

Discotic Liquid Crystals for Opto-Electronic Applications^{†,‡}

Bilal R. Kaafarani*

Department of Chemistry, American University of Beirut, Beirut 1107-2020, Lebanon

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Discotic liquid crystals (DLCs) have been exploited in opto-electronic devices for their advantageous properties including long-range self-assembling, self-healing, ease of processing, solubility in a variety of organic solvents, and high charge-carrier mobilities along the stacking axis. An overview of DLCs and their charge-carrier mobilities, theoretical modeling, alignment, and device applications is addressed herein. The effects of alignment on charge-carrier properties of DLCs are discussed. Particular attention is devoted to processing techniques that achieve suitable alignment of DLCs for efficient electronic devices such as zone-casting, zone melting, Langmuir–Blodgett deposition, solution-casting on preoriented polytetrafluoroethylene (PTFE), surface treatment, IR irradiation, application of a magnetic field, use of sacrificial layers, use of blends, application of an electric field, and others.

1. Introduction

Since their discovery by Chandrasekhar¹ in 1977, discotic liquid crystals (DLCs) have attracted the attention of many research groups. Serious efforts have been made to exploit DLCs in organic electronic devices. A typical discotic mesogen generally includes a central aromatic core functionalized with three to eight flexible chains. The two main types of mesophases DLCs form are nematic and columnar. In the nematic phase, discs have orientational order while in the columnar phase the discs pile into columns, see Figure 1, and are generally considered most useful for organic electronics applications.² A comprehensive review of the chemical aspects of DLCs was reported by S. Kumar,³ wherein the existence of six different columnar DLC phases: hexagonal columnar, rectangular columnar, columnar oblique, columnar plastic, helical, and columnar lamellar, are reported.³ On the other hand, indenes and pseudoazulenes were the first reported thermotropic DLCs that do not bear flexible chains.⁴ Moreover, DLCs with shape-persistent macrocyclic cores were also reported.⁵

Several review articles have addressed the design and important features of DLCs.^{2,3,5–19} In consideration of the increased interest in DLCs, this review not only focuses on the specific aspects of DLCs for potential use in opto-electronic devices but also highlights recent progress in the development of DLCs of promising performance in electronic devices. Scrupulous attention is devoted to alignment techniques of DLCs that improve such performance. Moreover, additional developments posterior

to the 2006–2007 seminal reviews by Geerts,¹⁴ Kumar,³ and Laschat¹³ are particularly highlighted.

DLCs may form efficient $\pi-\pi$ columnar stacks that produce high charge-carrier mobilities, the magnitude of which is fundamentally determined by the degree of order and $\pi-\pi$ molecular orbital overlap within the columnar stacks. Charge transport within the stack, i.e., in a one-dimensional manner, is therefore built into the design scheme. The ease of film formation is another key feature of smart materials for organic-based electronic and optoelectronic devices. Because some DLCs have a predisposition to self-assemble into columnar stacks, ease of processability is inherent, although orientation of the columnar stacks in the direction required for the device function can be challenging. Furthermore, because of their liquid-character, DLCs possess the capacity to self-heal structural defects such as grain boundaries and consequently have the ability of attaining several square millimeters large single domains of several micrometers film thickness.¹⁴ The advantageous properties of DLCs, therefore, include long-range self-assembling (order), self-healing (dynamics), ease of processing, high solubility in organic solvents, and high charge-carrier mobility.

The driving force for formation of columnar mesophases has been postulated to be shape anisotropy,^{4,20,21} microsegregation between flexible chains and rigid core,²² and core–core van der Walls attractions.² The core–core distance along the column direction is usually in the order of 3.5 Å whereas the distances between the centers of cores in adjacent columns is dictated by the size of the mesogens and is typically of the order of 20–40 Å. Flexible alkyl chains around the cores substantially insulate the column from the neighboring column. Conductivity is, therefore, anticipated to be significantly higher along the column axis; therefore, the DLC columns are sometimes referred to as quasi-one-dimensional

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*To whom correspondence should be addressed. E-mail: bilal.kaafarani@aub.edu.lb.

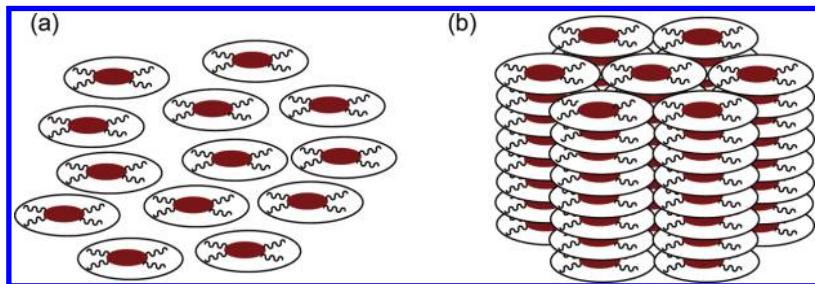


Figure 1. Schematic representations of (a) the discotic nematic and (b) the columnar phase.² Modified version of Figure 1 from the article: Kumar, S. *Liq. Cryst.* **2004**, *31*, 1037–1059. Reprinted by permission of the publisher (Taylor & Francis Group, <http://www.informaworld.com>).

conducting wires.² On the other hand, calamatic liquid-crystals exhibit two-dimensional charge transport analogous to that observed in pentacene and oligothiophene, which demonstrate herringbone packing.^{14,23} Moreover, the orbital overlap in DLCs is much larger than that of calamatics.²⁴

The structure of the conjugated core of the discoid materials govern their molecular-level electronic properties, whereas the change in the peripheral flexible chains and aromatic cores control their self-assembly in both solution and bulk phase; the overall electronic properties of the materials, therefore, depend on both core and substituent structure.²⁵ The supramolecular assembly of DLC materials can also be strongly affected by the processing method.²⁵

In this review, a short overview of DLCs, their charge mobilities, and their mesophase engineering is first addressed. This is followed by highlighting a particular aspect associated with DLCs, i.e., alignment. The different processing techniques to achieve suitable alignment for an efficient device (OFET, OLED, OPV) are discussed.

2. Overview of DLCs

Discotic liquid crystals have been reported with a large number of discoid cores including benzene,^{26–30} pyridine,³¹ triazine,^{28,30,32} triphenylene,^{2,12} diazatriphenylene,³³ hexaazatriphenylene,³⁴ pyrene,³⁵ dibenz[*g,p*]chrysene,^{36,37} dibenzo-naphthacene,³⁸ tristriazolotriazine,³⁹ rufigallol,^{40–42} truxene,⁴³ triazatruxene,⁴⁴ or triindole,⁴⁵ tricycloquinazoline,^{46,47} hexaazatruxene (HATNA),^{48,49} perylene,⁵⁰ coronene diimide,⁵¹ phthalocyanine (Pc),^{52–56} porphyrin,^{57,58} quinoxalinophenanthrophenazine (TQPP),^{59,60} pyrazinopyrazinoquinoxalinophenanthrophenazine (TPPQPP),⁶⁰ dodecaazatrianthracene (DATAN),⁶⁰ and hexa-*peri*-hexabenzocoronene (HBC),⁶¹ see Figure 2. Müllen's group has recently reported DLCs of large aromatic polycyclic hydrocarbons cores paving the road to stimulating research developments in the field of organic electronics such as the synthesis of thin graphene layers, see Figure 2.^{62,63}

The nature of the discoid core and flexible chains affect the self-assembly of DLCs.²⁵ Some examples are herein briefly illustrated. The substitution of hexaazatriphenylene with six alkyl or alkylthio groups does not result in columnar mesophases,³⁴ but the addition of H-bonding side groups induces mesophase behavior.⁶⁴ Recently, Armstrong's group reported the self-organization of a phthalocyanine derivative into columnar aggregates, which were attributed

to the H-bonding interactions between the benzamide groups of the side chains, see Figure 3.⁶⁵ Computational simulations attribute such behavior to the intermolecular electrostatic potential among the discoid cores; this is a crucial factor in stabilizing/destabilizing the columnar phases.⁶⁶ The self-assembly of HBC derivatives was further enhanced upon the introduction of H-bonding side groups to the core.⁶⁷ The change in position of functional group (carboxylic acid, methyl carboxylate, or nitro group) in a series of dibenzophenazine DLCs from the “top” to the “side” of the aromatic core strongly affects their stability and mesophases.⁶⁸ The effect of symmetry on the stability of columnar phase in dibenzophenazine and triphenylene derivatives was also studied wherein the melting temperatures of less symmetrical DLCs were found to be lowered by a much larger degree than clearing temperatures.⁶⁹ On the other hand, the substitution of the discoid core with electron-withdrawing groups stabilize the mesophases and increase the fluorescence quantum yield.⁷⁰

3. Charge-Carrier Mobilities

The mobility of charge carriers in organic semiconducting materials may determine their suitability for use in electronic devices. In crystalline materials, the mobility is strongly influenced by the properties of the solid state. In comparison to amorphous materials, single crystals of high-purity of planar organic compounds (such as the acenes, i.e., anthracene, pentacene) show higher mobility due to their well-organized stacking behavior. While staggeringly high mobilities have been reported in single crystal-devices, the major drawbacks in this approach are both the cost and time-effort associated with the growth of single crystals. Workers generally target systems programmed to self-assemble under wet-processing conditions. The mobility ultimately controls the switching speed of the field-effect transistor, the intensity of the light emitting diode, and the separation of charges in photovoltaic cells.⁷¹

Different techniques and geometries have been used to measure the mobility of charge-carriers in DLC materials. These include the pulse radiolysis time-resolved microwave conductivity technique (PR-TRMC),^{72–78} time-of-flight (TOF),^{79–82} steady-state space charge-limited current (SCLC),^{83–86} and field-effect mobility.^{87–89} PR-TRMC determines the mobility of charge-carriers at the local level and is relatively insensitive to defects

