a dipole moment associated with the kink this axis becomes the polar axis which is responsible for ferroelectricity. Macroscopic samples are achiral. If chirality alters from layer to layer in a sample, it is called racemic. If there are macroscopic domains with homogeneous chirality, the sample is homochiral.

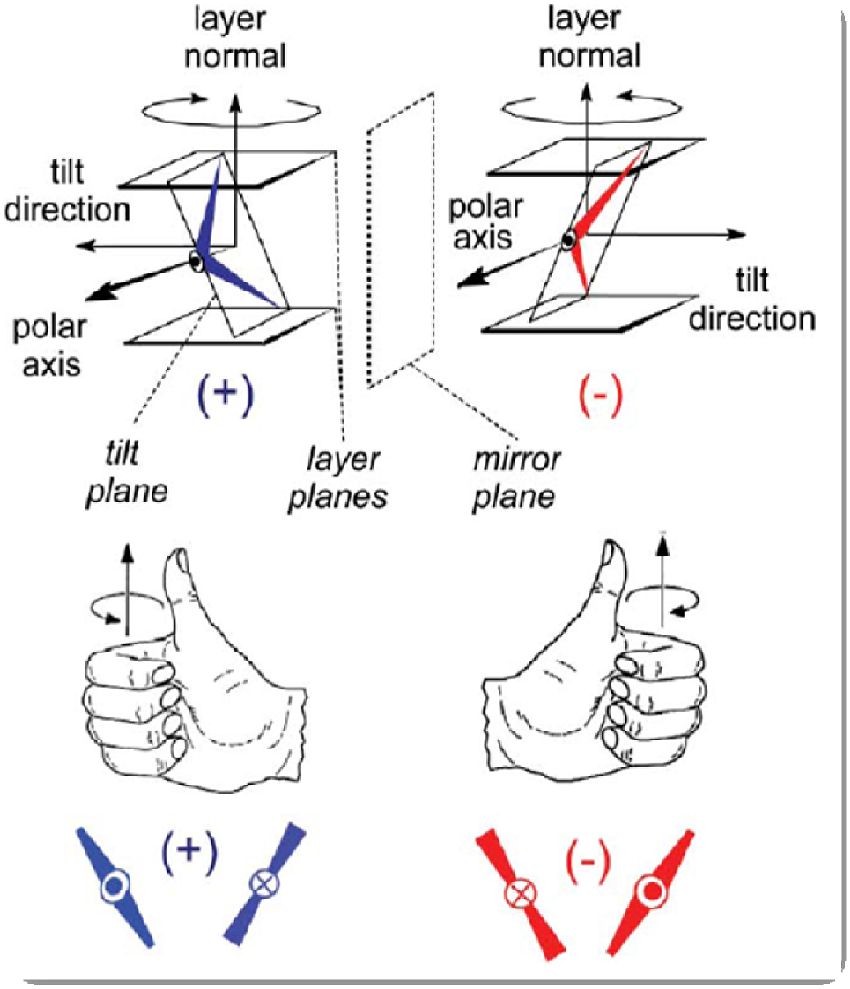

Figure 12. Origin of chirality in banana liquid crystals (Reproduced from Reddy, R. A. and Tschierske, C., *J. Mater. Chem.*, 16, 907, 2006).

1.4.2.3. Discotic liquid crystals

As this thesis is mainly concerned with discotic liquid crystals, it will be discussed in detail (section 1.5 to 1.14).

1.5. Discotic liquid crystals: the discovery

Before 1977 it was a general belief that disk-like or plate like molecules cannot demonstrate mesomorphism but in September 1977, 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*".[7] They synthesized a series of benzene hexa-*n*-alkanoate derivatives (**3**). A new class of mesomorphism was recognized on the basis of thermodynamic, optical and X-ray results. The suggested structure has stacking of molecules one on the top of other in column and these columns in turn arrange themselves in hexagonal lattice (Figure 13). This invention started a whole new field of fascinating liquid crystal research.

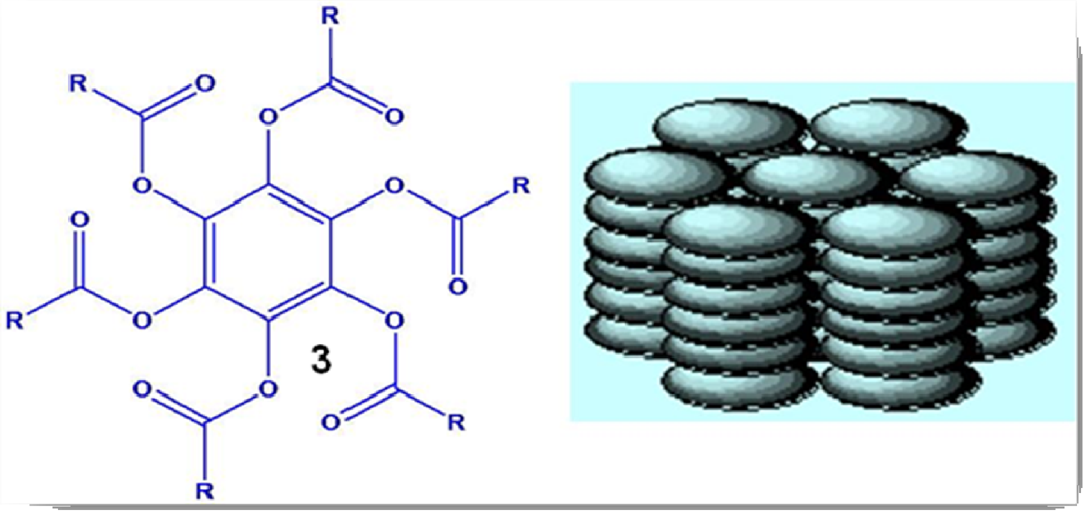

Figure 13. Structure of benzene-hexa-*n*-alkanoates and their columnar arrangement.

In 1924, Vorlander believed that leaf-shaped molecules[18] can exhibit liquid crystalline behavior. However, his efforts to realize any example with this behavior had been fruitless probably because the molecules investigated by him did not have any flexible chain. He pointed out 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 famous for forming columnar mesophases. In the early 1960s, anisotropic mesophases with nematic texture had

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[18] D. Vorlander, "*Chemische Kristallographic der Flussigkeiten*", Akademische Verlagsgesellschaff, Leipzig, pp. 34, **1924**.

been observed during the pyrolysis of graphitizable substances (Carbonaceous mesophase).[19] These mesophases were considered to be developed from flat polyaromatic molecules, however, and not by well-defined organic molecules. The complete characterization of these mesophases was not possible because of their non stability and non homogenous nature.

Benzene hexa-*n*-alkanotes discovered by Chandrasekhar *et al*. were an entirely new class of liquid crystals, reasonably different from the conventional liquid crystals constructed by rod-like or calamitic molecules. The disc-like molecules spontaneously form one-dimensional columnar stacks, which in turn, arrange themselves in two-dimensional lattices; the third dimension has no translational order-that shows liquid like characteristic (Figure 14).

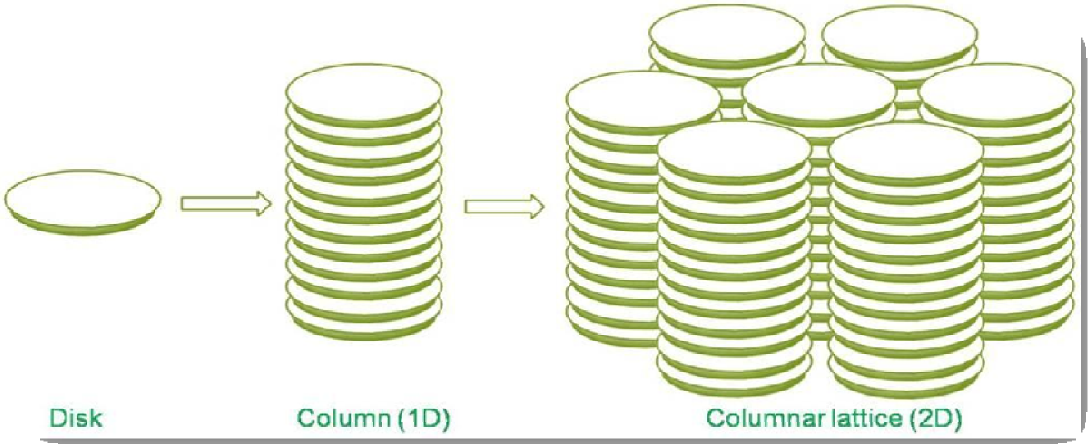

Figure 14. Self assembly of discotic liquid crystals into columnar phase.

1.6. Structures of the liquid crystalline phases formed by discotic mesogens

Discotic materials often have two- to six-fold rotational symmetry. The mesomorphism is the result of microsegregation of the two incompatible parts *i.e.* peripheral alkyl chains and rigid aromatic core. The crystalline character is encouraged by the interaction

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[19] (a) G. H. Taylor, *Fuel*, 40, 465, **1961**; (b) J. D. Brooks, G. H. Taylor, *Nature*, 206, 697, **1965**; (c) J. D. Brooks, G. H. Taylor, *Carbon*, 3, 185, **1985**; (d) J. D. Brooks, G. H. Taylor, *Carbon*, 4, 243, **1968**.

between the rigid conjugated cores whereas the melting of the peripheral alkyl chains in the mesophase results in the liquid character.

Most of the disc-shaped molecules display only one type of mesophase but few examples are known to exhibit polymorphism.[20] Mesophases formed by discotic molecules are primarily of four types:

(i) Nematic,
(ii) Smectic,
(iii) Columnar,
(iv) Cubic.

The columnar phase is most common in discotics followed by nematic phase whereas the other phases are rarely observed.

1.6.1. Nematic Phases of discotic mesogens

The nematic phases of disc-shaped molecules can be categorized into four different kinds depending on the molecular arrangements.

a. Discotic Nematic (N_D),
b. Chiral Nematic (N_D*),
c. Columnar nematic (N_{Col}),
d. Nematic lateral (N_L).

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[20] (a) S. Kumar, *Chem. Soc. Rev.*, 35, 83, **2006**; (b) T. Kato, T. Yasuda, Y. Kamikawa, M. Yoshio, *Chem. Commun.*, 729, **2009**; (c) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hagele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem. Int. Ed.*, 46, 4832, **2007**; (d) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.*, 36, 1902, **2007**; (e) J. Wu, W. Pisula, K. Mullen, *Chem. Rev.*, 107, 718, **2007**; (f) Y. Shimizu, K. Oikawa, K. Nakayama, D. Guillon, *J. Mater. Chem.*, 17, 4223, **2007**; (g) N. Boden, R. J. Bushby, J. Clements, B. Movaghar, *J. Mater. Chem.*, 9, 2081, **1999**; (h) R. J. Bushby, O. R. Lozman, *Curr. Opin. Solid State Mater. Sci.*, 6, 569, **2002**; (i) R. J. Bushby, O. R. Lozman, *Curr. Opin. Colloid Interface Sci.*, 7, 343, **2002**; (j) H. Takezoe, K. Kishikawa, E. Gorecka, *J. Mater. Chem.*, 16, 2412, **2006**; (k) K. Ohta, K. Hatsusaka, M. Sugibayashi, M. Ariyoshi, K. Ban, F. Maeda, R. Naito, K. Nishizawa, A. M. van de Craats, J. M. Warman, *Mol. Cryst. Liq. Cryst.*, 397, 25, **2003**; (l) P. H. J. Kouwer, W. F. Jager, W. J. Misj, S. J. Picken, *Macromolecules*, 34, 7582, **2001**; (m) S. Chandrasekhar, *Liq. Cryst.*, 14, 3, **1993**; (n) S. Chandrasekhar and G. S. Ranganath, *Rep. Prog. Phys.*, 53, 57, **1990**.

This phase is denoted by the symbol 'N_D'. In N_D phase, the molecules have orientational order but no long range positional order (Figure 15a). The molecules stay more or less parallel to each other. The nematic phase of disc-shaped molecules is generally non-miscible with the nematic phase of rod-shaped molecules. However, the symmetry of the nematic phase formed by disc-shaped molecules is indistinguishable from that formed by rod-shaped molecules. In discotic nematic phase the director is along the short molecular axes of the molecule since the disc normals are orientationally ordered.

Similar to chiral calamitic nematic or cholesteric phase, chiral discotic nematic mesophase N_D* also exists. The structure of this phase is characterized by nematic arrangement of molecules within one plane, but on going from one plane to the other plane the overall director of molecules rotates. The mesophase occurs in mixtures of discotic nematic and mesomorphic or non-mesomorphic chiral dopants as well as in pure chiral discotic molecules. Chiral discotic nematic phase is characterized by a helical structure.

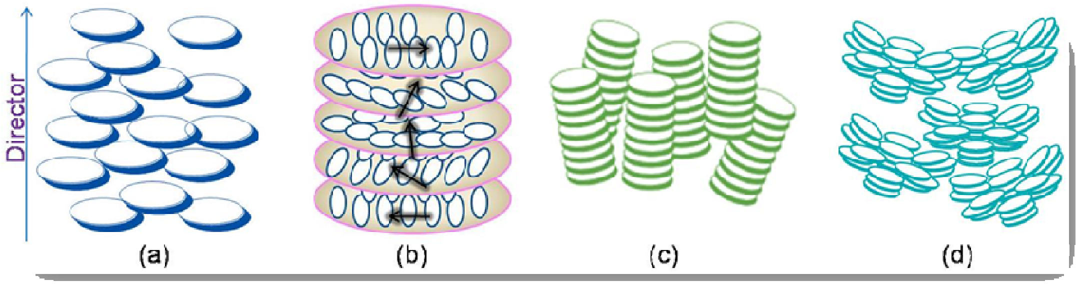

Figure 15. Schematic representations of (a) discotic nematic, (b) helical structures of chiral nematic, (c) nematic columnar and (d) nematic lateral phase.

The structural unit in columnar nematic phase is the stack of discotic molecules in the form of column. Individual column in turn arranges in nematic fashion *i.e.* columns do not form two-dimensional (2D) lattice structures (Figure 15c). They exhibit an orientational long-range order and a positional short-range order. This phase is denoted by N_{Col}.

Recently, another nematic phase has been reported, where the disc shaped molecules aggregate into large disc-shaped superstructures, and these aggregates show a nematic arrangement (Figure 15d). The phase is referred as the nematic lateral phase (N_L) due to strong lateral interactions.[20]

1.6.2. Smectic phases of discotic mesogens

The unequal distribution of the peripheral alkyl chains or reduced number of peripheral chains around the disk is responsible for the formation of discotic smectic mesophase (Figure 16). In analogy to calamitic smectic mesophases, in discotic smectic mesophases the discs are arranged in a layered manner separated by sub layers of peripheral chains.[21] Since the molecular rotations about their long molecular axes will be restricted in the layers, they are expected to exhibit biaxial smectic phases. Unlike columnar phases, smectic phases are rare in discotic LCs.

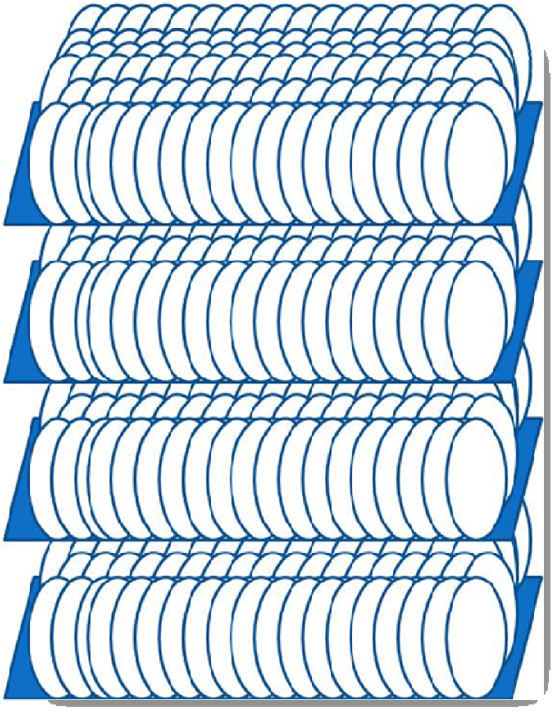

Figure 16. Smectic phase of discotic liquid crystals.

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[21] (a) D. W. Bruce, D. A. Dunmur, L. S. Santa, M. A. Wali, *J. Mater. Chem*., 2, 363, **1992**; (b) B. Alameddine, O. F. Aebischer, W. Amrein, B. Donnio, R. Deschenaux, D. Guillon, C. Savary, D. Scanu, O. Schidegger, T. A. Jenny, *Chem. Mater*., 17, 4798, **2005.**

1.6.3. Columnar phases of discotic mesogens

Due to strong π-π interaction, discotic molecules stack one on the top of the other to construct columns. These columns arrange themselves in various two-dimensional lattices. Within each column arrangement of molecules may be in a regular ordered (periodic) manner or disordered pattern (aperiodic). Periodic or aperiodic order of discs within the column is determined by the extent of π-π overlap along the column. Depending on the degree of order in the molecular stacking, orientation of the molecules along the columnar axis, the dynamics of the molecules within the columns and the two-dimensional lattice symmetry of the columnar packing, the columnar mesophases may be classified in seven classes.

(i) Columnar hexagonal mesophase (Col_h),
(ii) Columnar rectangular mesophase (Col_r),
(iii) Columnar oblique phase (Col_{ob}),
(iv) Columnar plastic phase (Col_p),
(v) Columnar helical phase (H),
(vi) Columnar square (tetragonal) phase (Col_{tet}),
(vii) Columnar lamellar phase (Col_L).

1.6.3.1. The hexagonal columnar mesophase (Col_h)

In this mesophase, molecular columns are arranged in hexagonal pattern. Hexagonal columnar mesophases are often denoted as Col_{ho} (Figure 17) or Col_{hd} where 'h' stands for hexagonal and 'o' and 'd' for ordered or disordered stacking of the molecules, respectively. 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_h". Hexagonal columnar mesophase is the most occurring phase among all varieties of columnar phase exhibited by discotic molecules. All the synthesized compounds belonging to this thesis work displayed Col_h phase for a broad temperature range.

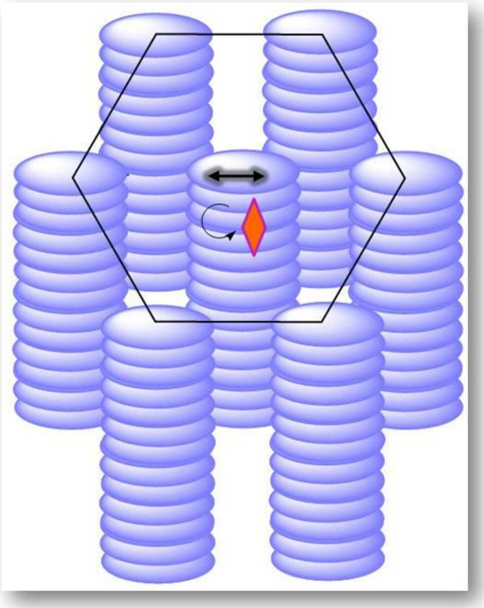

Figure 17. Schematic representation of hexagonal columnar mesophase.

The planar space group of a hexagonal columnar mesophase is *p6/mmm*, which is equivalent to *p6/m2/m* in the International System (Figure 18a) and belongs to the point group D_{6h} in Schoenflies notation. The symmetry elements are shown in Figure 18b.

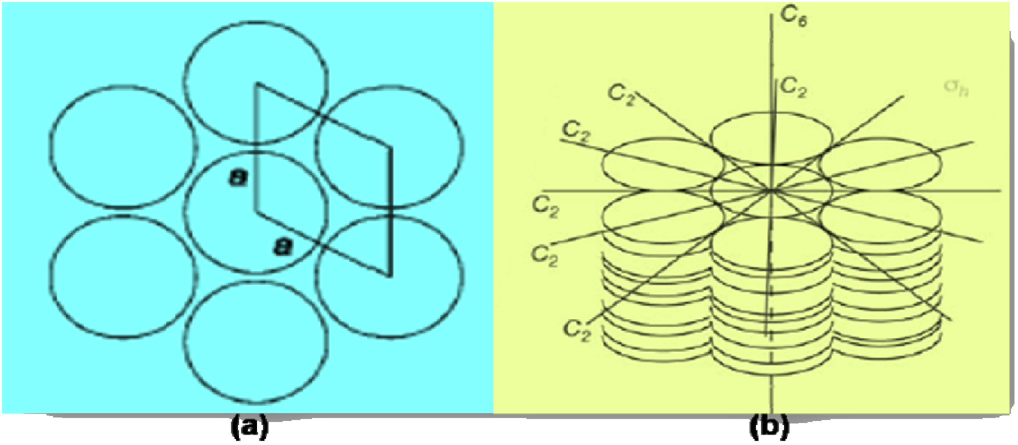

Figure 18. (a) Plan views of the 2D lattices in hexagonal (b) symmetry elements of a Col_h mesophase: the point group D_{6h} has one C_6 axis and perpendicular to this axis, six C_2 and a mirror plane σ_h.

1.6.3.2. The rectangular columnar mesophase (Col_r)

This phase is denoted by Col_r. Columns are arranged in a rectangular pattern (Figure 19).

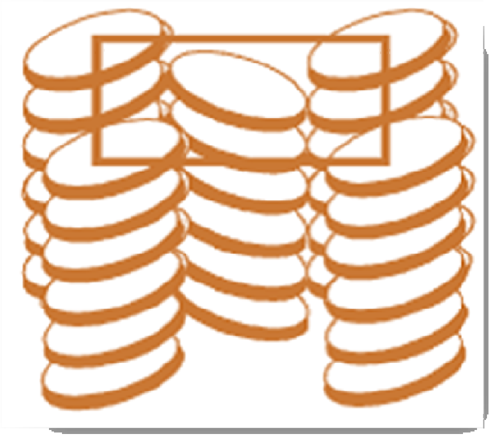

Figure 19. Schematic representation of a rectangular columnar mesophase.

Three different types of rectangular mesophase Col_r have been identified (Figure 20a-c).[22] In general, the molecules are tilted with respect to the column axis,[23] whereby the cross section, orthogonal to the axis of a column, is elliptic.

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[22] A. M. Levelut, *J. Chem. Phys*., 80, 149, **1983**.

[23] F. C. Frank, S. Chandrasekhar, *J. Phys*., 41, 1285, **1980**.

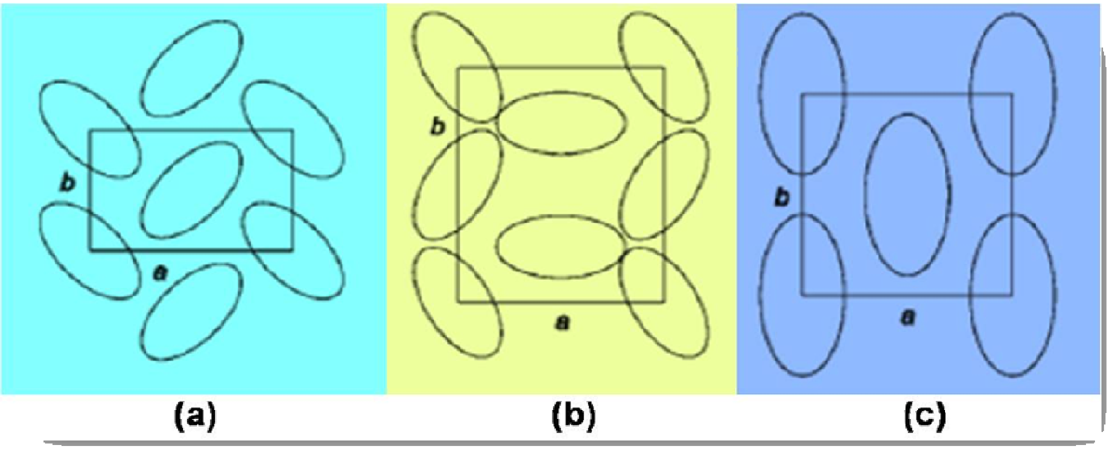

Figure 20. Different types of rectangular columnar phases (a) Col_r ($P2_1/a$) ; (b) Col_r (P2/a) and (c) Col_r (C2/m).

The symmetries of the 2D lattices are specified by three different planar space groups $P2_1$/a, $P$2/a, and $C$2/m,[22,24] 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 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.

1.6.3.3. The columnar oblique mesophase (Col_{ob})

Figure 21 illustrates the arrangement of the columns in a columnar oblique mesophase. In this phase, the tilted columns are represented by elliptic cross sections. The symmetry of

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[24] C. Destrade, P. Foucher, H. Gesparoux, H. T. Nguyen, A. M. Levelut, J. Malthete, *Mol. Cryst. Liq. Cryst.*, 106, 121, **1984**.

this 2D lattice corresponds to the space group P_1. Examples for columnar oblique mesophases are rare because of strong core-core interactions.[24,25]

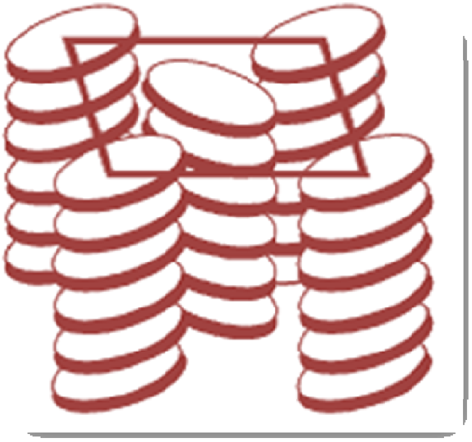

Figure 21. Columnar oblique phase.

1.6.3.4. The columnar plastic mesophase ($\mathrm{Col_p}$)

This phase is denoted as $\mathrm{Col_p}$ and was noticed recently in discotic liquid crystals.[26] In this phase molecules arrange as three-dimensional crystal-like order in a hexagonal lattice, while the discs within the columns are able to rotate about the columnar axis (Figure 22). Contrary to this, in the case of $\mathrm{Col_h}$ 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 $\mathrm{Col_p}$ phase is restricted.