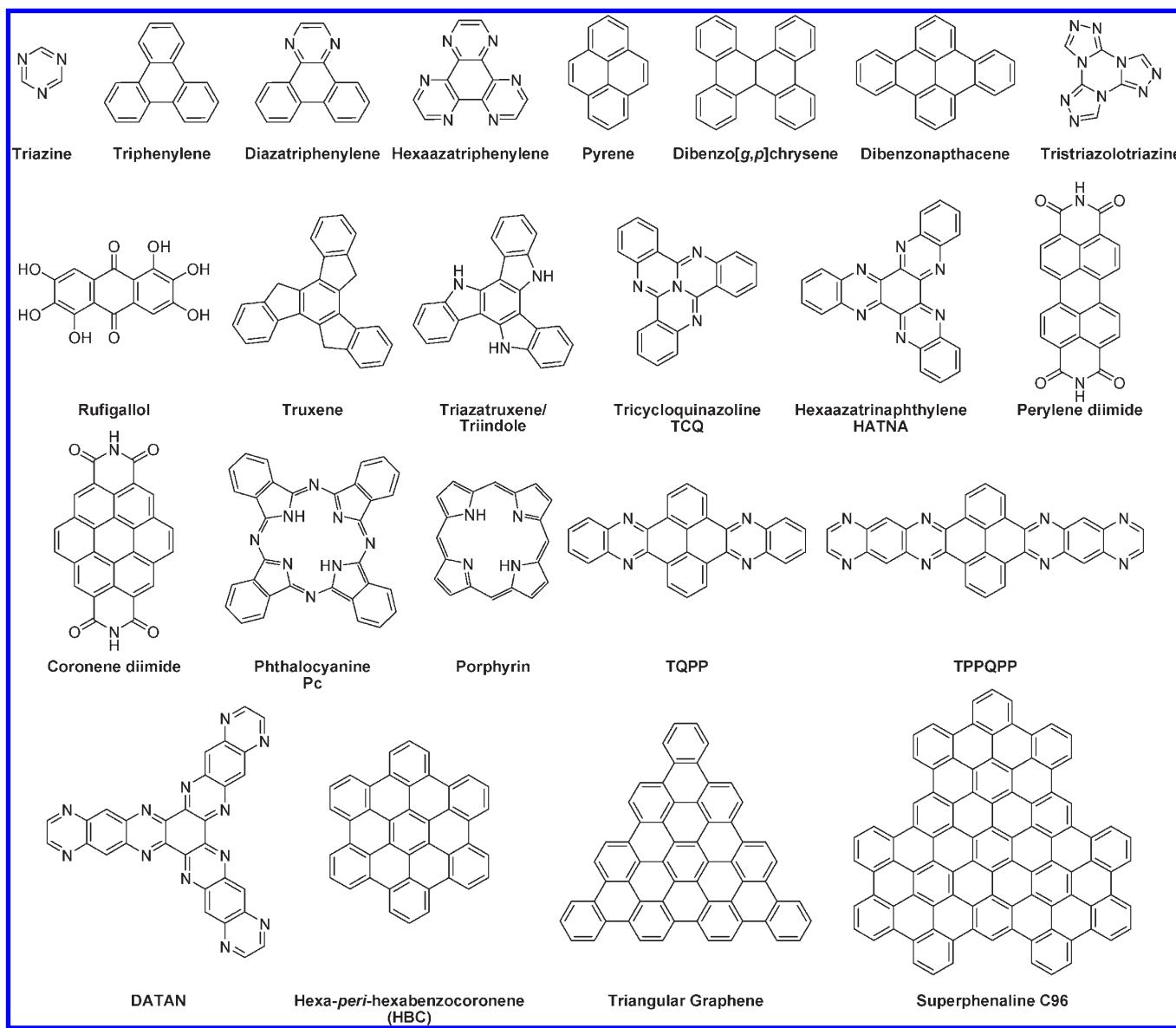


Figure 2. Selected aromatic cores used in discotic mesogens.

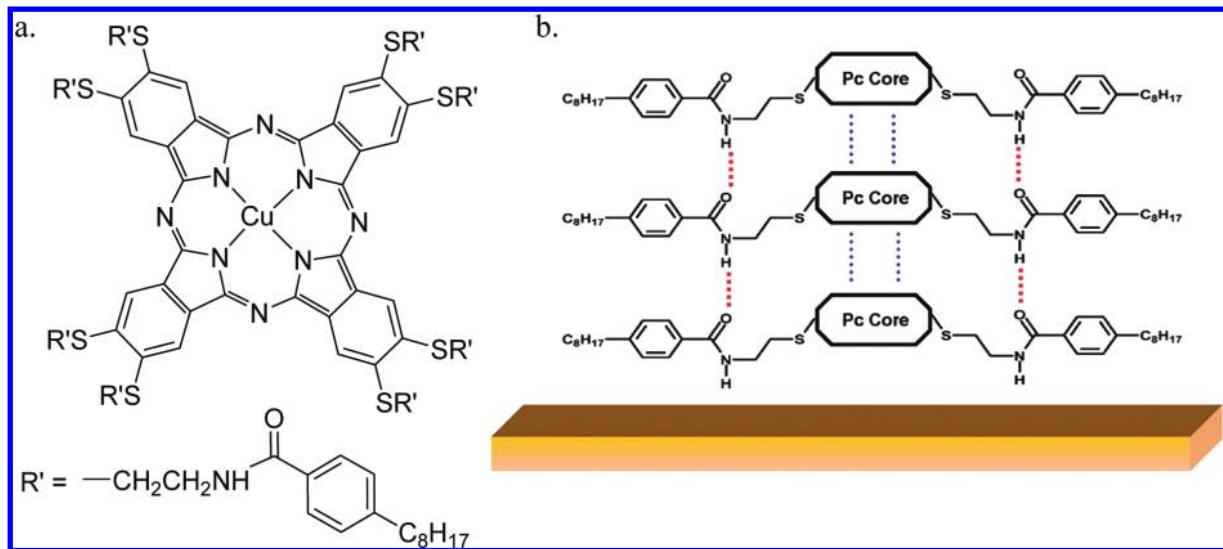


Figure 3. (a) Chemical structure of 2,3,9,10,16,17,23,24-octa(2-(4-octylbenzamide ethylsulfanyl) phthalocyanato copper(II)). (b) Schematic view of the aggregation of the molecules through hydrogen bondings exerted via amide units in the side chains, $\pi-\pi$ stacking between the aromatic rings, and S-S interactions.⁶⁵ Reprinted from ref 65. Copyright 2010 American Chemical Society.

(shows mobility within spatial limited domains) or, in the case of 1D conductors such as columnar DLCs, to the orientation(s) of the column axes. Thus, the method often gives values larger than those seen on the macroscopic scale; on the other hand, it can be regarded as giving a measure of what might be achievable if defect-free well-aligned samples could be obtained. In contrast, TOF and field-effect mobilities measure the macroscopic values and are strongly dependent on the presence of defects.¹⁵ SCLC mobility is calculated from the current–voltage characteristics of thin organic films sandwiched between injecting electrodes.⁹⁰ Recent review articles collected the TOF¹⁵ and PR-TRMC^{71,74} mobilities of selected discotics. Studies comparing mobilities using some of the aforementioned techniques were also reported.^{74,90}

van de Craats and Warman reported that a lower charge mobility in the columnar hexagonal phase (Col_h) was generally observed when alkyl chains are connected to the core via an oxygen atom as opposed to those for which the chains are coupled either directly (i.e., via methylene moiety) or via a sulfur.⁷⁵ The authors developed eq 1, based on previous PR-TRMC experimental results on triphenylene, porphyrin, coronene monoimide, azocarboxyldiimido-perylene, phthalocyanine, and *peri*-hexabenzocoronene, to predict the maximum mobility.

$$\sum \mu_{\max} \approx 3e^{-83/n} \text{ cm}^2/\text{V s} \quad (1)$$

where n is the total number of C, N, and O atoms in the core.⁷⁵

However, Müllen's group showed that mobility values predicted in eq 1 are limited to core sizes of $n < 40$ in HBC derivatives.⁷⁷ The relationship between core size, side chain length, and supramolecular organization of polycyclic aromatic hydrocarbon (PAH) cores, ranging from 42-carbon HBC core to a larger PAH core of 132-carbon atoms, was also investigated by the Müllen's group.⁹¹ The authors reported the lateral packing of PAH cores to increase with the molecular masses of the core, which form the columnar stacks, and of the side chains which fill the core periphery.⁹¹

In addition, the nature of the substituents linked to the discoid core may affect the solubility, supramolecular order, and thus the charge-carrier mobility of DLCs. Branching side chains closer to the point of attachment to the HBC results in a decrease of the isotropic temperature and the $\pi-\pi$ interaction between the discoids. However, the intramolecular order remains high at room temperature with charge-carrier mobility in the order of $0.73 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁹² Doping 2,3,6,7,11-(hexakis(hexyloxy)triphenylene (HAT6) with 1% (w/w) methylbenzenethiol-coated gold nanoparticles increased the conductivity in the Col_h phase by 3 orders of magnitude ($\sim 10^{-12}$ to $\sim 10^{-9} \Omega^{-1} \text{ cm}^{-1}$), as well as in the crystalline and isotropic phases.⁹³ The authors also reported a further 3–4 orders of magnitude ($\sim 10^{-6} \Omega^{-1} \text{ cm}^{-1}$) increase in conductivity upon the application of a field.⁹³ Such increase in conductivity is attributed to the formations of chains of gold nanoparticles.⁹³

Recently, a saturation hole mobility of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was reported in TQPP-[SC₁₂H₂₅]₄,⁸⁹ which showed

multiple crystalline phases, but no mesophase behavior was observed.⁹⁴ However, TQPP-[*t*-Bu]₂-[OR]₄ exhibited multiple DLC phases as observed by differential scanning calorimetry (DSC), polarized light microscopy (PLM), and wide-angle X-ray diffraction (WAXD); however, no charge-carrier mobilities have yet been reported on this series.⁶⁰

The TOF hole mobility of hexapentyloxytriphenylene in the Col_h phase was reported to be temperature and electric-field dependent with charge-carrier mobilities up to $2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 85 °C. Drift velocity was reported to be linearly dependent on the electric field below 10^{-5} V/cm reaching saturation at higher fields.⁹⁵ On the other hand, hexahexylthiotriphenylene exhibited both electron and hole mobility in the order of $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the helical Col_h phase at 45 °C.⁹⁶ A high SCLC hole mobility of $0.09 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was reported in 10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]-carbazole (indole) in its crystalline phase at 22 °C whereas the mobility in the Col_h phase decreased by a 3–4 factor.⁴⁵ The authors attributed the lower mobility in the Col_h phase to the higher motional freedom of the side chains and thus increasing the structural disorder in the columns.⁴⁵ An SCLC charge-carrier mobility as high as $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was reported for *N,N'*-di[3,4,5-tri(doceoxy)benzyl]-3,4,9,10-perylene diimide in its disordered columnar hexagonal phase (Col_{hd}) at room temperature.⁵⁰ The authors showed the strong dependence of SCLC mobilities on the morphology of the films which is itself affected by the processing technique.⁵⁰ TOF measurements of 1,3,6,8-tetrakis(3,4-dioctyloxyphenyl)pyrene indicated an ambipolar charge transport with mobility in the order of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in its Col_h phase at 60 °C.⁹⁷ In addition, the TOF carrier mobility of molecular aligned DLC Cu-phthalocyanine was as high as $2.60 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, whereas a metal-free phthalocyanine DLC exhibited an OFET hole mobility up to $2.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁵² The gelation of 2,3,6,7,10,11-hexa(hexyloxy)triphenylene with hydrogen-bonded fibrous aggregates increased the hole mobility from 4.5×10^{-4} to $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; the mobility was independent of temperature and electric field strength.⁹⁹ The columnar phase of a derivative of coronenedimide substituted with perfluoroctyl chains, obtained by cooling from isotropic phase, exhibited a remarkable SCLC electron mobility of $6.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at ambient temperature.⁵¹ The H-bonding in hexacarbox-amido hexaazatriphenylene (HAT-CONHC₁₂H₂₅] induced the columnar order in these discotics leading to an inter-disc distance of 3.18 Å with a $\sum \mu_{1D}$ values varying from $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at -80 °C to $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 200 °C.¹⁰⁰ The Col_h mesophase of coronenemonoimide showed a mobility of $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature; this value increased gradually to $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ just below the clearing temperature of 160 °C.¹⁰¹

Recently, Müllen's group reported the synthesis of a triangularly shaped polyaromatic hydrocarbon, see Figure 4, of 3-fold symmetry leading to a helical packing structure and 60° rotation angle and therefore forming the optimal local arrangement for charge transport.