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[25] F. Morale, R. W. Date, D. Guillon, D. W. Bruce, R. L. Finn, C. Wilson, A. J. Black, M. Schroder, B. Donnio, *Chem. Eur. J.*, 9, 2484, **2003**.

[26] B. Glusen, W. Heitz, A. Kettner, J. H. Wendorff, *Liq. Cryst.*, 20, 627, **1996**.

Figure 22. Columnar plastic phase.

1.6.3.5. The columnar helical (H) phase

This exceptional mesophase structure with helical order was observed in a triphenylene derivative namely hexahexylthiotriphenylene (HHTT).[27,28] In this so-called H phase helical columns develop with interdigitate in groups of three columnar stacks. X-ray diffraction experiments have proved that the helical H phase is distinctive to HHTT and certain mixtures of compounds with an average chain length close to 6 carbons.[29] The H phase found in HHTT is shown in Figure 23.

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[27] E. Fontes, P. A. Heiney, W. H. De Jeu, *Phys. Rev. Lett.*, 61, 1202, **1988.**

[28] P. A. Heiney, E. Fontes, W. H. De Jeu, A. Riera, P. Carroll, A. B. Smith III, *J. Phys. France*, 50, 461, **1989**.

[29] S. H. J. Idziak, P. A. Heiney, J. P. McCauley, Jr. P. Carroll, A. B. Smith III, *Mol. Cryst. Liq. Cryst.*, 237, 271, **1993**.

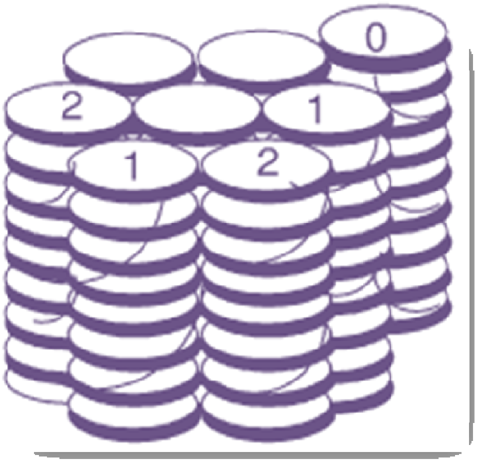

Figure 23. Structure of the helical H phase.

1.6.3.6. The columnar lamellar mesophase

The mesophase of some discotic compounds *e.g.* bis(*p*-n-decylbenzoyl)methanato copper(II), some perylene derivatives[30] has layered structure. This phase is called columnar lamellar phase and is denoted by the symbol Col_L. In this phase discotic molecules stack to form columns and these columns are arranged in layers, where the columns in layers can slide. But the columns in different layers do not possess any positional (translational) correlation (Figure 24).

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[30] (a) K. Ohta, H. Muroki, A. Takagi, K. I. Hatada, H. Ema, I. Yamamoto, K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 140, 131, **1986**; (b) H. Sakashita, A. Nishitani, Y. Sumiya, H. Terauchi, K. Ohta, I. Yamamoto, *Mol. Cryst. Liq. Cryst.*, 163, 211, **1988.**

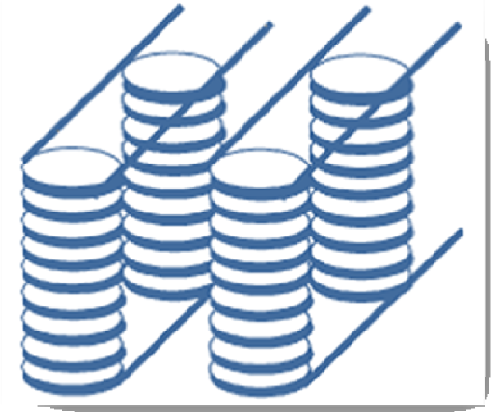

Figure 24. Columnar lamellar phase.

1.6.3.7. The columnar square (tetragonal) phase

The columnar square phase is also known as tetragonal phase (Col_{tet}). The structure of this phase is represented in Figure 25. In this mesophase the columns are upright and they are arranged in a square lattice. Similar to columnar hexagonal phase, this phase also exhibit spontaneous homeotropic alignment of the columns. This phase is exhibited by sugar molecules, phthalocyanines and supramolecular fluorinated liquid crystals.[31a-f]

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[31] (a) T. Vlad-Bubulak, J. Buchs, A. Kohlmeier, M. Bruma, and D. Janietz, *Chem. Mater.,* 19, 4460, **2007**; (b) K. Ohta, T. Watanabe, H. Hasebe, Y. Morizumi, T. Fujimoto, I. Yamamoto, *Mol. Cryst. Liq. Cryst.*, 196, 13, **1991**; (c) K. Hatsusaka, K. Ohta, I. Yamamoto, H. Shirai, *J. Mater. Chem*., 11, 423, **2001**; (d) M. Ichihara, A. Suzuki, K. Hatsusaka, K. Ohta, *Liq. Cryst*., 34, 555, **2007**; (e) K. Praefcke, P. Marquard, B. Kohne, W. Stephan, A. -M. Levelut, E. Watchtel, *Mol. Cryst. Liq. Cryst*., 203, 149, **1991**; (f) *Handbook of Liquid Crystals*, eds. D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill, Wiley-VCH, Weinheim, Vol I-III, **1998**; (g) Md. A. Alam, J. Motoyanagi, Y. Yamamoto, T. Fukushima, J. Kim, K. Kato, M. Takata, A. Saeki, S. Seki, S. Tagawa, T. Aida, *J. Am. Chem. Soc.*, 131, 17722, **2009.**

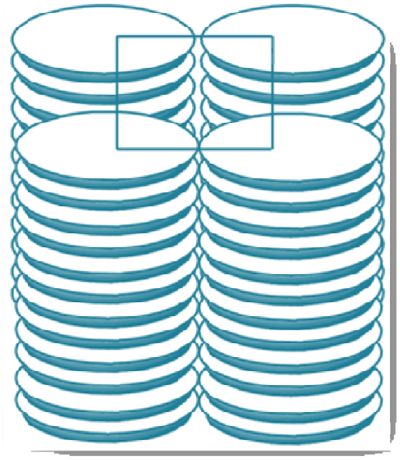

Figure 25. Columnar tetragonal phase.

1.6.4. Cubic phase

Cubic phases are omnipresent in lyotropic liquid crystals, however some thermotropic discotic phthalocyanine derivatives[31c,d] and discotic ionic triphenylene derivatives[31g] exhibit bicontinuous cubic phase which consist of interwoven but not connected branched columns.

1.7. Structure of the discotic mesogens

Molecules forming discotic mesophases are classically made of a central rigid conjugated core substituted by 3-8 saturated aliphatic chains. These materials frequently have two, three, four or six-fold rotational symmetry. However, there are many exceptions and materials with low symmetry, a non-planar, non-aromatic core having shorter number of chains are also documented to display discotic mesophase. The mesomorphism is the result of the microsegregation of the two constituents: the face on interaction between the conjugated rigid cores promotes the crystalline character while the liquid character originates from the melting of the saturated peripheral alkyl chains in the mesophase. Contrary to crystalline materials, discotic liquid crystals have capacity of repairing structural defects because of the fact that, molecules in this phase organize spontaneously under the form of one-dimensional columns, which can be oriented easily and possess self-healing properties. The search for such mesophase is mostly regulated by delicate changes in the number, size and nature of the lateral chains in addition to the central core. A general template for discotic mesogens is shown in Figure 26.

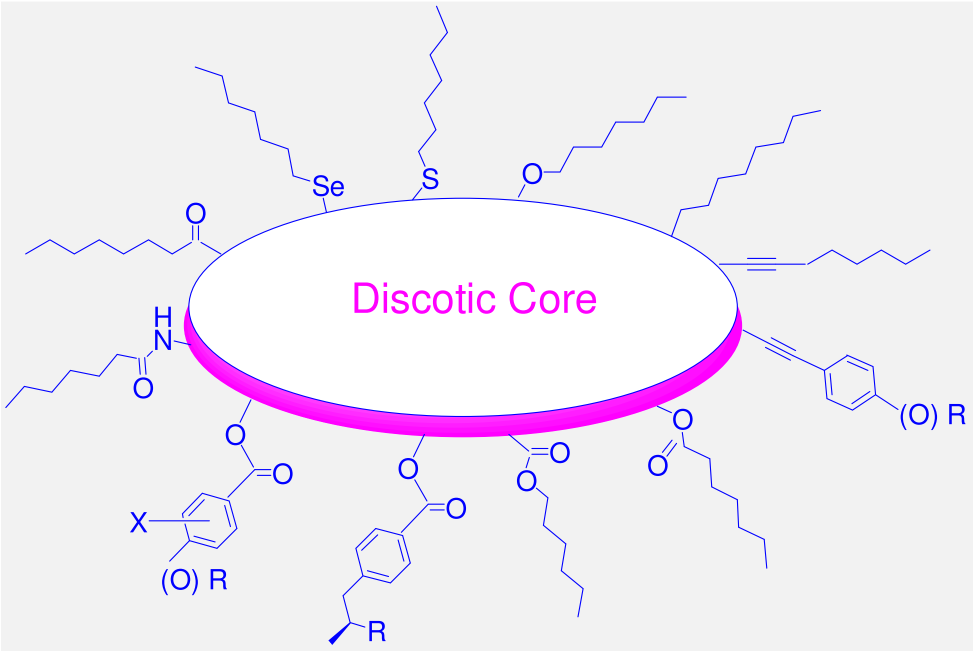

Figure 26. General template of discotic liquid crystals.

By tailoring the shape, size and nature of the central core as well as the type of the attached side chains, compounds with different ability to self-organize into different mesophase morphologies can be obtained.

1.8. Chemistry of discotic liquid crystals

The most common method for the synthesis of discotic mesogenic materials is the assemblage of a rigid aromatic core which is then followed by nucleophilic or electrophilic aromatic substitutions around the conjugated core. General methods for their synthesis have recently been described in the *Handbook of Liquid Crystals*.[20a,31f] The preparation and purification of discotic compounds is generally difficult and tedious, primarily because of incomplete substitution of all the functional groups. Partial substitution of polyfunctional groups gives a mixture of structurally similar products having almost indistinguishable R_f values on a chromatographic plate and their separation is often difficult even by HPLC. Reaction can be pushed towards completion by taking excess of the reagent and/or longer reaction time. Secondly, in many cases, excess of the reagent or longer reaction time may cause side reactions resulting in a complex mixture of products. Finding optimum reaction conditions is the central part of the synthesis. Highly regio-selective and high yielding methods are now available particularly for the synthesis of triphenylene based discotic liquid crystals. 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, benzpyrone, oxatruxene, thiatruxene, benzotrisfuran, tricycloquinazoline, bispyran, hexaazotriphenylene, pyrillium salt, coroneneimide, triazine, tetrathiofulvalene,

(d) **metallomesogens** such as, β-diketone complexes, triketone complexes, dioxime complexes, tetraketone complexes, dithiolene complexes, benzalimine complexes, tetrabenzo-tetraazacyclohexadecine, dibenzaldiimine 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.

There are various methods for the synthesis of a range of discotic mesogens. Those are as follows; Flexible aliphatic chains can be appended 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. Polyfunctionalized core or directly mesomorphic materials have been generated by direct electrophilic aromatic substitution of polycyclic aromatic hydrocarbons in some cases. These examples are also not common because of regioselectivity problem. 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, because of sensitivity of many functional groups towards drastic reaction conditions, this choice is also restricted. The most widespread method to prepare DLCs involves construction of the core with protected functional groups (ether or ester), followed by cleavage of the protecting groups and finally grafting pendant chains. Efforts have been made to avoid the protection and deprotection steps in case of discotics with ether linkage. The long flexible aliphatic chains necessary to induce mesogenity were attached in the starting molecules and these then transformed directly to liquid crystalline materials using classical or modern synthetic methods. A number of alkyl substituted DLCs have also been synthesized by this method.

1.9. Characterization of discotic liquid crystal phases

The mesomorphic behavior of discotic liquid crystals is frequently examined by using differential scanning calorimetry (DSC), polarized optical microscopy (POM), wide-angle X-ray scattering (WAXS) and solid-state NMR.[20c] DSC is used to determine the temperatures of phase transitions and enthalpy changes related to each transition. The fluid character of mesophases and in many cases the characteristics textures are easily monitored by POM. The supramolecular organization and the corresponding packing parameters in each phase can be studied in detail by X-ray diffraction, in particular by 2D-WAXS of macroscopically orientated samples. This technique allows one to obtain a detailed insight into the intra and intercolumnar order. It is possible to determine not only the intercolumnar spacings but also to obtain information about the arrangement of discs within the columns, such as tilting and helical packing and also to provide much more dipper insight into the various microstructures adopted in the self assembly of the mesogens in the mesophase. Solid state NMR is mainly used for the study of the molecular dynamics.[32] This technique allows one to derive independent conclusions about the rotation of the core or about peripheral mobility of side chains. Moreover, because of the different electronic environments of the aromatic protons in the intracolumnar packing, the tilted arrangement of the discs in the solid phase can be determined as well. In general it is necessary to apply all these complementary experimental methods in order to obtain a clear, comprehensive and unambiguous picture of the bulk behavior of discotic mesogens. The phase transition from crystalline to the mesophase is accompanied by a significant increase in molecular dynamics such as the rotation of the discs around the columnar axis, lateral and axial displacement of the discs etc. The centers of gravity of the molecules in the columnar LC mesophases are positioned along the column axis and columns can slide relative to each other giving rise to the fluid character of the phase. It is important to stress that the molecular fluctuations in the liquid crystalline mesophases support the self-healing of structural defects and hence enhance the charge carrier transport along the columnar stacks.