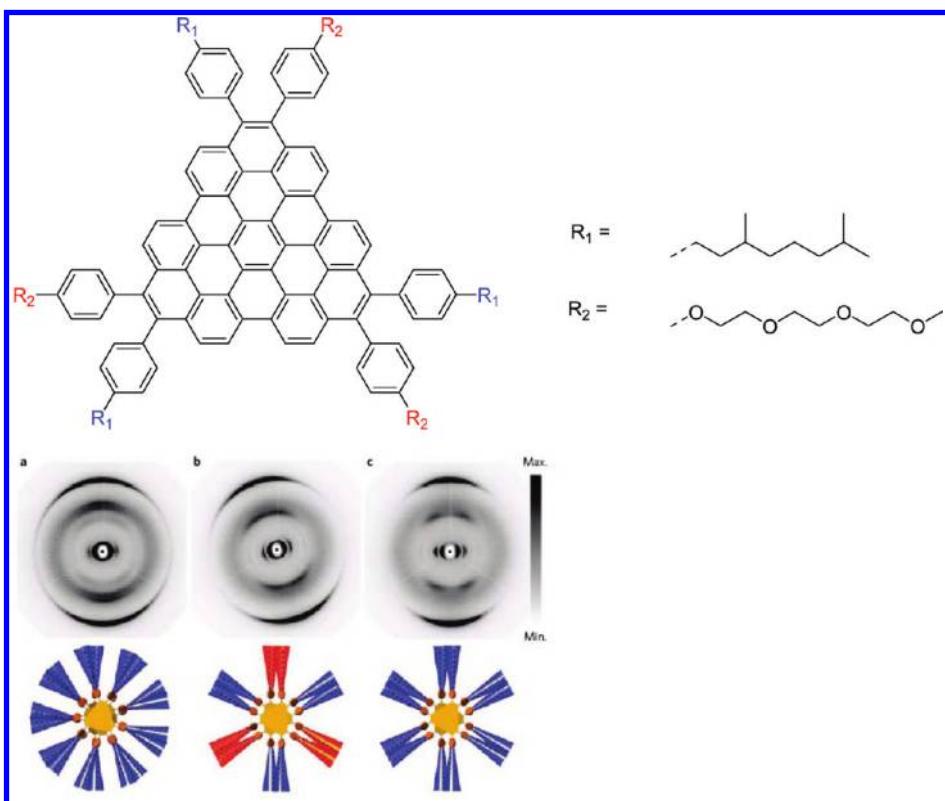


Figure 4. Two-dimensional wide-angle X-ray scattering patterns and corresponding schematic illustrations of top-viewed triangularly shaped polyaromatic hydrocarbon molecules stacked on top of one another.¹⁰² Reprinted by permission from Macmillan Publishers Ltd: Feng, X.; Marcon, V.; Pisula, W.; Hansen, M. R.; Kirkpatrick, J.; Grozema, F.; Andrienko, D.; Kremer, K.; Müllen, K. *Nat. Mater.* **2009**, *8*, 421–426, copyright (2009).

PR-TRMC measurements of this compound showed a mobility of $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹⁰² The authors argued that mobility is limited by structural defects and that an ideal defect-free assembly of materials may lead to a mobility up to $15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹⁰²

Finally, Wöll and co-workers lately presented evidence for bandlike transport of electrons in highly ordered self-assembled monolayers (SAMs) of HBC materials anchored to Au substrate via S–Au bonds.¹⁰³ The authors proposed that the poor charge-carrier mobilities, which are governed by lateral hopping transport, increase considerably in the presence of a high degree of molecular ordering with estimated electron mobilities in the order of $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K within highly ordered HBC-based SAMs.¹⁰³

The aforementioned synopsis of charge-carrier mobilities of selected DLCs demonstrates the prospective of designing a DLC of high charge-carrier mobility. The challenge remains producing defect-free films over large areas for DLCs exhibiting high charge-carrier mobility.

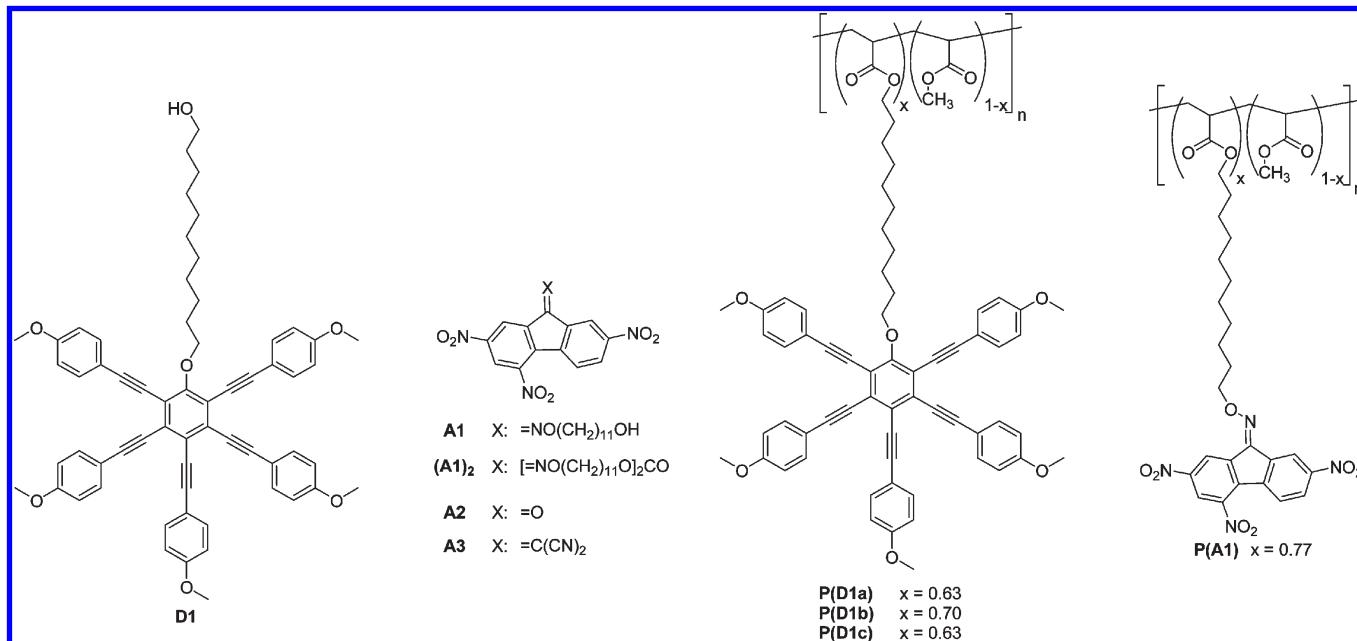
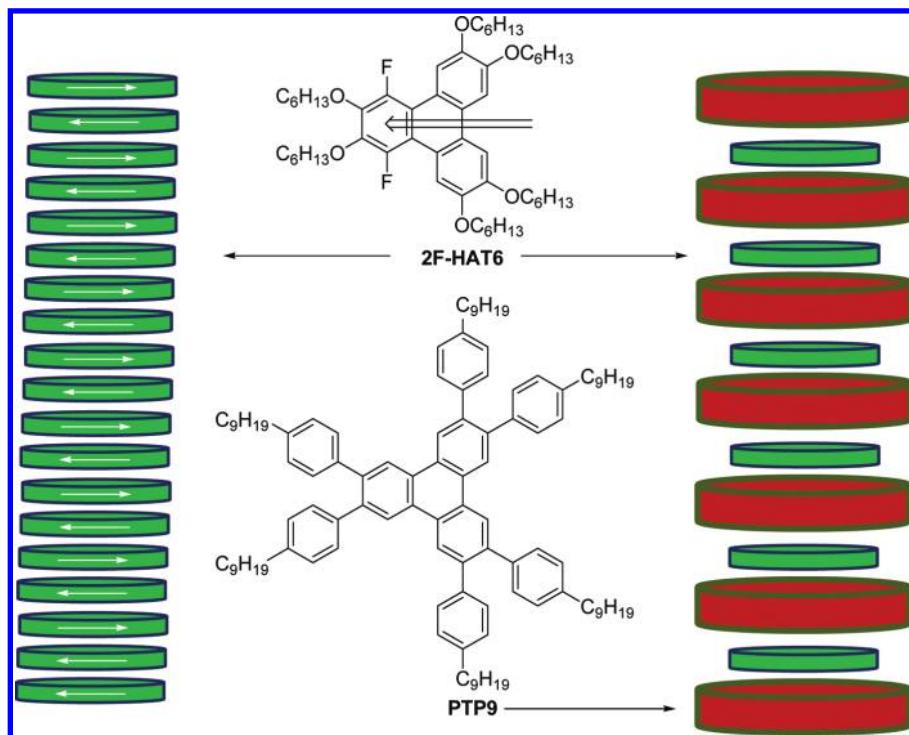
4. Transition and Mesophase Engineering

Researchers were also able to engineer DLC mesophases via different approaches. Aida's group reported the controlled self-assembly of amphiphilic HBC derivatives.^{104–107} Amphiphilic HBC derivatives substituted with trinitrofluorene (TNF) moieties form coaxial nanotubular structure (16 nm in diameter and several micrometers long), wherein the electron-donating graphitic layer of π -stacked HBC are coated by a layer of the electron-accepting TNF, allowing photochemical generation of charge-carriers

and a rapid photoconductive response with an on/off ratio larger than 10^4 .¹⁰⁴ Electron-rich discoids when doped with TNF may form charge-transfer (CT) complexes leading to supramolecular assemblies and mesophases. Such CT complexes were reported in 1:1 mixtures of pentakis(phenylethynyl)phenol and TNF and resulted in different mesophases with higher clearing temperature.¹⁰⁸ The addition of a series of trinitrofluorene-based acceptors to a discotic mesogen carrying five methoxy groups and one functional tail (see Figure 5) has led to CT complexes of a wide range of mesophase behavior.¹⁰⁹ The interaction of multyne DLC with TNF was studied using deuterium NMR by measuring the peaks quadrupolar splitting. This provides information about the orientational order of the complex of the deuterated compounds.¹¹⁰

The introduction of a lateral nuclear dipole moment in 1,4-difluoro-2,3,6,7,10,11-hexakis(hexyloxy)triphenylene (2F-HAT6), see Figure 6, resulted in a Col_h mesophase from below room temperature to 121 °C as opposed to a Col_h mesophase between 70 and 100 °C in HAT6.¹¹¹ This has increased the TOF mobility from $7.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in HAT6 to $1.6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in 2F-HAT6. The authors also reported the increase of the TOF mobility to $1.5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in a 1:1 stoichiometric mixture of 2F-HAT6 and 2,3,6,7,10,11-hexakis-(4-nonylphenyl)triphenylene (PTP9).¹¹¹

In addition, functionalizing dendrons at their ends with different electron donor (D) and acceptor (A) groups, see Figure 7, self-assemble into supramolecular liquid crystals phases, which exhibit hole mobility up to

**Figure 5.** Studied materials.¹⁰⁹**Figure 6.** Schematic representation of the stabilization of a columnar phase through antiferroelectric alignment of molecular dipoles as in 2F-HAT6 or by formation of a CPI compound as in 2F-HAT6 + PTP9.¹¹¹ Modified version of Figure 2 from the article: Bushby, R. J.; Donovan, K. J.; Kreouzis, T.; Lozman, O. R. "Molecular engineering of triphenylene-based discotic liquid crystal conductors" *Opto-Electron. Rev.* **2005**, 13, 269–279. Reproduced with permission.

$10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the D-dendrons and electron mobility up to $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the A-dendrons.¹¹²

Arene–perfluoroarene interactions were exploited to control the mesophase behavior of functionalized triphenylene monomers/polymers in a 1:1 mixture with perfluorotriphenylene.¹¹³ The authors reported the stabilization of the DLC mesophase by perfluoroarene–arene interactions with an increase of 70 °C in the clearing temperature.¹¹³

Furthermore, doping triphenylene discotics with electron deficient ferrocenium ion formed a charge transfer complex leading to an increase in the charge-carrier mobility along the discoids without affecting the Col_h mesophase.¹¹⁴ Blending HBC derivative with electron-donating perylenediimide and terrylenediimide derivatives led to a considerably higher level of order within the self-assembled columnar stacks.¹¹⁵

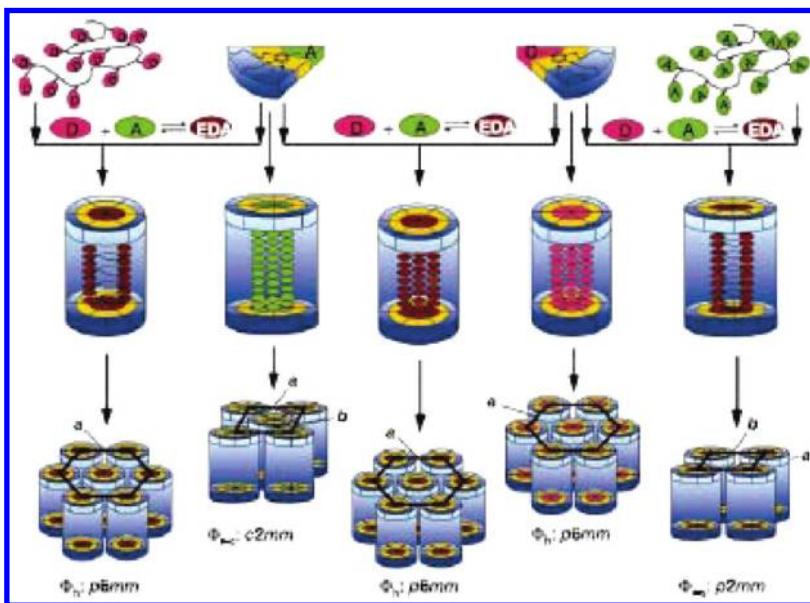


Figure 7. Schematic illustration of the LC assembly process in fluorinated dendrons functionalized at their tips with electron donor (D) and electron acceptor (A).¹¹² Reprinted by permission from Macmillan Publishers Ltd: Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shlyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H. W.; Hudson, S. D.; Duan, H. *Nature* **2002**, *419*, 384–387, copyright (2002).

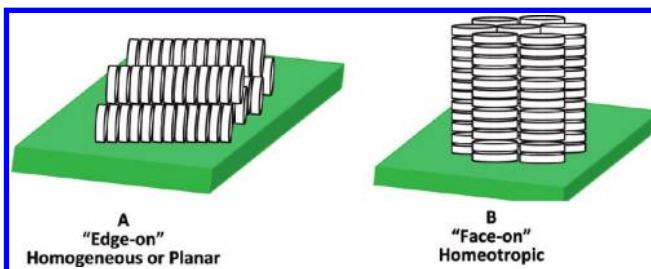


Figure 8. (A) “Edge-on”, homogeneous, or planar unidirectional alignment; (B) “face-on” or homeotropic alignment.

5. Alignments

There are two distinct alignments of columnar DLCs: (a) homogeneous, edge-on or uniaxial planar (column axis parallel to a substrate) and (b) homeotropic or face-on (column axis perpendicular to a substrate), see Figure 8. Unidirectional planar alignment is ideal for OFETs while the homeotropic alignment is ideal for OPV or OLED applications.^{116–118} For rectangular columnar ordered mesophases, Liu et al. proposed two limiting orientations of the molecular columns wherein the columns are either parallel or perpendicular to the substrate with a slight tilt.¹¹⁹ Slow cooling of DLCs from the isotropic phase may lead to homeotropic alignment since the face-on orientation of the first molecular layers act as nucleation sites for the further self-assembly of discs perpendicular to the substrate.¹²⁰

The ability to control the structural order and alignment of semiconducting materials is critical to attain high charge-carrier mobility.^{121–123} A plethora of techniques has been used to align DLCs, some of which are described below in more detail.

5.1. Zone-Casting. Zone-casting allows alignment of organic materials in a homogeneous fashion. DLC material, dissolved in solvent, is continuously supplied through a

nozzle on a moving substrate with a temperature gradient. Homogeneous alignment is achieved due to a concentration gradient in the meniscus formed between the nozzle and the moving substrate. With a change in the parameters of the casting (solvent, concentration, temperature, nozzle/substrate distance, rate of supply, and substrate velocity), well-aligned layers can be obtained on the area of several square centimeters, see Figure 9.¹²⁴ Zone-casting was used to align HBC-C12 and resulted in a mobility of $1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, an order of magnitude higher than oriented HBC derivatives on a PTFE layer.¹²⁵ This was consistent with Warman’s findings that the photoconductivity of HBC-C12 aligned by zone-casting was 10-fold higher in the columnar alignment direction than in the perpendicular direction.¹²⁶ The optical anisotropy of an aligned HBC derivative, by the zone-casting technique, was reversibly switched on/off by changing the temperature in the region of the crystal to mesophase transition. This led to the reorientation of the molecules from a tilted to an orthogonal stacking arrangement.¹²⁷

5.2. Zone-Melting. In the zone-melting technique, an electrically heated wire generates a narrow molten zone (0.5–2 mm wide) on the organic layer sandwiched between two pieces of glass or indium–tin oxide-coated glass, see Figure 10. When the molten zone of tetrakis-*n*-undecylporphyrin was moved slowly (3–120 $\mu\text{m}/\text{min}$) across the layer from one end of the cell to the other, a single-crystal film was produced after one pass. The steady-state short-circuit photocurrent of tetrakis-*n*-undecylporphyrin was improved by several orders of magnitude after such treatment.¹²⁸ It should be noted that the zone-melting technique also purifies the material; therefore, the improved properties may be attributed to better alignment in addition to higher purity of the material.

5.3. Langmuir–Blodgett Deposition. Alignment of amphiphilic HBC derivatives was achieved using Langmuir–Blodgett (LB) techniques.^{129,130} Hexaalkylhexa-*peri*-hexabenzocoronene bearing one alkyl substituent terminated

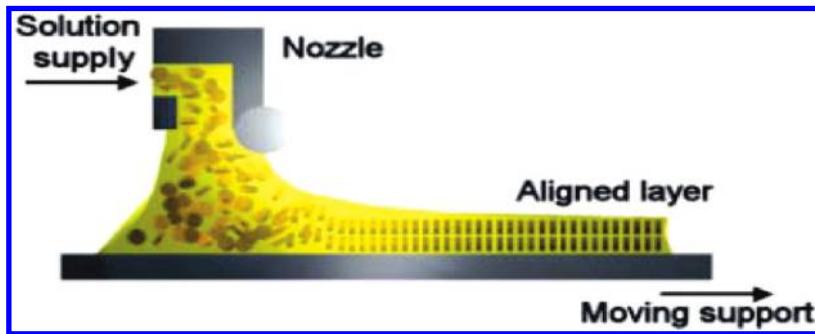


Figure 9. Schematic presentation of the zone-casting technique.¹²⁵ Pisula, W.; Menon, A.; Stepputat, M.; Lieberwirth, I.; Kolb, U.; Tracz, A.; Sirringhaus, H.; Pakula, T.; Müllen, K. “A zone-casting technique for device fabrication of field-effect transistors based on discotic hexa-*peri*-hexabenzocoronene”, *Adv. Mater.* **2005**, *17*, 684–689. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

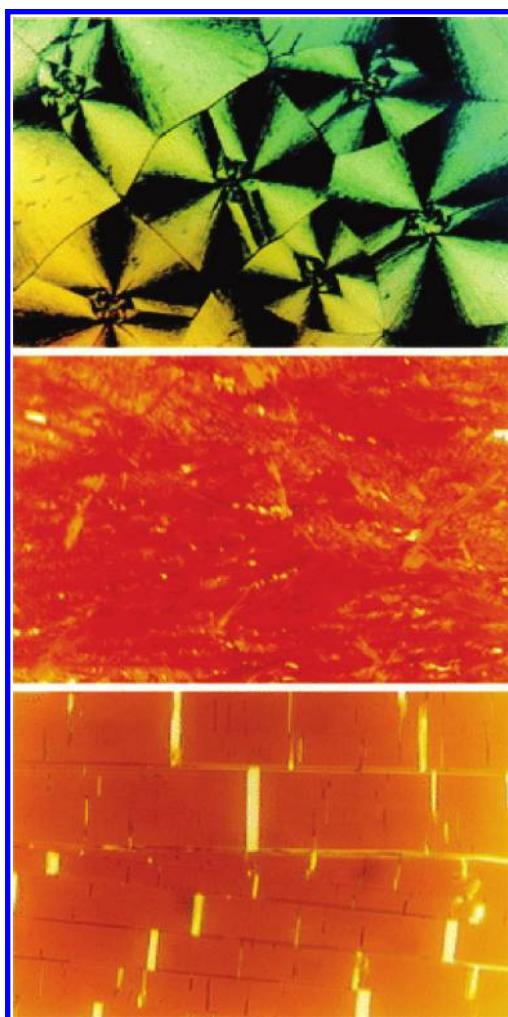


Figure 10. Micrographs of a porphyrin thin film (area of view, 0.3 mm × 0.5 mm). (top) Crystals grown by capillary filling and imaged between two crossed polarizers. (middle) Crystals first grown by capillary filling and then remelted briefly with the heating wire and quickly cooled by turning the power off. (bottom) Crystals regrown by the zone-melting technique (growth rate, 6 $\mu\text{m}/\text{min}$).¹²⁸ Reprinted with permission from ref 128. Copyright 2000 American Chemical Society.

with a carboxylic group were reported to form well-defined LB films upon growing from solution at the water–air interface.¹³⁰ The authors reported the competition of π – π stacking and alkyl chain packing leading to two distinct phases.¹³⁰ Moreover, benzyl-terminated octa-substituted phthalocyanines¹³¹ form highly ordered LB thin films of

significant thermal stability while edge-on orientation was observed in LB films of DLCs formed of one/two triphenylenes linked to TNF.¹³²

5.4. Solution-Casting on Preoriented Polytetrafluoroethylene (PTFE). Another tool used to align DLCs involves highly oriented polytetrafluoroethylene (PTFE). This technique was successfully applied in aligning HBC,¹³³ triphenylene,¹³⁴ phthalocyanine,¹¹⁷ pyrene, and benzoperylene¹³⁵ derivatives into uniaxial columns along the direction of PTFE on the substrate.