1.10. Why discotics ?

Potent π-π interaction of polyaromatic cores is the main reason for the formation of columnar mesophases is majority of discotic liquid crystals. The core-core (intracolumnar) separation in a columnar mesophase is usually of the order of 3.6 Å so that there is considerable overlap of π-orbitals. As flexible long aliphatic chains surround the core, the inter-columnar distance is usually 20-40 Å, depending on the lateral chain length and number of lateral chains. The number of aliphatic chains around the discotic core varies from 3-8 to produce columnar mesophase. Therefore, interactions between neighboring molecules within the same column would be much stronger than interactions between neighboring columns. As a result, charge migration in these materials is anticipated to be quasi-one-dimensional. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than the same observed in the perpendicular direction. Thus the columns may be described as *molecular wires* or more appropriately *molecular cables* since

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[32] (a) I. Fischbach, F. Ebert, H. W. Spiess, I. Schnell, *ChemPhysChem,* 5, 895, **2004**; (b) M. Lehmann, I. Fischback, H. W. Spiess and H. Meier. *J. Am. Chem. Soc.*, 126, 772, **2004**.

the conducting aromatic cores are surrounded by insulating aliphatic chains in the columnar phase as shown in the Figure 27.

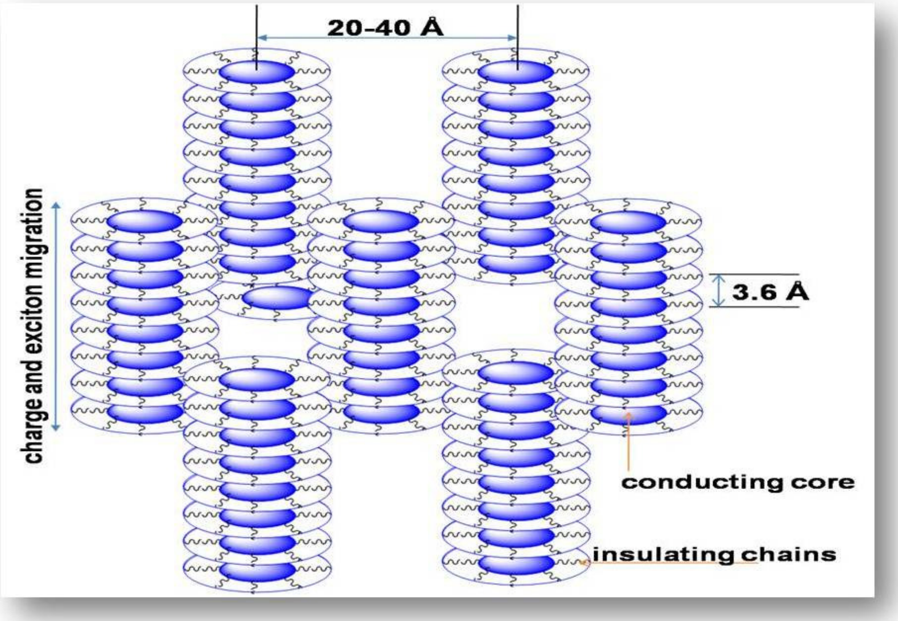

Figure 27. Energy and charge migration in discotic liquid crystals.

1.11. Discotics as semiconductor: molecular concepts, one-dimensional electrical & photoconductivity

As expressed previously, 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 hold intrinsic charges.[20h] To investigate the charge transport along the columns, charges were created by doping or through photogeneration. Vaughan *et al.*[33] doped hexahexylthiotriphenylene (HHTT) **4** with iodine, which increased the conductivity by several orders of magnitude. Boden *et al*. used hexapentyloxytriphenylene **5** with $AlCl_3$, which transformed the insulating

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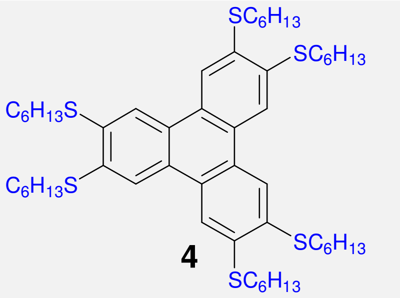
[33] G. B. M. Vaughan, P. A. Heiney, J. P. McCauley, Jr., A. B. Smith III, *Phys. Rev. B* 46, 2787, **1992**.

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 undoubtedly signifies the high anisotropy of conduction in the columnar phase and the columnar phase can be considered as a practical quasi one-dimensional conductor along the columnar axis.



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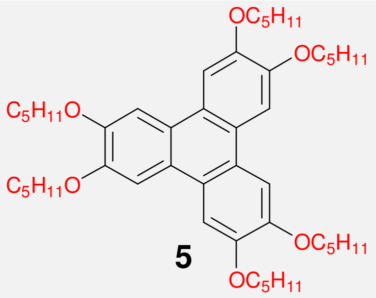

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The other discotic liquid crystalline materials which have been subjected to the measurement of charge carrier mobility are Porphyrins, Phthalocyanines, Hexabenzocoronenes (HBC) Hexaazatrinaphthylene (HATNA) etc.[34] Carrier mobility as high as 1.0 cm^2/Vs is observed in the crystalline phase and in the liquid crystalline phase the value reaches to 0.38 cm^2/Vs in HBCs. The highest values for Porphyrins and Phthalocyanines in the liquid crystalline phases are 0.07 and 0.08 cm^2/Vs respectively and for HATNA the highest is 0.20 cm^2/Vs. With an increase in core size the carrier mobilities increase but for very large core sizes containing 60 or more carbon atoms in the aromatic core the value decreases because of large amplitude of fluctuation disorder.

For studying charge transport (CT) in discotic liquid crystals the time-of-flight (TOF) technique, which relies on charge photoregeneration, is most widely used.[34] Charges are created by light irradiation of discotic films in a typical sandwich-cell configuration as shown in Figure 28. 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

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[34] (a) J. M. Warman, A. M. van de Craats, *Mol. Cryst. Liq. Cryst.*, 396, 41, **2003**; (b) H. Eichhorn, *J. Porphyrins Phthalocyanines*, 4, 88, **2000**; (c) J. M. Warman, M. P. de Hass, G. Dicker, F. C. Grozema, J. Piris and M. G. Debeje, *Chem. Mater.*, 16, 4600, **2004**; (d) J. M. Warman, J. E. Kroeze, P. G. Schouten, and A. M. van de Craats, *J. Porphyrins Phthalocyanines*, 7, 342, **2003.**

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.

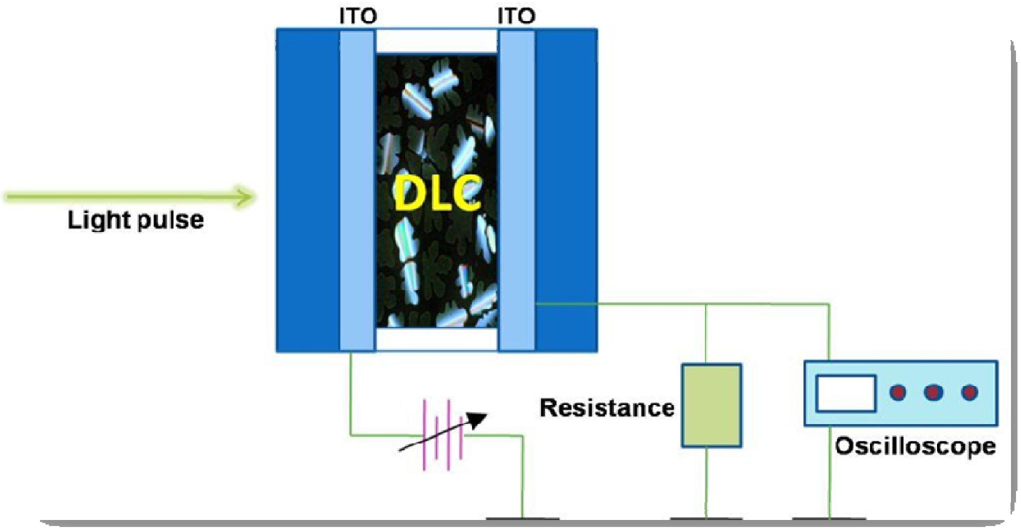


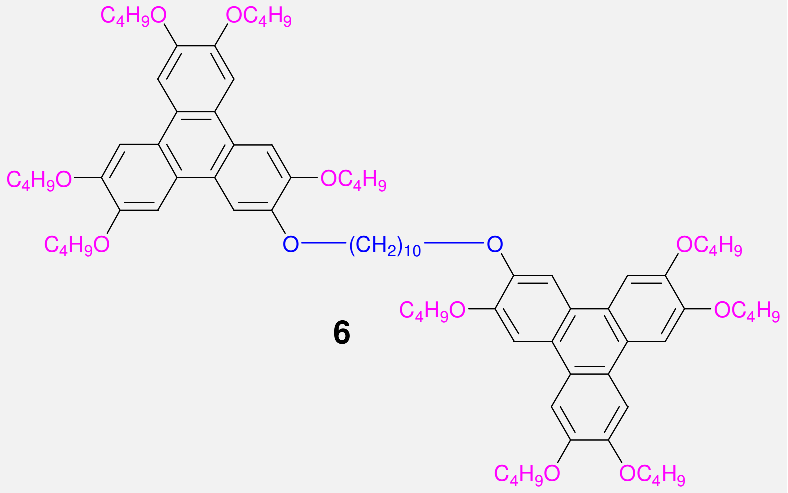
Figure 28. Set up of the TOF experiment.

The time that these charges take to travel between the electrodes allows the mobility μ to be recorded. In fact, μ 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 drawback of the TOF method is that, monodomains with the columns aligned perpendicular to the electrodes (homeotropic alignment) are necessary. Any defect in the path has a strong outcome 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 explore by the TOF method.

Transport in triphenylenes was modeled by Haarer and co-workers.[35] Despite the remarkable results in terms of mobility because of the high degree of order in the columns, the transport appears not to be described by a band-like 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 correctly aligned, the pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC) has been employed.[34] 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 homogeneous 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

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[35] I. Bleyl, C. Erdelen, H. –W. Schmodt, D. Harrer, *Philos. Mag. B*, 79, 463, **1999**.

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 29.

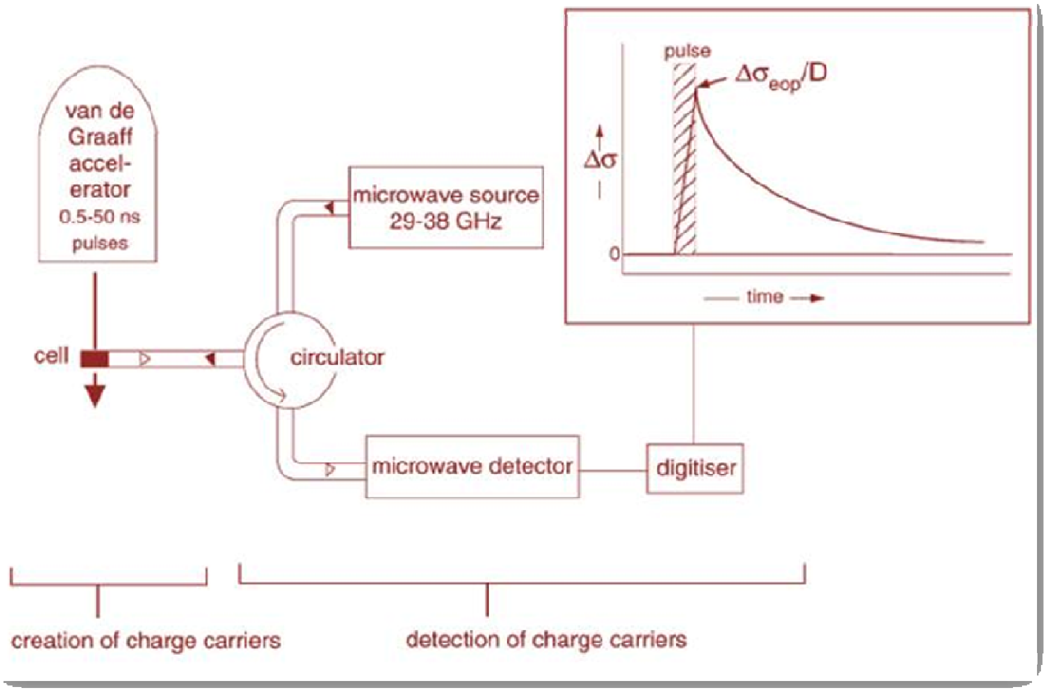

Figure 29. Set up of PR-TRMC experiment (Reproduced from Warman, J. M. and van de Craats, A.M., *Mol. Cryst. Liq. Cryst.*, 396, 41, 2003).

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

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

where μ_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[36] was confirmed by van de Craats *et al*. using electrode-less pulse-radiolysis time resolved microwave conductivity method.[37]

The PR-TRMC technique has its limitations, for example, the individual contributions of the positive and negative charge carriers cannot be separately determined but it is a method that can be readily applied to any material irrespective of its morphology or optical properties, thus allowing a large number and variety of materials to be inspected and compared. Because of the low electric field strength (<100 V/cm) and the ultra high frequency (ca. 30 GHz) the random diffusional motion of charge carriers is only slightly perturbed. This together with the nanosecond time response of detection, ensures that the mobilities determined are effectively zero-field, trap-free values, characteristic of the most well-organised (highest mobility) domains within a sample.[34]

Discotic mesophases do not exhibit perfect order; as a result charge carriers tend to localize to an extent that depends on the degree of order. Thus a coherent band like description is inappropriate and a phonon-assisted hopping picture is more appropriate as a starting point to describe charge transport in discotics. In this case, the charge carriers are localized on single molecules and jump from disc to disc along the stacks. The frequency of charge hopping between two adjacent discs can be approximately estimated on the basis of semi classical Marcus theory.[38] For such a self-exchanging electron (hole) transfer process the rate of charge hopping depends on two main parameters: the *reorganization energy* and the intermolecular *transfer integral*. High transfer rates and hence high charge mobility, requires small values for the former and large values for the latter.[39] The reorganization energy is sum of two terms: the inner reorganization energy of the molecule and reorganization energy of the surrounding medium. For discotic liquid crystals in the bulk state the inner reorganization energy plays a significant role since there is no other surrounding medium. The reorganization

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[36] (a) M. C. Nuss, P. M. Mankiewich, M. L. O'Malley, E. H. Westerwick, P. B. Littlewood, *Phy. Rev. Lett.*, 66, 3305, **1991**; (b) D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, D. Haarer, *Nature*, 371, 141, **1994**.

[37] A. M. van de Craats, J. M. Warman, M. P. de Hass, D. Adam, J. Simmerer, D. Haarer, P. Schuhmacher, *Adv. Mater*., 8, 823, **1996**.

[38] R. A. Marcus, *Rev. Mod. Phys*., 65, 599, **1993.**

[39] V. Lemaur, D. A. da Silva Filho, V. Coropceanu, M. Lehmann, Y. Geerts, J. Piris, M. G.. Debije, A. M. van de Craats, K. Senthilkumar, L. D. A. Siebbeles, J. M. Warman, J. –L. Bredas, J. Cornil, *J. Am. Chem. Soc*., 126, 3271, **2004**.

energy reflects the geometric changes in the molecule when going from the neutral to ionized (ionic or radical) state or vice versa. The intermolecular transfer integral characterizes the strength of the electronic coupling between the molecules; the absolute values can be estimated to a good approximation as half the electronic splitting of the HOMO (LUMO) levels for holes (electrons) in a dimer made of two neutral molecules. For discotics the transfer integral has been shown to be very susceptible to the relative position and orientation of the neighboring molecules. Most favorable for charge transport is the co-facial orientation. 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.[34]

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 morphology and transition temperatures all play significant role to have a good discotic semiconductor.

1.12. Structure property relationship; phase behavior and transition temperatures

It is well understood that, discotic mesogens are made up of central rigid core surrounded by flexible alkyl chains. Mesomorphic as well as many properties of DLCs are affected by a balance between rigid and flexible part. An increase in rigid aromatic core causes an increase in transition temperatures. On the other hand increase in number, length or branching of flexible aliphatic chains results in decrease in transition temperature. A proper balance between rigid core and flexible alkyl chain determines the existence and structure of liquid crystalline phase. The replacement of normal alkyl chains by branched alkyl chains in hexaalkynylbenzene[40] and tricycloquinazoline[41] produces room temperature discotic nematic and columnar phases, respectively. In hexaalkyl-HBC series of discotic mesogens **7**, the

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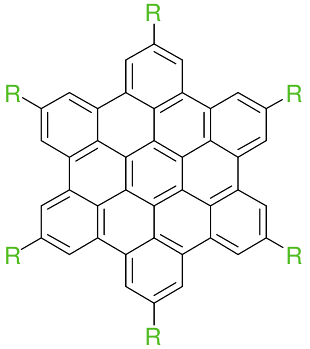
[40] S. Kumar, S. K. Varshney, *Angew. Chem.*, 112, 3270, **2000**.

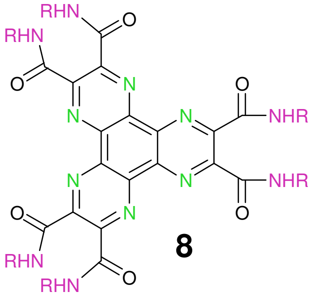
[41] S. Kumar, D. S. Shankar Rao, S. K. Prasad, *J. Mater. Chem.*, 9, 2751, **1999.**

compound **7a** forms mesophases only above 100 ºC with a very high clearing point.[42] On the other hand compound **7b** with longer and more sterically substituents is liquid crystalline at room temperature. Octa-alkoxycarbonyl phthalocyanines with branched chains are reported to be room-temperature liquid crystals in literature.[43] It is obvious that introduction of branching produce steric hindrance within the chains and thus has an important influence on the phase behavior of the discotic molecules. Similar behavior was observed for the family of tetra-alkoxy phthalocyanines.[44] It clearly appears that the steric hindrance introduced by branching of the side chains has a significant influence on the phase behavior of discotic mesogens. However, the role of stereoheterogeneity due to branched chains is not negligible, as demonstrated for the HBC derivative **7c**. The temperature of Cr-to-mesophase transition for the stereohomogeneous (all-*S*)-**7c** is 15 ºC higher than that of **7c** bearing the racemic side chains and comprising multiple diastereoisomers.[45] Compounds displaying LC properties at all temperatures, while rare, are of considerable interest because of their ready processibility and self-healing properties at room temperature.



7a-c

(a); R = $CH_2CH(CH_2CH_3)C_4H_9$
(b); R = $CH_2CH(C_6H_{13})C_8H_{17}$
(c); R = $CH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)CH_3$



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Connecting groups are also important for thermotropic behavior. Changing the oxygen atom of hexahexyloxytriphenylene to sulphur atom results in the formation of a highly ordered helical columnar phase. When connecting groups are involved in some specific non-covalent intermolecular interactions, such as intermolecular hydrogen bonding for example in

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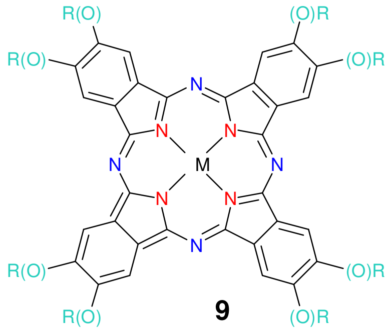
[42] W. Pisula, M. Kastler, D. Wasserfallen, T. Pakula, K. Mullen, *J. Am. Chem. Soc*., 12, 8074, **2004**.

[43] S. Sergeyev, E. Pouzet, O. Debever, J. Levin, J. Gierschner, J. Cornil, R. Gomez-Aspe, Y. H. Geerts, *J. Mater. Chem*., 17, 1777, **2007**.

[44] (a) J. F. van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte, W. Drenth, J. Aerts, R. Visser, S. J. Picken, *Liq. Cryst*., 6, 577, **1989**; (b) K. Ohta, L. Jacquemin, C. Sirlin, L. Bosio, J. Simon, *New J. Chem*., 12, 751, **1988**; (c) D. Guillon, A. Skoulios, C. Piechocki, J. Simon, P. Weber, *Mol. Cryst. Liq. Cryst*., 100, 275, **1983**.

[45] A. Fechtenkotter, N. Tchebotareva, M. Watson, K. Mullen, *Tetrahedron*, 57, 3769, **2001**.

case of hexamide derivative of hexaazatriphenylene **8**, a inter-disc distance as short as 0.318 nm *i.e.* smaller than the Van der Walls radii of carbon atoms in PAH has been observed.[46] It has been proposed that increasing the size of conjugated core would reduce the core-core separation and hence enhance the charge mobility.[47] Extraordinary thermal and photochemical stability of phthalocyanines **9** (M = Metal) and porphyrin **10** discotics in the field of dyes and pigments have also been reported.[48]



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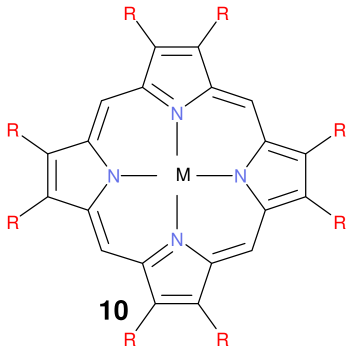

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1.13. Alignment of discotic liquid crystals

The key physical process for the applications of DLCs in electronic devices is the formation, transport and recombination of electrical charges. In particular the mobility of charge carriers in solid state materials is one of the most important parameters determining device performance. The electronic mobility not only depends on the intrinsic electronic properties of the materials but also on the macroscopic order of the molecules in thin and thick films.[20,34] Therefore the control of their supramolecular order over macroscopic dimensions is a key issue to obtain optimized performance. The control of the molecular arrangement on/between the surfaces is also an important issue during the discotic material processing. For field effect transistors, an edge-on organization (Figure 30b) of the discotics in uniaxially oriented columns is required. In this arrangement, charge carriers drift through the columns from the source electrode to the drain electrode, under controlled gate voltage. In contrast, the large mono-domain face-on arrangement (Figure 30a) of the discs leads to a

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[46] R. J. Gearba, M. Lehmann, J. Levin, D. A. Ivanov, M. H. J. Koch, J. Barbera, M. G. Debije, J. Piris, Y. H. Geerts, *Adv. Mater.*, 15, 1614, **2003.**

[47] S. Kumar, J. J. Naidu, D. S. Shankar Rao, *J. Mater. Chem.*, 12, 1335, **2002**.

[48] C. -Y. Liu, A. J. Bard, *Acc. Chem. Res.*, 32, 235, **1999.**

homeotropic alignment which allows faster charge transport between the top and bottom electrodes and favors the photovoltaic and light emitting performance.

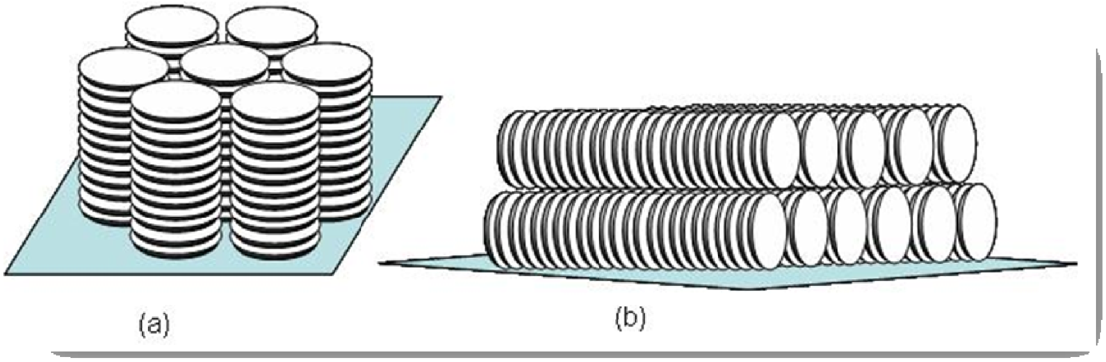

Figure 30. (a) Homeotropic and (b) planar alignment of discotic liquid crystals.

1.14. Applications of discotic liquid crystals

1.14.1. Discotic liquid crystals in display devices

In addition of having miscellaneous applications such as, solvents in chemical reactions, temperature sensing, in spectroscopy, in holography, in chromatography, etc., liquid crystals are above all accepted by their ubiquitous presence in electro-optical display devices such as watches, calculators, telephones, personal organizers, laptop computers, flat panel television, etc.[49] The liquid crystal layer in the foremost display devices (twisted nematic, TN and super twisted nematic STN) is exclusively the calamitic liquid crystal (composed of rod-shaped molecules). Narrow and non-homogeneous viewing cone are the main disadvantages of current liquid crystal displays. Numerous development efforts have been focused to achieve higher quality wide viewing angle LCDs. These efforts are the multidomain technique,[50] the introduction of an optical compensator to reduce the amount of light leakage in the dark state,[51] the application of an electric field parallel to the plane of the substrates,[52]

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[49] Bahadur, B. (ed.). *Liquid Crystals: Applications and Uses*, Vols. 1–3, World Scientific, Singapore, **1990.**
[50] T. Sugiyama, T. Hashimoto, K. Katoh, Y. Iimura, S. Kobayashi, *Jpn. J. Appl. Phys*., 34, 2396, **1995.**
[51] H. Mori, *Jpn. J. Appl. Phys*., 36, 1068, **1997.**

the so-called ‘amorphous’ twisted nematic liquid crystals,[53] 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. Recently, discotic nematic liquid crystals have been found to be useful as an alternative of calamitic nematic liquid crystals to overcome this problem.[54] Hexaalkynylbenzene based discotic nematic liquid crystal has been employed in LCD. This device exhibits wide and symmetrical viewing angle and no reversal of contrast ratio in any direction.[54] Nevertheless, the device is extremely slow because of the very high viscosity of discotic nematic liquid crystal.