Uniaxial alignment of a peritetrastubstituted phthalocyanine Pc was achieved by confining Pc in a mesh of crisscrossed nanogrooves, see Figure 11.¹³⁶ This is due to the anisotropy of boundary tension between the mesophase and the nanogrooves’ walls.¹³⁶ An aligned polyimide layer surface was also used to assemble triphenylene-based DLCs.¹³⁷

5.5. Surface Treatment. The successful alignment of DLCs by annealing is achieved when the material is stable at and slightly above the clearing temperature and when it wets the substrate in both its isotropic and DLC phase.¹³⁸ An ITO surface treatment was reported to stabilize DLC thin films, in which one treated the ITO substrate with argon plasma, annealing, and UV-ozone. This led to good wetting conditions attaining homogeneous organic thin films. Such films were obtained by heating up the DLC material above the clearing temperature and cooling down with a controlled rate to obtain large, well-aligned domains.¹³⁸ Recently, the control of planar alignment of a Pc derivative, with control of the azimuthal angle, was achieved by dewetting the compound in its isotropic phase over a substrate patterned with organothiol self-assembled monolayers on gold.⁵⁶ Alignment of DLCs can also be affected by their specific surface interactions.^{120,139,140} Geerts’ group reported the homeotropic alignment of a phthalocyanine derivative, attached to eight oligo(ethyleneoxy) peripheral substituents, on a hydrophilic surface whereas a planar alignment of random arrangement of column directors was observed on a hydrophobic surface.¹²⁰ The authors attributed the variation in alignment to the different interactions of the peripheral chains of the Pc molecule with the different surfaces, e.g., oligo(ethyleneoxy) chains H-bond to a hydrophilic surface causing homeotropic alignment.¹²⁰

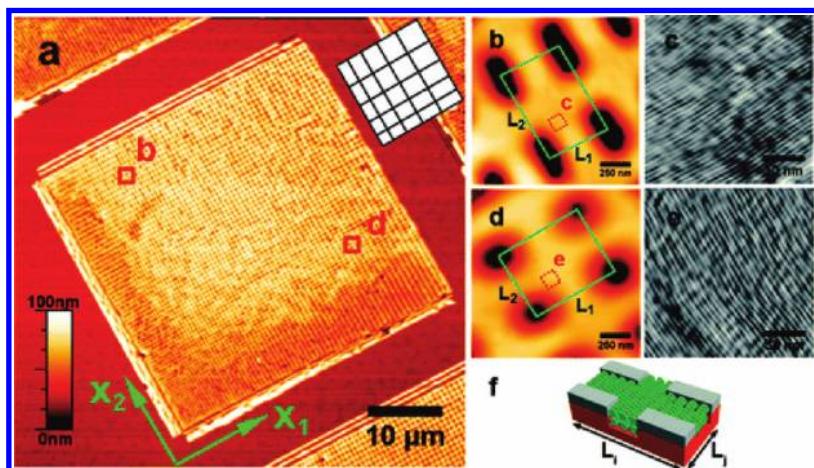


Figure 11. (a) AFM topography image of the $40\text{ }\mu\text{m} \times 40\text{ }\mu\text{m}$ PC network used to screen column alignment. The periods of the grooves increases progressively, as shown schematically in the inset. (b,d) AFM topographic zoom on the region marked in part a. The column alignment is observed in the corresponding AFM phase images shown in parts c and e. (f) Schematic drawing of the alignment of columns in a rectangular cell of the network.¹³⁶ Reprinted from ref 136. Copyright 2007 American Chemical Society.

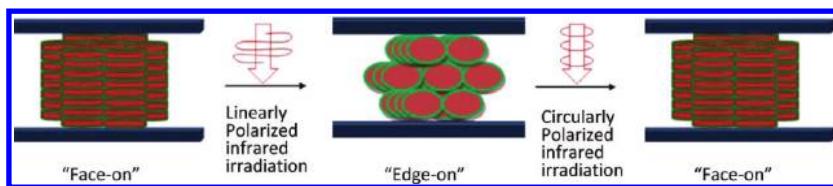


Figure 12. Schematic representation of alignment change upon circularly polarized IR irradiation.¹⁵⁰ Modified version of TOC from the article: Monobe, H.; Awazu, K.; Shimizu, Y. "Alignment control of a columnar liquid crystal for a uniformly homeotropic domain using circularly polarized infrared irradiation" *Adv. Mater.* **2006**, *18*, 607–610. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

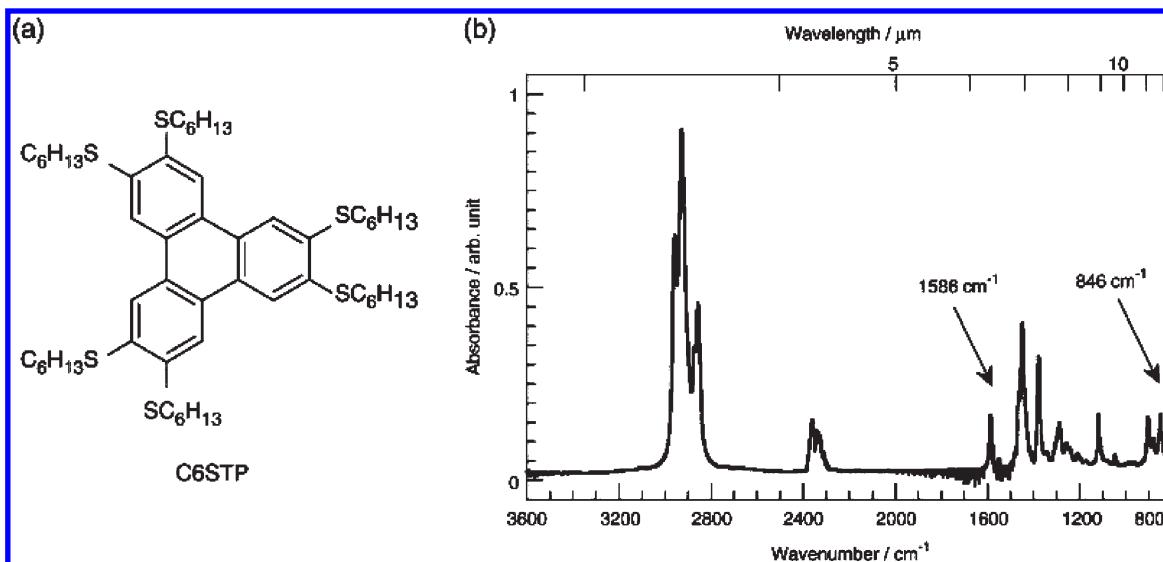


Figure 13. (a) Molecular structure of hexahexylthiotriphenylene (C6STP) and (b) its infrared spectrum of a film in H phase ($66\text{ }^\circ\text{C}$).¹⁵¹ Reprinted from *Thin Solid Films*, **518**, Monobe, H.; Awazu, K.; Shimizu, Y., "Alignment change of hexahexylthiotriphenylene in the helical columnar phase by infrared laser irradiation", 762–766, Copyright (2009), with permission from Elsevier.

5.6. IR Irradiation. Shimizu's group has used circularly polarized infrared irradiation to control the alignment of DLCs, see Figure 12.^{141–151} The vibrational mode of a selected chemical bond in a mesogen is excited using polarized infrared irradiation from a free electron laser leading to a change of DLC alignment.¹⁴⁶ The selected combination of the polarization direction of the incident photon as well as that of the transition dipole moment for the vibrational excitation allows achieving the molecular

alignment. Such alignment can only be obtained with the higher-ordered DLC phase, Col_h mesophase, owing to its high viscosity.¹⁴⁶ The polarized infrared light irradiation of the C–C stretching absorption band of hexahexylthiotriphenylene (C6STP) (1586 cm^{-1}) led to a uniform and anisotropic alignment change of domains, see Figures 13 and 14.¹⁵¹

5.7. Magnetic. Lee et al. reported the first magnetic uniaxial alignment of the columnar structures of discotic

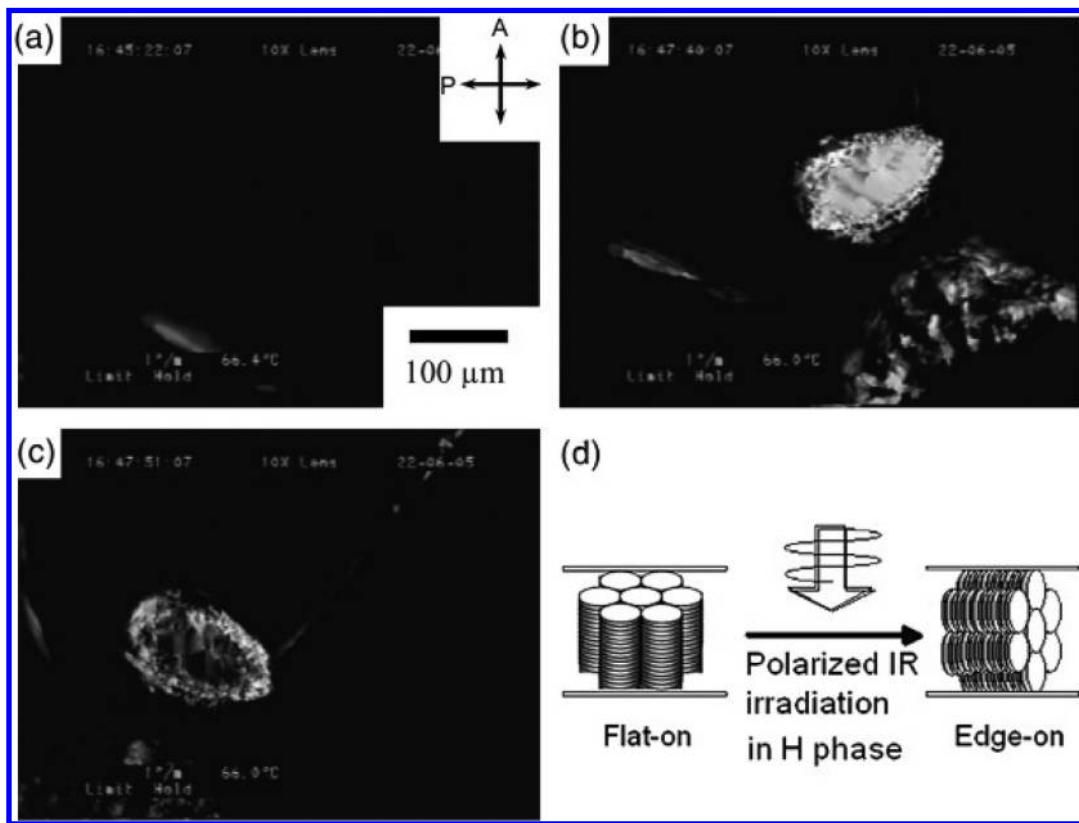


Figure 14. Microscopic textures observed for a C6STP film in H phase at 66 °C cooled from I.L. followed by Col_h (a) before infrared irradiation (homeotropic alignment), (b) after irradiation with 6.30 μm infrared FEL and (c) after rotation of the sample on the stage by 45° counterclockwise. (d) A schematic representation of the alignment change of columns in H phase of C6STP with infrared laser irradiation.¹⁵¹ Reprinted from *Thin Solid Films*, 518, Monobe, H.; Awazu, K.; Shimizu, Y., “Alignment change of hexahexylthiotriphenylene in the helical columnar phase by infrared laser irradiation”, 762–766, Copyright (2009), with permission from Elsevier.