Compensation films having negative birefringence can be employed to overcome 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. Discotic mesogens have opposite optical anisotropy as compared to calamitic liquid crystals. They are the most promising materials for negative birefringence films. The optical anisotropy of disk-like molecules compensates the optical anisotropy of calamitic mesogens so, the optical behavior of the combination becomes equivalent to isotropic. Because of this reason linearly polarized light passing through the combination will not suffer from any distortion and hence viewing angle dependence will be neglected.

Recently, triphenylene-based discotic cross linked polymer has been used in an optical phase-compensation film, which was commercialized by Fuji Photo Films.[55] 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.

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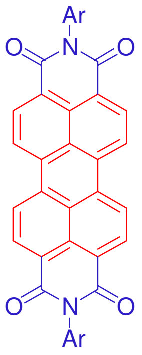
[52] M. Oh-e, M. Yoneya, K. Kondo, *J. Appl. Phys.*, 82, 528, **1997**.
[53] Y. Toko, T. Sugiyama, K. Katoh, Y. Iimura, S. Kobayashi, *J. Appl. Phys.*, 74, 2071, **1993**.
[54] S. Chandrasekhar, S. Krishna Prasad, G. G. Nair, D. S. Shankar Rao, S. Kumar, M. Manikam, *Euro Display ’99, The 19th International Display Research Conference Late-news papers* (Berlin-Germany), pp.9, **1999**.
[55] (a) K. Kawata, *Chem. Rec.*, 2, 59, **2002**; (b) H. Mori, Y. Ioh, Y. Nishiura, T. Nakamura, Y. Shinagawa, *Jpn. J. Appl. Phys.*, 36, 143, **1997**; (c) F. Leenhouts, *Jpn. J. Appl. Phys.*, 39, L741, **2000.**

1.14.2. Discotics in Xerographic processes

Xerography is a technique used in recent photocopier machines. This is a dry procedure for copying by applying heat. A commercially available photocopier or laser scanner consists of a rotating cylinder that is covered with a photoconducting surface. This surface moves over the original document with simultaneous irradiation.[56] 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 (dry ink) 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.

For a compound to be a good candidate for xerographic applications, it has to meet several prerequisites along with its photo conducting property. In order 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. Therefore, 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.



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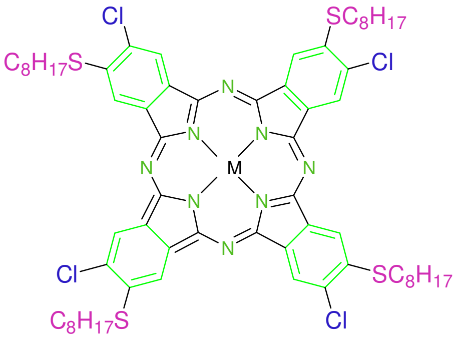

12

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[56] K. –Y. Law, *Chem. Rev.*, 93, 449, **1993.**

Perylene bisimide derivative **11** absorbs in visible region. These types of materials are particularly well examined for photoconducting devices that operate in the visible region.[57] Alternatively, phthalocyanine derivatives have a strong absorption both in the visible and near infrared region. Eichhorn *et al.* discovered that mixtures containing amphotropic phthalocyanines such as **12** with a different substitution pattern, show much higher inter- and intracolumnar order than the single compounds.[58] Additionally, macroscopic homeotropic alignment was simply achieved by mechanical shearing, thus providing an easy way to orient the material for laser printers.

1.14.3. Discotics in holographic optical data storage

Cis-trans or E/Z isomerization around double bond in dye molecules (eg. azobenzenes, stilbenes) is the main working principle in optical data storage. The imprinting with two linear polarized laser-light beams causes a reorientation in 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 the writing laser beam, can be read out by a reading laser beam.

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[57] F. Wurthner, C. Thalacker, S. Diele, C. Tschierske, *Chem. Eur. J.*, 7, 2245, **2001**.

[58] H. Eichhorn, D. W. Bruce, D. Wohrle, *Adv. Mater.*, 10, 419, **1998**.

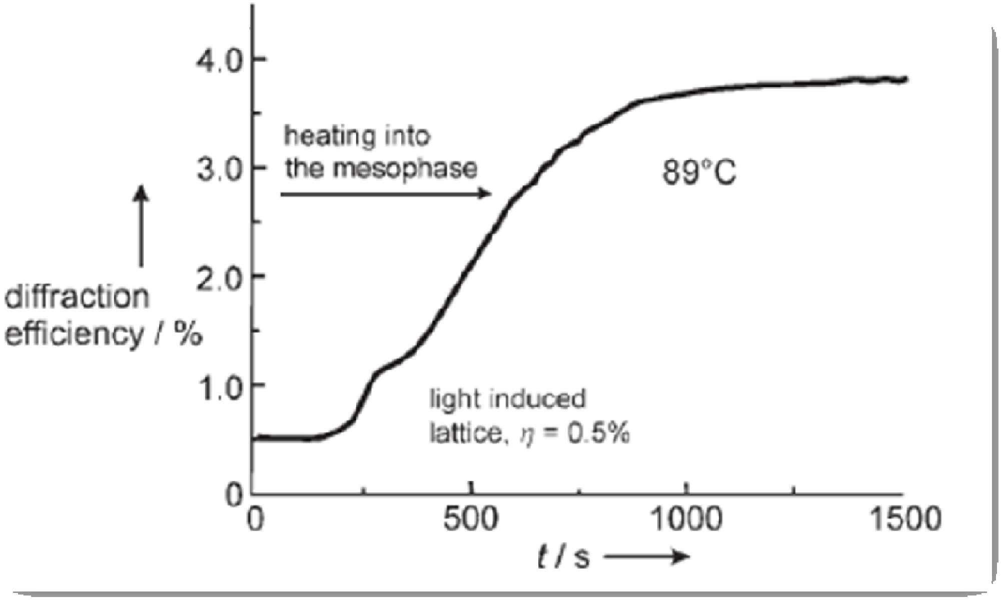

Figure 31. Thermal gain effect of the diffraction efficiency (Reproduced from A. Stracke, J. H. Wendroff, D. Janietz, S. Mahlstedt, *Adv. Mater*., 11, 667, **1999**).

Stracke *et al*. reported columnar donor-rod-acceptor triple compound **13**, having an azobenzene moiety as the chromophoric group in middle of the molecule.[59] The stability of the columnar nematic phase was improved by combination of strong electron-acceptor TNF with the electron donor pentakis(phenylalkynyl)benzene. The storage process occurs via the isomerization of functional azo group in a transparent film. As can be seen in the Figure 31, 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%. Stracke *et al*. found that trisazomelamine **14** is not only suitable for the light-induced isomerization of the azobenzene units to give rise to photo-reorientation, but also causes surface modulations.[60] The gain effect of these surface modulations was achieved by thermal treatment.

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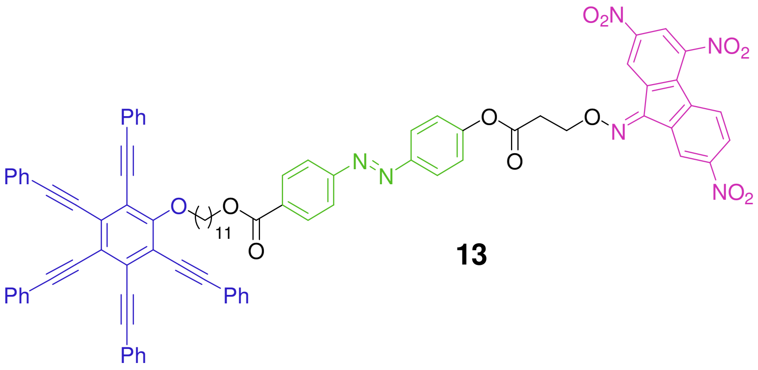
[59] (a) D. Hertel, C. D. Muller, K. Meerholz, *Chem. Unserer Zeit*., 39, 336, **2005**. (b) A. Stracke, J. H. Wendroff, D. Janietz, S. Mahlstedt, *Adv. Mater*., 11, 667, **1999**.

[60] A. Stracke, J. H. Wendroff, D. Goldmann, D. Janietz, B. Stiller, *Adv. Mater*., 12, 282, **2000**.



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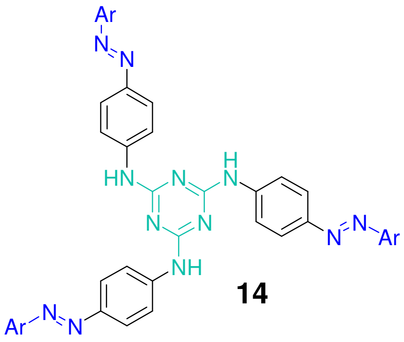

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1.14.4. Discotics in organic light-emitting diodes

Light-emitting diodes (LEDs) are mainly semiconducting light sources, which are used as indicator lamps in many devices, and are now employed for lighting. When electrons are enforced to combine holes, they release energy in the form of photon. This effect is called electroluminescence, which is the fundamental principle of LEDs. In case of organic light emitting diodes (OLEDs), semiconducting organic molecules are used as light source. The presence of conjugated π-bonds/electrons is essential prerequisite for an organic material to be a good candidate for OLEDs.

A single-layer OLED consists of a layer of organic material, placed between two electrodes, the transparent anode (ITO) and metallic cathode,[61] while a multilayer device (Figure 32) 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. Because of electrostatic attraction between electron and hole, closer to the emissive layer, they recombine to form 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.

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[61] M. O'Neill, S. M. Kelly, *Adv. Mater.*, 15, 1135, **2003.**

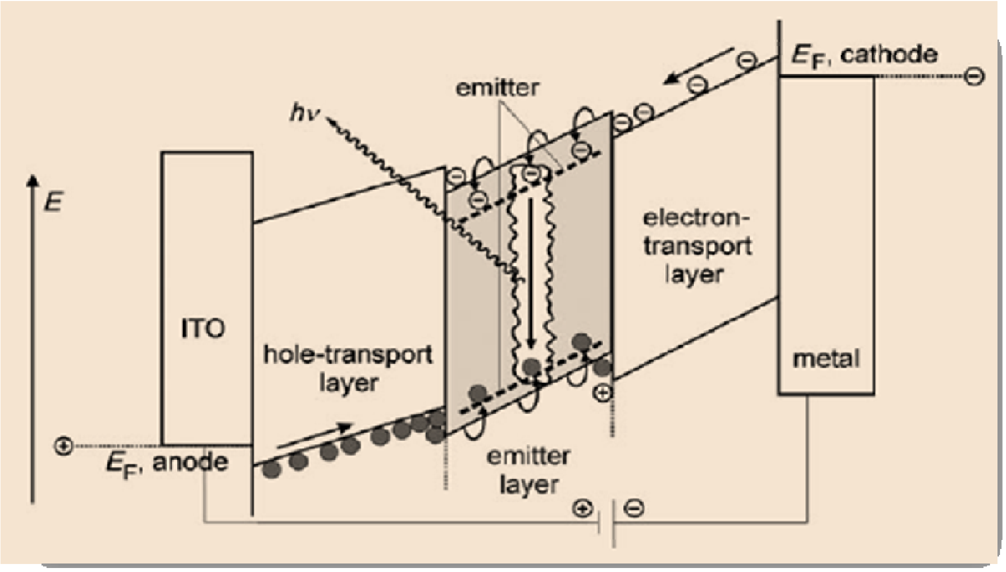
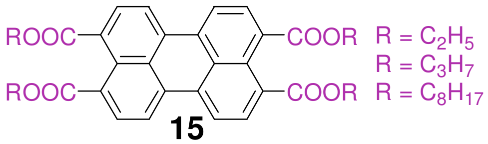


Figure 32. Energy diagram of multilayered diode.



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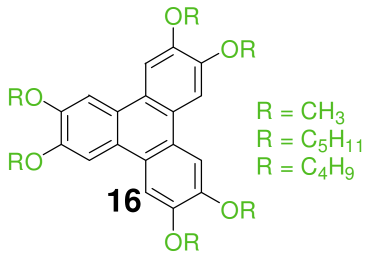

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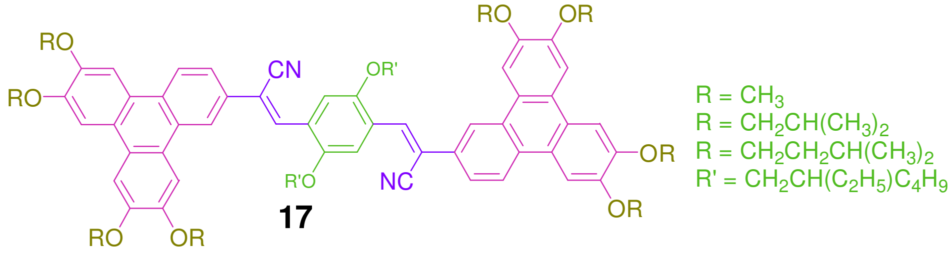

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Columnar liquid crystals of perylene derivatives have been successfully employed in OLED applications. The research groups of Kitzerow and Bock reported an all-columnar bilayer OLED containing fluorescent discotic 3,4,9,10-tetra(alkoxycarbonyl)perylenes **15** as the luminescent electron transport layer combined with columnar hexaalkoxytriphenylenes **16** as the hole transport layer.[62] A particular benefit of columnar LCs in such devices is their ability to expel defects in an annealing process leading to increased lifetimes. Freudenmann *et al*. obtained and examined the mesomorphic and electroluminescent properties of triphenylene based dimer **17** in which two tetraalkoxytriphenylene disks were linked to central benzene ring through a double bond having cyano group *i.e.* both the triphenylene rings were in conjugation with each other through central *p*-phenylene vinyl group.[63] As compared to monomeric triphenylene systems these dimers exhibited strong bathochromic shift of more than 250 nm along with bright orange to red electroluminescence which fulfills the requirements for the fabrication of OLEDs using these materials as emissive layer. Alibert-Fouet *et al*. have reported the electroluminescence property of different but closely related derivatives of perylene based molecules (differing only in substitution pattern).[64] Selective electron transporting or predominantly hole transporting property can be induced by having difference in substituents around perylene based skeletons.

1.14.5. Discotics in organic field–effect transistors

Columnar liquid crystalline arrangement of discotic molecules is a reasonable candidate for organic field effect transistors (OFETs) because of its self assembling behavior and also because of the fact that these materials provide anisotropic charge-carrier transport along the columnar channel. A typical OFET device is represented in Figure 33.

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[62] (a) S. Benning, H. –S. Kitzerow, H. Bock, M. –F. Achard, *Liq. Cryst.*, 27, 901, **2000**; (b) T. Hassheider, S. A. Benning, H. –S. Kitzerow, M. –F. Achard, H. Bock, *Angew. Chem.*, 113, 2119, **2001**; (c) I. Seguy, P. Destruel, H. Bock, *Synth. Met.*, 111, 15, **2000**.

[63] R. Freudenmann, B. Behnisch, M. Hanack, *J. Mater. Chem.*, 11, 1618, **2001**.

[64] S. Alibert-Fouet, S. Dardel, H. Bock, M. Oukachmih, S. Archambeau, I. Seguy, P. Jolinat, P. Destrue, *ChemPhysChem*, 4, 983, **2003**.

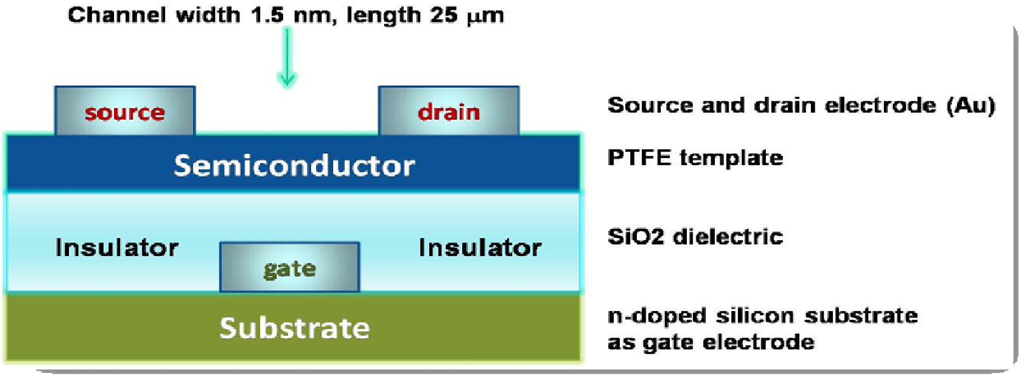

Figure 33. Schematic representation of an organic field effect transistor.

In case of p-type semiconductors, the gate voltage plays effective role for the conduction of charge between the source and the drain electrodes. 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.[20g] Pisula el al**.** reported the use of zone casting method for the fabrication of long range oriented hexadodecyl substituted hexabenzocoronene **18** films in order to achieve highly ordered active layers in field effect transistors (FETs).[65] The overall performance of the FET device constructed using this method was about one order of magnitude greater than the earlier reported values.

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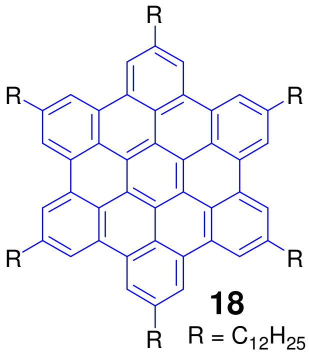
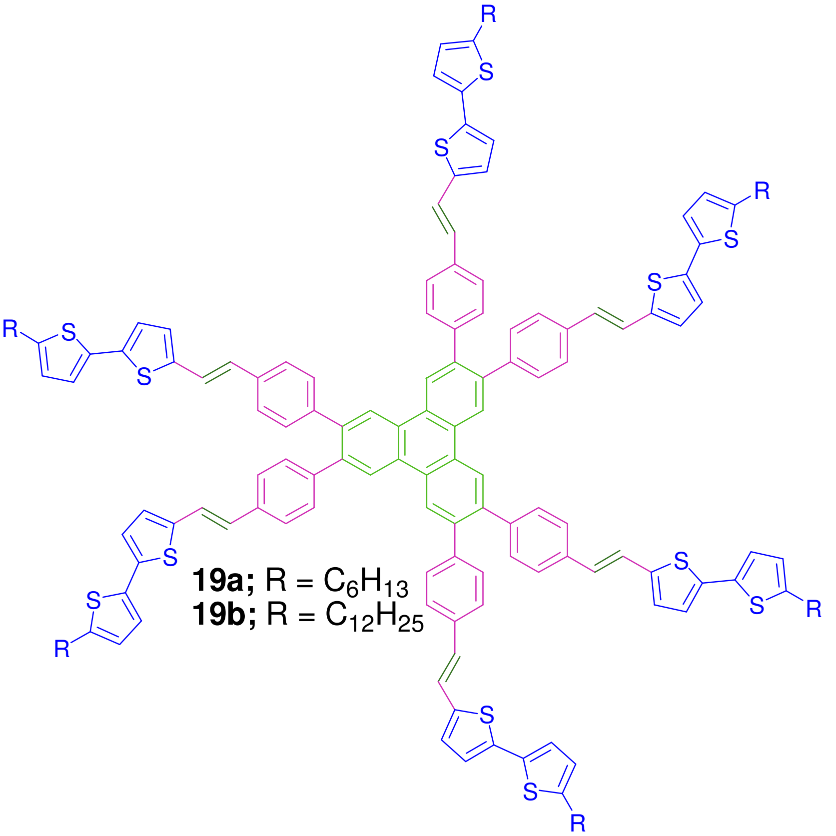
[65] W. Pisula, A. Menon, M. Stepputat, I. Lieberwirth, U. Kolb, A. Tracz, H. Sirringhaus, T. Pakula and K. Mullen, *Adv. Mater*, 17, 684, **2005**.



18 R = $C_{12}H_{25}$



19a; R = C_6H_{13}
19b; R = $C_{12}H_{25}$

The first example of OFETs, based on discotic triphenylene derivatives appeared recently in 2009, when Hoang *et al*. prepared a series of two discotic mesogens **19** in which π-conjugation of triphenylene aromatic ring was extended with phenyl, alkene and thiophene.[66] As compared to the formerly reported triphenylene discotics these materials had better crystallization property and lower band gap energy. Lower band gap energy of these compounds certifies these materials as a strong candidate for OFET fabrication.

1.14.6. Discotic liquid crystals as photosynthetic light harvesting materials

The most important and essential phenomenon for the conversion of light (solar cells) to electric or chemical energy (photosynthesis) are the light-stimulated generation, separation

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[66] M. H. Hoang, M. J. Cho, K. H. Kim, M. Y. Cho, J. –s. Joo, D. H. Choi, *Thin Solid Films*, 518, 501, **2009.**

and migration of electrons and holes. Photosynthesis (conversion of light to chemical energy) is the basis of life on earth. Three steps are involved in photovoltaic effect;

(i) the absorption of solar radiation and the photogeneration of electrons and holes,
(ii) the charge separation,
(iii) transport of electrons and holes for collection at the cathode and anode, respectively.

The energy-level diagram for a typical blended device under short-circuit conditions is represented in Figure 34.[67]

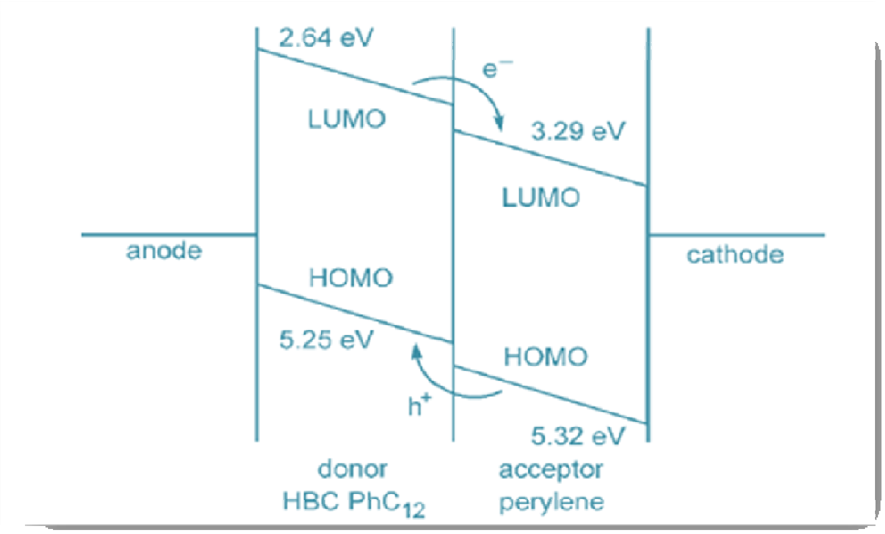

Figure 34. Energy level diagram showing charge separation and transport to electrodes.

A well-organized consequence of all the above actions is crucial for effective photovoltaic process. Frequent charge recombination should be avoided and to be kept at a minimum. Absorption is achieved by exciton formation. Charge separation is the result of ionization of an exciton over a distributed interface between electron-donating and electron-

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[67] (a) S. Kumar, *Curr. Sci.*, 82, 256, **2002**; (b) N. R. Armstrong, B. Kippelen, D. F. O'Brien, S. M. Marder, J. –L. Bredas, *Proceedings-NCPV Program Review Meeting, Lakewood*, 328, **2001.**

accepting species. The separated carriers float to external electrodes in the built in field introduced by dissimilar electrodes. In order to optimize photoinduced charge separation, the photosensitivity of semiconducting organic materials can be enhanced by blending donor and acceptor molecules.

Fullerene (C_{60}) and its derivatives were blended with semiconducting polymers in order to improve carrier collection efficiency and energy conversion efficiency of polymer photovoltaic cells. As compared to device made of pure conjugated polymer, composite film of semiconducting polymer (donor) and fullerene (acceptor) displayed efficiencies which were improved by more than two orders of magnitude.[68] The efficiency was further improved by blending a soluble methanofullerene into the conjugated polymer film. Molecular morphology was proved to be effective for efficient power conversion of organic photovoltaic devices based on a blend of conjugated polymer with methanofullerene. Shaheen *et al*.[69] has engineered photovoltaic devices having power conversion efficiency of 2.5%. Zinc based mesomorphic porphyrin material has been used for atypical photovoltaic behavior in symmetrical cells containing indium-tin oxide (ITO) electrodes.[70] Liquid crystalline property of this compound was used to fill the cells and to promote macroscopic order, which on cooling, forms polycrystalline films. Photocurrent was measured which was directly proportional to intensity of the incident light and was independent on the wavelength of light. High performance in optoelectronic device has been achieved by the utilization of intermolecular and mesoscopic ordering of HBC-based discotic liquid crystals in perylene-HBC system.[71] Perylene dye (electron transporting layer) and discotic liquid crystalline hexabenzocoronene (hole transporting layer) has been employed to assemble this p/n type photovoltaic solar cell. The maximum achieved energy conversion efficiency was 1.95% at 490 nm. In an influential contribution, Mullen and coworkers[72] have discovered that thin film prepared by self-organization of a mixture of columnar LC and crystalline-conjugated

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[68] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science*, 270, 1789, **1995**.

[69] S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, J. C. Hummelen, *Appl. Phys. Lett.*, 78, 841, **2001**.

[70] B. A. Gregg, M. A. Fox, A. J. Bard, *J. Phys. Chem*., 94, 1586, **1990**.

[71] L. Schmidt-Mende, A. Fechtenkotter, K. Mullen, E. Moons, R. H. Friend, J. D. Mackenzie, *Science*, 293, 1119, **2001**.