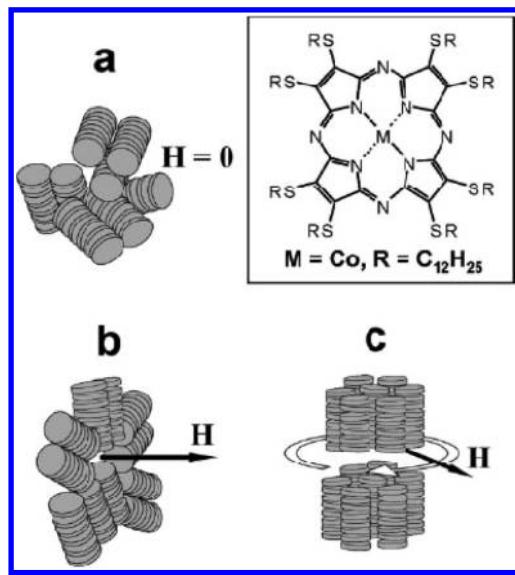


Figure 15. Uniaxial alignment concept using a rotating magnetic field.¹⁵² Lee, J.-H.; Choi, S.-M.; Pate, B. D.; Chisholm, M. H.; Han, Y.-S. “Magnetic uniaxial alignment of the columnar superstructure of discotic metallomesogens over the centimetre length scale”, *J. Mater. Chem.* **2006**, *16*, 2785–2791. Reproduced by permission of the Royal Society of Chemistry.

metallomesogens, cobalt octa(*n*-dodecylthio)porphyrazine (CoS12), see Figure 15, over a centimeter length scale.^{152,153} Because the DLC aromatic core possesses a diamagnetic interaction with an external magnetic field,

uniaxial alignment can be achieved by cooling a constantly spinning sample from the isotropic phase to the liquid crystalline phase in the presence of a static applied magnetic field.¹⁵² Edge-on alignment in CoS12 DLC was achieved using an external magnetic field (~1.0 T) and a substrate functionalized with octadecyltrichlorosilane (OTS), which increases the affinity of the substrate to the alkyl side chains.¹⁵⁴ The magnetic alignment of HBC derivative resulted in a charge-carrier mobility up to 10⁻³ cm² V⁻¹ cm⁻¹ in an FET device.¹⁵⁵

5.8. Use of a Sacrificial Layer. Geerts’ group reported the use of a sacrificial polymer layer for confinement of an alkoxy phthalocyanine DLC to achieve homeotropic alignment.¹⁵⁶ After spin coating the Pc on the substrate, the sacrificial polymer is spin-cast. Thermal annealing followed by cooling to room temperature induces the homeotropic alignment. The sacrificial polymer is then washed carefully with methanol, see Figure 16.¹⁵⁶

5.9. Blends. The morphological studies of blends of different mesogenic binary discotic systems leading to spontaneous alignment without application of external stimuli are recently reported.^{157–161} The columnar phase of blends of more than 40% of disk-shaped electron-donor phthalocyanine and the lath-shaped perylenetetracarboxidiimide derivatives was shown to be more ordered with the increase of phase stability of 100 °C in comparison to pure Pc.¹⁵⁹ The authors proposed the random insertion of lathlike molecules inside molecules of disks in

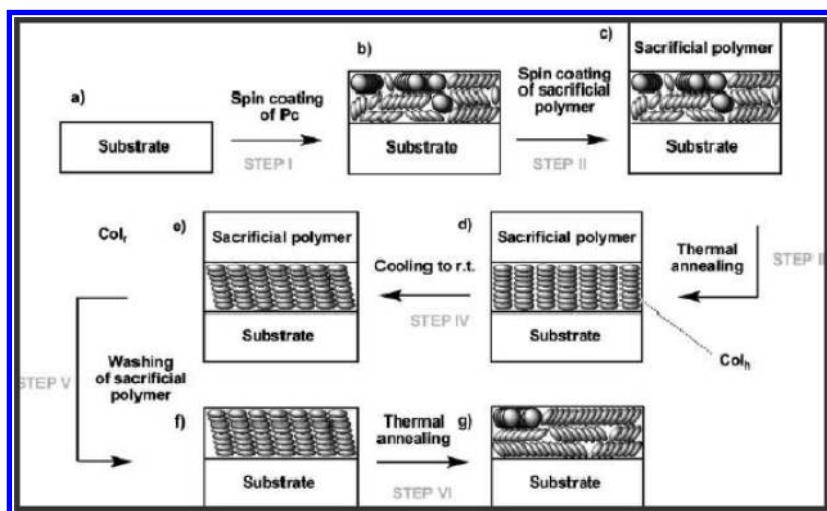


Figure 16. Fabrication process of homeotropically aligned films of the phthalocyanine derivative. The last step serves only to demonstrate the function of the sacrificial layer.¹⁵⁶ Reprinted from ref 156. Copyright 2009 American Chemical Society.

the columnar phase leading to self-aligned homeotropic alignment between two electrodes.¹⁵⁹ Geerts' group demonstrated that homeotropic alignment in blends of two metal-free *Pc* mesogens is only possible when one of the compounds exhibits a *Col_h* phase.¹⁵⁸ Complementary polytopic interaction (CPI),¹⁶² which is defined as the sum total of a large number of atom-by atom van der Waals interactions between a discotic mesogen and a larger core polyaromatic compound,¹⁶³ in a 1:1 mixture of 2,3,6,7,10, 11-hexakis(hexyloxy)triphenylene (has *Col_h* phase between 70 and 100 °C) and hexakis(4-nonylphenyl)dipyrazino-[2,3-*f*:2',3'-*h*]quinoxaline (has two crystal forms that melt at 71 and 81 °C) resulted in a *Col_h* phase with a clearing temperature of 240 °C.⁹ Recently, C₆₀-discotic dyads forming mesophases were reported.^{164,165} C₆₀, anchored to two triphenylene moieties via dodecyloxy side chains, produced a CPI columnar phase when mixed with dipyrazino[2,3-*f*:2',3'-*h*]quinoxaline derivative.¹⁶⁴ The authors proposed the clustering of fullerenes around one of the seven columns forming this *Col_h* phase.¹⁶⁴ Monte Carlo simulations of the phase behavior and molecular organization of the triphenylene-C₆₀-triphenylene mesogenic unit showed mesomorphism with isotropic, nematic, and columnar phases wherein the fullerenes are closely packed.¹⁶⁶

5.10. Influence of Electric Field on Alignment. The response of DLC materials to an applied electric field was also investigated.^{167–175} The design of a ferroelectric columnar DLC requires the stabilization of one-directional stacking of molecules in the column and the reduction of the intercolumnar dipole–dipole interaction to reduce the repulsive interaction between the columns in the ferroelectric arrangement.¹⁷⁰ Kishikawa's group reported the *Col_h* mesophases of *N,N'*-bis(3,4,5-trialkoxyphenyl)-ureas (*R* = *n*-C₁₂H₂₅ and *n*-C₁₆H₃₃), in which the urea molecules are stacked in one direction in each column with strong H-bonding, to exhibit a sharp peak of spontaneous polarization in response to an applied triangular electric field (0.1–18 Hz), see Figure 17.¹⁷⁰ Homeotropic

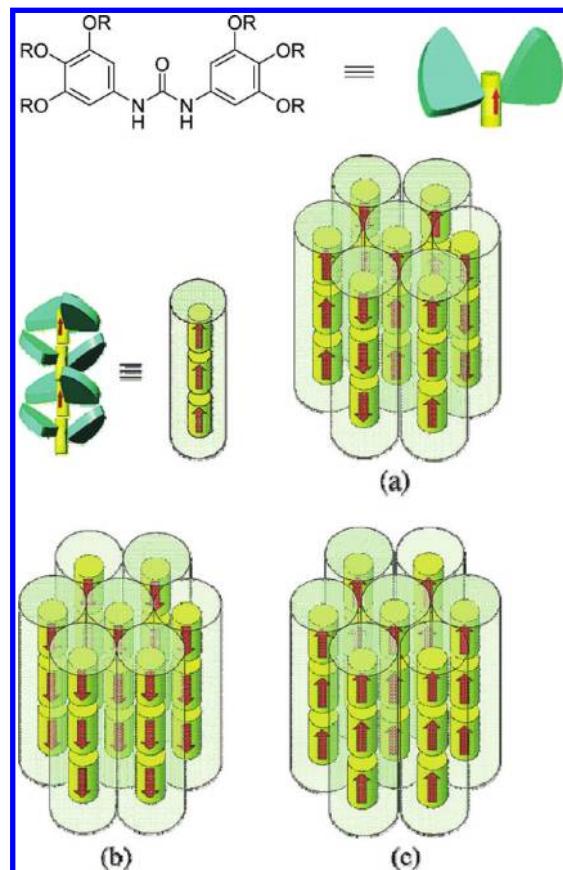


Figure 17. Schematic representation of columnar DLC columns of *N,N'*-bis(3,4,5-trialkoxyphenyl)ureas (*R* = C_{*n*}H_{2*n*+1}) in the switching experiment. (a) Columns at 0 V; (b and c) columns in an applied field.¹⁷⁰ Reprinted from ref 170. Copyright 2005 American Chemical Society.

alignment of DLC materials was also achieved upon the application of an electric field.^{173,174}

5.11. Others. Dewetting of columnar DLCs of triphenylene and phthalocyanine derivatives on chemically patterned surfaces resulted in planar alignment.^{172,175} Bock's group reported the competition of homeotropic and planar alignment in DLCs which can be controlled by the film thickness and cooling rate.^{176,177} The induced