[72] (a) J. Jung, A. Rybak, A. Slazak, S. Bialecki, P. Miskiewicz, I. Glowacki, J. Ulanski, S. Rosselli, A. Yasuda, G. Nelles, Z. Tomovic, M. D. Watson and K. Mullen, *Synth. Met.*, 155, 150, **2005**; (b) J. P. Schmidtke, R. H. Friend, M. Kastler and K. Mullen, *J. Chem. Phys*., 124, 174704, **2006**.

materials showed a photovoltaic response with higher external quantum efficiency at 490 nm. Surface potential decay technique was applied to resolve photogeneration quantum yield in layers of HBC-based discotic liquid crystals (hole transport material), perylene derivative (electron transport material) and of their mixtures.[72a] A very weak photogeneration in the visible range was perceived in case of pure DLC, in pure perylene derivative, photogeneration of only negative mobile charge carriers occurred. However, a mixture of above two materials resulted in cooperative effect of photogeneration of both positive and negative mobile charge carriers. The formation of vertically segregated non-mesomorphic electron-accepting perylene bismide and the columnar phase forming hole accepting hexa-peribenzocoronene with a high interfacial surface was shown by AFM and optical polarizing microscopy (Figure 35).[72b] Efficient photoinduced charge transfer between the two molecules and an effective charge transport through the layered structure was responsible for the high efficiency. Hirota *et al.* have proved on the basis of electrochemical measurement that mesomorphic triheptanoyl decacyclene derivative functions as electron acceptor material in polymer photovoltaic devices.[73] Electron acceptor property of this material was again verified by photo-induced electron transfer on combining with a p-type semiconducting polymer. The energy conversion efficiency was increased to double after annealing at liquid crystalline transition temperature. Transparent films of discotic liquid crystalline hexaalkyl substituted superphenalene has been used as electrode in organic solar cells.[74] Li *et al.* has reported synthesis and mesomorphism of light harvesting discotic porphyrins.[75] A blend of porphyrin with C_{60} derivative has been used to fabricate bulk-heterojunction solar cell. Homeotropic alignment of these porphyrin-based compounds has been proved with the help of synchrotron X-ray diffraction, which is enormously important for photovoltaic applications. Very recently, for the first time, Thiebaut *et al.* has discussed about heterojunction based on two immiscible but liquid crystalline materials.[76] Perylene derivative was employed as electron acceptor, while tetraester of pyrene acted as a role of electron donor. Both the compounds were one after the other deposited (on bare or ITO-covered glass slides or on silicon wafers with their oxide) by spin-coating method. The bilayer was then heated up to ~150 °C. Thermal annealing of this bilayer

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[73] K. Hirota , K. Tajima, K. Hashimoto, *Synth. Met.*, 157, 290, **2007.**
[74] X. Wang, L. Zhi, N. Tsao, Z. Tomovic, J. Li, K. Mullen, *Angew. Chem. Int. Ed.*, 47, 2990, **2008.**
[75] L. Li, S. –W. Kang, J. Harden, Q. Sun, X. Zhou, L. Dai, A. Jakli, S. Kumar, Q. Li, *Liq. Cryst.*, 35, 3, 233, **2008.**
[76] O. Thiebaut, H. Bock, E. Grelet, *J. Am. Chem. Soc.*, 132, 6886, **2010.**

resulted in the formation of an oriented bilayer heterojunction with macroscopic self-assembly of two discotic liquid crystals. Hexasubstituted triphenylene based discotic liquid crystal has been employed as additive for poly(3-hexylthiophene):[6,6]-phenyl-C_{61}-butyric acid methyl ester based bulk-heterojunction organic photovoltaics.[77] An increment in average power conversion efficiency was observed after incorporating 3 wt % of triphenylene based discotic liquid crystals in both conditions (pre-annealing and post-annealing).

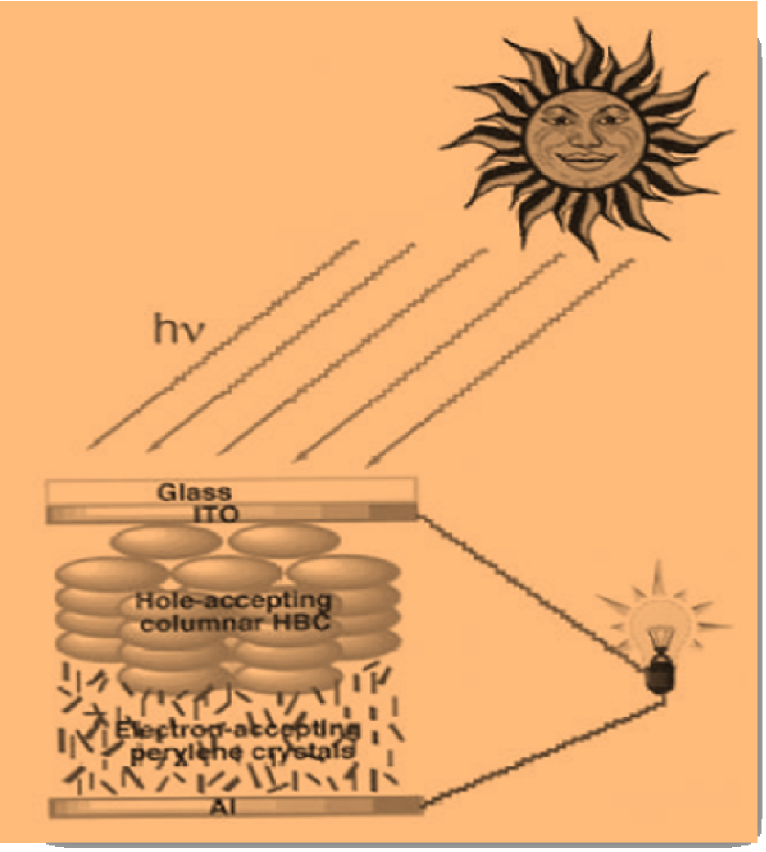

Figure 35. Schematic diagram of a discotic-based photovoltaic solar cell (Reproduced from S. Kumar, *Curr. Sci.*, 82, 256, **2002**).

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[77] S. Jeong, Y. Kwon, B. –D. Choi, H. Ade, Y. S. Han, *Appl. Phys. Lett.*, 96, 183305, **2010**.

1.14.7. Discotics as gas sensors

Extra degrees of freedom can be expected near the free surface of liquid crystals where the absence of interacting neighbors should give rise to new and exciting ordering phenomena. The absence of neighbors on one side actually promotes crystallization in case of smectic liquid crystals. On the other hand the surface of discotics has more degrees of freedom which encourage disorder in the stacks. On application of a lateral field to a homeotropic film, conduction is expected to be dominated by that of the disordered surface since in the bulk state it would be perpendicular to the columns. Efforts have been made to examine the conductivity of discotic liquid crystal surface films using the interdigitated electrode geometry by filling the cells with homeotropically aligned discotic liquid crystals. If it is possible to measure the effect of exposure to gas on the fluctuation and thermodynamics of liquid crystal surfaces, the response could be simply and cheaply measured by looking at the conductance change giving a simple gas sensor. Structural changes do not require strong electronic coupling or charge transfer reactions to surface states, so sensor built on these principles could also work for detecting weakly interacting non-polar gases. A change in the order of the surface is produced by the adsorbate which results in change in the polarisation response or conductivity values. This is reasonably easy to measure. Additionally, charge and uncharged impurities remain near the free surface of the liquid crystals due to self-organized molecular dynamics of mesophase. Discotic liquid crystals can therefore be used as very sensitive gas sensors for both polar and non-polar molecules.[78]

NO_2 sensing by L. B. films of phthalocyanines, NO_2 sensing properties of discotic liquid crystalline phthalocyanines, and NO_2 sensing properties of films of crowned phthalocyanines has been investigated by Wright *et al*.[79a] Quick response and reversal to NO_2 at room temperature has been demonstrated by semiconducting films of crown-ether substituted metal-less phthalocyanines.[79b] Very recently, nanowires of columnar discotic liquid crystals have been employed to construct an electronic nose device, which is able to

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[78] (a) J. Clements, N. Boden, T. Gibson, R. Chandler, J. Hulbert and E. A. Ruck-Keene, *Sens. Actuators*, 47, 37, **1998**; (b) N. Boden, R. J. Bushby and A. N. Cammidge, *J. Am. Chem. Soc.*, 117, 924, **1995.**

[79] (a) Wright, *Chem. Funct. Dyes, Proc. Int. Symp.*, 2nd, 207, **1993**; (b) J. D. Wright, P. Roisin, G. Patricia Rigby, R. J. M. Nolte, M. J. Cook, S. C. Thorpe, *Sensors and Actuators B: Chemical*, 13, 1-3, 276, **1993.**

determine the composition and concentration of volatile organic compdounds in a sample with very high sensitivity.[80]

1.14.8. Discotics as precursors of novel carbonaceous nanostructures

In bulk state disk-like molecules stack one upon the other to form ordered columnar superstructures. Because of high stability of columns discotic liquid crystals are considered as precursors toward novel carbon nanostructures. It is assumed that pyrolysis under restricted conditions may uphold the order existing in the mesophase during formation of the carbonaceous materials. Novel carbon nano and microstructures are the result of pyrolysis of well-defined discotic molecules in the bulk state. Carbonization of the discotic mesogens in their columnar phase led to the formation of carbon nanotubes (CNTs) without metal catalysts and with desired graphene layer orientations. The temperatures are much lower than the normally used graphitization temperature (2000-3000 ^{o}C). Recently pyrolysis of graphitic hexabenzocoronene (HBC) in porous alumina membranes has been used as a template method for the uniform fabrication of carbon nanotubes. The preorganized ordered columnar superstructures can be converted into nanotubes by carbonization under a controlled heating process. Mullen *et al.* have produced nanotubes from thermotropic discotic liquid crystals.[81] A unique approach to self-assembled graphitic nanotubes from an amphiphilic hexabenzocoronene is demonstrated. The structure of nanotubes consists of graphitic wall created from numerous molecular graphene sheets stacked parallel to the longer axis of the tube. It has helically rolled-up bilayer tapes composed of π-stacked HBC units, where the inner and outer HBC layers are connected by interdigitation of the hydrophobic alkyl chains while the hydrophilic ethylene oxide chains are located on both sides of the tubular wall. The π-stacked HBC units supply a charge carrier transport pathway. Nanotubes with a range of

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interesting physical and chemical properties can be obtained by appropriate chemical functionalization of the amphiphilic HBCs.[82]

1.15. Non-conventional liquid crystals

Non-conventional liquid crystals are those materials whose structure and property deviate from ordinary or conventional LCs. One can get materials of interesting properties by combining more than one contrasting or different functionalities within a molecule. A lot of combinations are possible *e.g.* thermotropic/lyotropic, hydrophilic/hydrophobic, non-polar/polar, hydrocarbon/fluorocarbon, rigid/flexible, disc/rod, electron donor/electron acceptor, mesogenic/dimeric, mesogenic/oligomeric, mesogenic/polymeric etc.[83] Non-conventional mesogens bridge the gap between entirely different chemical or physical properties.

Mesomorphic compounds of the conventional types were employed for practical applications in early years. Later on the synthetic efforts of most scientific groups started focusing on the development of new materials of unconventional types.[84] Apart from their prospective applications, non-conventional liquid crystals are in particular crucial for the theoretical understanding of the mesomorphic phenomenon. The detailed study of novel non-conventional materials may result in knowledge about novel liquid crystalline phases and deeper insights in the driving forces of their self-organisation. It is well known that anisotropic molecular shape and space filling play vital role in self assembly of mesogens. However, nanoscale segregation of irreconcilable molecular parts *i.e.* micro segregation has also been realized to play an important role in mesogenic self assembly, resulting in to new mesophase morphologies.[83,85] On account of their astonishing self-assembly into complex soft materials, non-conventional liquid crystals are of massive interest at present.

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On the basis of molecular structure and functional group present in the mesogen, low molar mass liquid crystals can be categorized in to two classes' *i.e.* anisotropic nonamphiphilic molecules and amphiphilic molecules. The aggregation and assembly of the first class of molecules (calamitic, discotic and banana) results in the formation of thermotropic liquid crystals.[86] Amphiphilic molecules can form thermotropic liquid crystals in absence of any other component, while in presence of solvent (in most cases water) they lead to lyotropic mesomorphism.[87] The above types of mesogens can either be integrated in the main chain of polymer (main chain liquid crystalline polymer) or can be linked as side chain to a polymer backbone (side chain liquid crystalline polymer) to give high molar mass non-conventional liquid crystals.[88]

One can have molecules of intermediate shape and size (polycatenar) between disk-like and rod-like to bridge the gap between discotic and calamitic mesogens. In pure condition amphiphilic mesogens show a variety of liquid crystalline phases. Addition of appropriate solvent affects the mesomorphic property and results in the formation of lyotropic liquid crystals. Water loving hysrophilic and hydrophobic elements of amphiphilic molecules have tendency to segregate in to separate microdomains. Because of having chemical linkage between the parts of opposite behavior the phase separation does not happen on macroscopic level. The separation of chemically different segments results in formation of interfaces separating two or more than two domains.

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