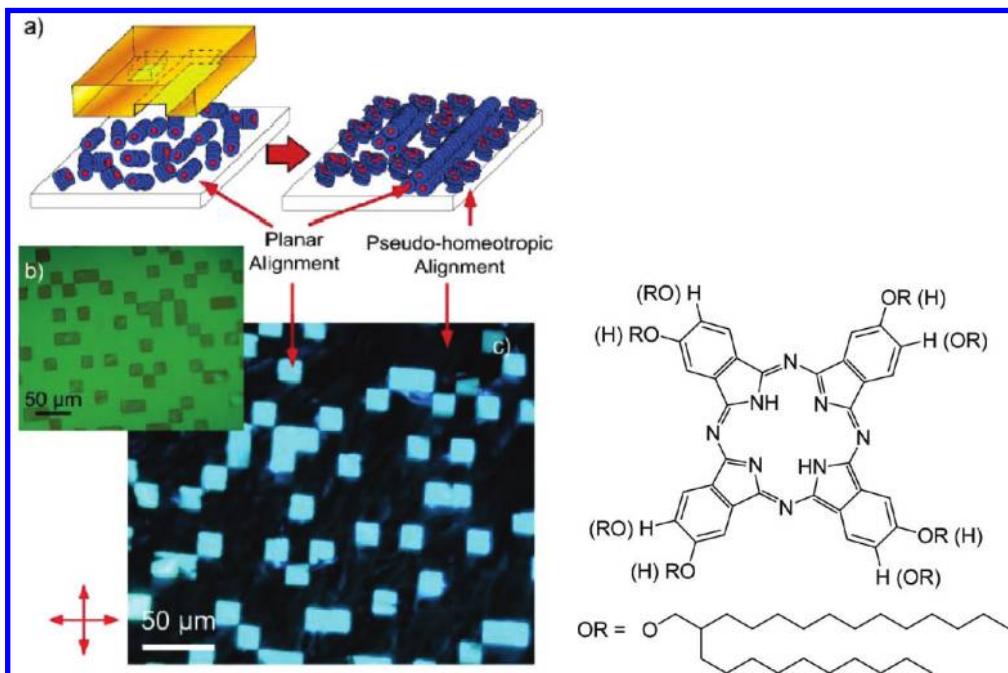


Figure 18. LCW induces a spatially controlled columns orientation in continuous thin films. a) Scheme of LCW applied on isotropic (fluid) phase. b) Optical microscopy images in bright field of the stamp and c) with cross polars of the patterned *Pc* film.¹⁸⁵ Cavallini, M.; Calo, A.; Stolar, P.; Kengne, J. C.; Martins, S.; Matacotta, F. C.; Quist, F.; Gbabode, G.; Dumont, N.; Geerts, Y. H.; Biscarini, F. “Lithographic Alignment of Discotic Liquid Crystals: A New Time-Temperature Integrating Framework”, *Adv. Mater.* **2009**, 21, 4688–4691. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

birefringence observed between crossed polarizers is indicative of planar alignment whereas the absence of birefringence is typical of hometropic alignment since the direction of light propagation is parallel to the optical axis of the liquid crystal.¹⁷⁶

Substitution of triphenylene with fluoroalkylated groups further resulted in a greater tendency for homeotropic alignment.¹⁷⁸ The presence of fluoroalkylated chain spacer, linked to the pentakis(phenylethynyl)-phenoxy core, was also reported to stabilize the nematic phase of this DLC.¹⁷⁹ The gelation of hexahexyloxy-triphenylene has resulted in a 3-fold increase of its hole mobility up to $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,¹⁸⁰ which was attributed to the suppression of fluctuation of the triphenylene molecules and increase of the molecular order in the gelled discotics.^{180,181}

Triphenylene DLCs were also photoaligned on the surface of thin films of photoirradiated azobenzene-containing polymer¹⁸² and photo-cross-linkable polymer with cinnamoyl side groups.¹⁸³ When an azobenzene-containing polymer film was exposed to oblique nonpolarized light, photoisomerization and reorientation of azobenzene was achieved. This resulted in tilted DLC orientation forming a columnar nematic phase. However, the exposure of the film to linearly polarized light led to the homeotropic alignment of the triphenylene DLC.¹⁸⁴

Recently, the lithographic controlled wetting (LCW) technique was exploited to align the metal-free mesogenic phthalocyanine DLC, see Figure 18.¹⁸⁵ The authors reported the films to be patterned with no effect of aging at ambient temperature.¹⁸⁵ LCW is an unconventional lithographic method that is capable of forming a patterned nanostructure from a liquid layer.^{186,187}

Moreover, Geerts’ group reported the substrate-independent nature of the homeotropic alignment of mesogenic phthalocyanine.¹⁸⁸ The authors demonstrated homeotropic alignment of *Pc* even with substrates of different surface roughness, surface correlation lengths, and surface energies.¹⁸⁸ They also showed that it is the confinement induced by solid substrates, rather than the nature of substrates, that controls the homeotropic alignment.¹⁸⁸

Finally, atomic force microscopy (AFM)^{159,189–197} and scanning tunneling microscopy (STM)^{198–203} were largely used to characterize the hierarchical self-assembly of DLCs on conductive substrates. STM allows the study of the dynamics of monolayers in addition to the depiction of molecular ordering.²⁰⁰ Piot et al. showed the spontaneous hierarchical self-assembly of edge-on nanocolumnar stacks of HBC-C12 at the liquid–solid interface on highly oriented pyrolytic graphite (HOPG).¹⁹⁸ The authors attributed the complex 3D supramolecular multilayered architectures (HOPG/face-on/edge-on/edge-on) and (HOPG/face-on/edge-on/face-on) to the strong tendency of HBC-C12 to aggregate in π -stacks or mesophases.¹⁹⁸

6. Theoretical Calculations

Brédas and co-workers reported a seminal quantum-chemical study correlating structures and properties of DLCs and the subsequent effect on their charge-transport properties.^{204,205} The estimation of phonon-assisted hopping between the discoid mesogens in DLCs is based on the idea that electrons (or holes) are localized on the discs and they hop from one disk to another along the stacking axis. Two main parameters govern charge transport in DLCs at the molecular scale: the reorganization energy

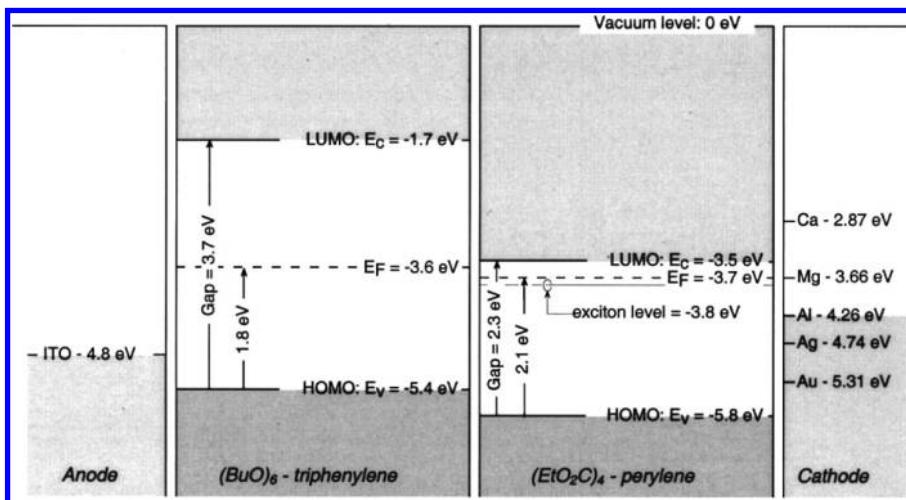


Figure 19. Schematic band diagram of OLED made of triphenylene and perylene.²⁰⁹ Reprinted with permission from Seguy, I.; Jolinat, P.; Destruel, P.; Farenc, J.; Mamy, R.; Bock, H.; Ip, J.; Nguyen, T. P. *J. Appl. Phys.* **2001**, *89*, 5442–5448. Copyright 2001, American Institute of Physics.

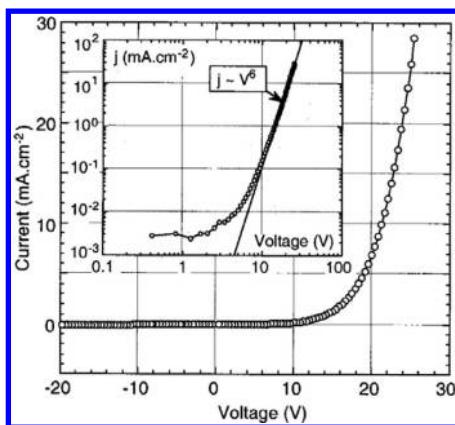


Figure 20. Current density-voltage characteristics of the EL device.²⁰⁹ Reprinted with permission from Seguy, I.; Jolinat, P.; Destruel, P.; Farenc, J.; Mamy, R.; Bock, H.; Ip, J.; Nguyen, T. P. *J. Appl. Phys.* **2001**, *89*, 5442–5448. Copyright 2001, American Institute of Physics.

(λ) and the intermolecular transfer integral (t). The reorganization energy is the sum of the internal reorganization energy, which is related to the geometric differences between neutral and charged species and that of the surrounding medium. In a dimer of two neutral molecules, the strength of electronic coupling, t , between them can be estimated as half the electronic splitting, respectively, of the HOMO and LUMO levels for holes and electrons. To achieve high charge-carrier mobilities in DLCs, small values of λ and large values of t are desired.²⁰⁵ The authors reported the magnitude of the transfer integrals in model dimers to be strongly governed by the rotational angle between two adjacent π -stacked molecules and hence the increase in the discoid size would not necessarily result in higher charge-carrier mobility. Furthermore, the authors demonstrated that the shape of the molecules does not influence the calculated electronic coupling as much as that of the character of the electronic wave function.²⁰⁵ Electron-transport DLCs should, therefore, have a small value of λ , large value of t , and an electron deficient core to facilitate the electron injection/collection. Hexakis(alkylsulfanyl)hexaazatriphosphine

HATNA-[SR]₆ mesogens were designed with the aforementioned requirements to act as potential electron-transport materials.⁴⁹ PR-TRMC mobilities of HATNA-[SR]₆ showed the strong dependence on the nature of the side chains with a $0.26\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ for HATNA-[SC₁₀H₂₁]₆ at 180 °C.⁴⁹ The charge-transport parameters of HBC derivatives were estimated at different temperatures using a simplified INDO method²⁰⁶ and a combination of quantum chemical calculations, molecular dynamics, and kinetic Monte Carlo simulations.²⁰⁷ Molecular dynamic simulations of tetraalkoxy-substituted metal-free phthalocyanines show the association between charge transport mechanism and the dynamics of mesophases.²⁰⁸ The hole mobility is 2 orders of magnitude higher (10^{-1} vs $10^{-3}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) when accounting for the rotational and translational dynamics (dynamic vs static approach).²⁰⁸

7. Optoelectronic Devices

A red organic light emitting device made from the electron-rich 2,3,6,7,10,11-hexabutoxytriphenylene and the electron-poor fluorescent tetraethylperylene-3,4,9,10-tetracarboxylate, both of which show DLC phases at high temperature, was recently reported.²⁰⁹ The device structure was ITO/triphenylene hexaether/perylene tetraester/aluminum. Electrons are injected from the aluminum cathode into the perylene layer, whereas holes are injected from the ITO anode, see Figure 19. The charge recombination occurs in the perylene layer near the heterojunction, and the emission leads to red light with $\lambda_{\max} = 615\text{ nm}$. The current density was reported to reach as high as 28 mA cm^{-2} at 26 V. At 28 V, a maximum luminance of 45 cdm^{-2} was recorded with the light turning on at 16 V, see Figure 20.²⁰⁹

Schmidt-Mende et al. reported the first use of DLC materials in an OPV device.²¹⁰ The authors used the self-assembly properties of hexabenzocoronene DLC derivative and perylene diimide to fabricate an OPV device with a maximum external quantum efficiency of more than 34% near 490 nm and a power efficiency up to 2%.²¹⁰ The authors attributed the high efficiency to photoinduced

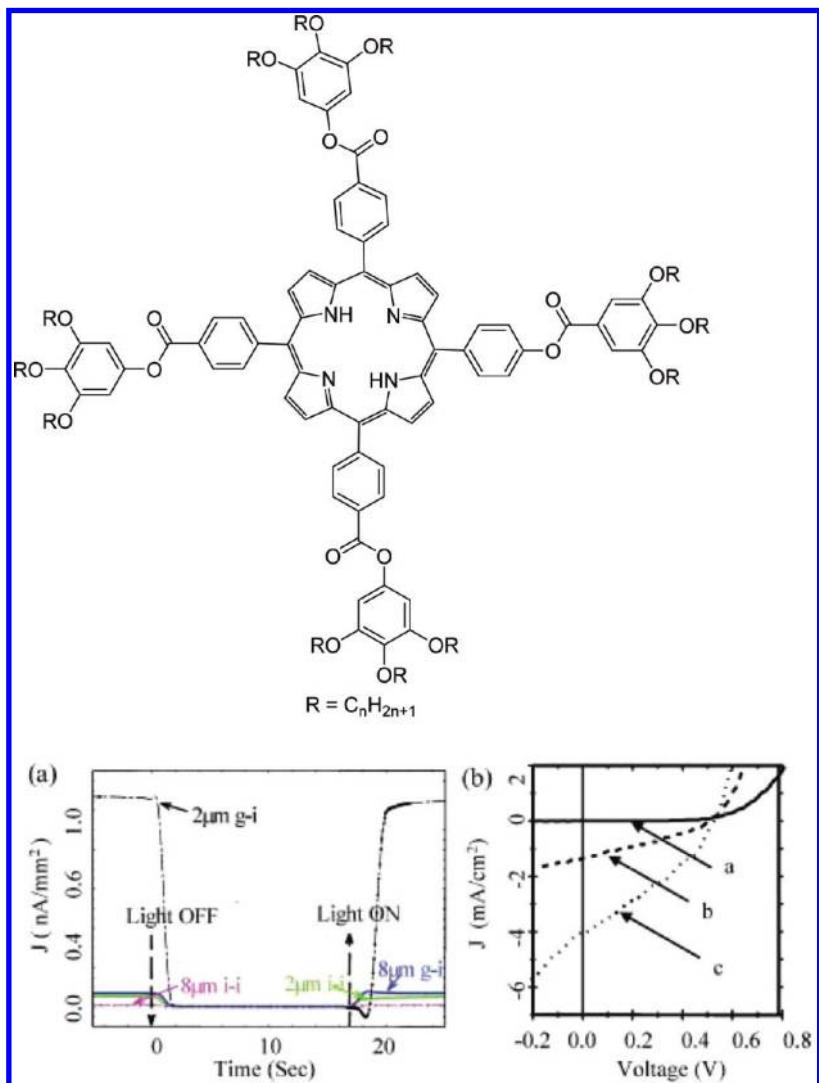


Figure 21. *J-V* characteristics of the bulk heterojunction cell.²¹¹ Li, L.; Kang, S.-W.; Harden, J.; Sun, Q.; Zhou, X.; Dai, L.; Jakli, A.; Kumar, S.; Li, Q. *Liq. Cryst.* **2008**, *35*, 233–239, reprinted by permission of the publisher (Taylor & Francis Group, <http://www.informaworld.com>).

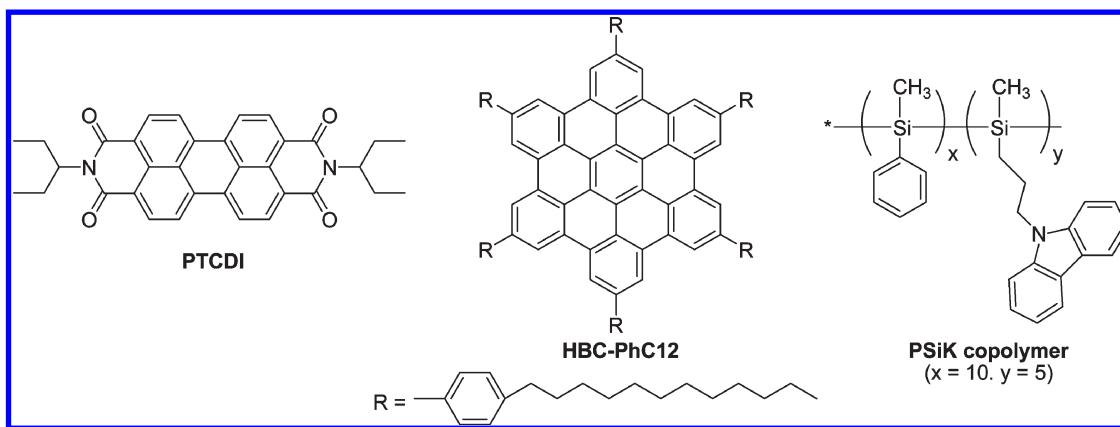


Figure 22. Structures used in Müllen's PV device.²¹²

charge transfer between the hexabenzocoronene and perylene along the π -system.²¹⁰ The investigation of a bulk heterojunction PV cell formed from a 1:1 (w/w) blend of a DLC porphyrin electron donor (see Figure 21, R = C₁₂H₂₅) and the C₆₀ derivative (PCBM) as an electron acceptor, where the ITO anode was coated with a conducting polymer poly(3,4-ethylenedioxythiophene)

(PEDOT) and the cathode was Ca/Al, showed a power conversion efficiency (PCE) of 0.222%.²¹¹ The PCE increased to 0.712% upon postannealing treatment leading to a better alignment of the porphyrin.²¹¹

Moreover, Müllen's group reported preparation of a PV device by spin-coating a 40:60 mixture of HBC-PhC12–PTCDI (see Figure 22), dissolved in chloroform,

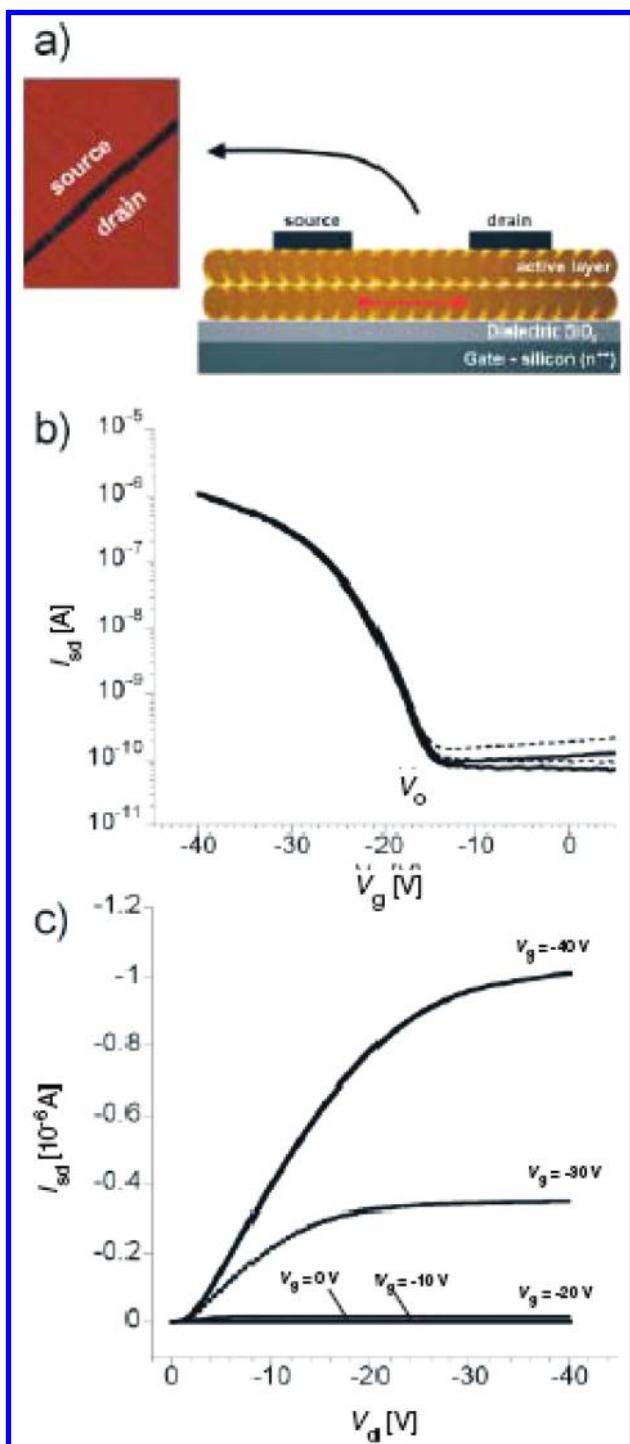


Figure 23. a) Schematic presentation of the top-contact device configuration (channel length $L = 25 \text{ mm}$, width $W = 1.6 \text{ mm}$, and depth $d = 200 \text{ nm}$) onto a 20 nm thick zone-cast HBC-C₁₂ aligned film. A 200 nm SiO₂ dielectric gate and an n-doped silicon substrate as a gate electrode were used in this device configuration. b) Transfer characteristic (gate voltage $V_g = -40 \text{ V}$). c) Current-voltage ($I-V$) output characteristics. Both dependences are measured along the columnar alignment. V_d : drain voltage; I_{sd} : source-drain current.¹²⁵ Pisula, W.; Menon, A.; Stepputat, M.; Lieberwirth, I.; Kolb, U.; Tracz, A.; Sirringhaus, H.; Pakula, T.; Müllen, K. “A zone-casting technique for device fabrication of field-effect transistors based on discotic hexa-peri-hexabenzocoronene”, *Adv. Mater.* **2005**, *17*, 684–689. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

on ITO-coated glass substrate and covering it with a 20 nm thin film of poly(ethylenedioxothiophene) doped

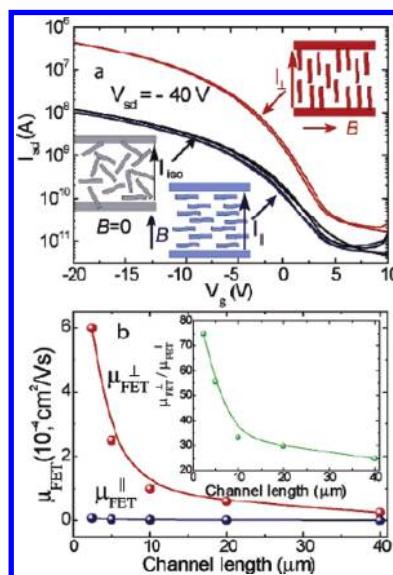


Figure 24. Electrical performance of HBC-PhC₁₂-based FET ($L = 10 \text{ m}$; $W = 10 \text{ mm}$). (a) Transfer characteristics for oriented HBC layers (I_{\perp} , red line), parallel (I_{\parallel} , blue line) to the magnetic direction and active HBC layers without the application of magnetic field (I_{iso} , black line). Insets show the direction of the field direction B and HBC-PhC₁₂. (B) Dependence of field-effect mobility on the channel length.¹⁵⁵ Reprinted from ref 155. Copyright 2005 American Chemical Society.

with polystyrene sulfonic acid (PEDOT-PSS).²¹² The performance of the photodiode was shown to be dependent on film morphology wherein the highest short circuit current JSC density was obtained with 1 wt % addition of the photoconducting copolymer PSiK.²¹²

The control of morphology of a PV device formed of blends of electron-acceptor perylene tetracarboxdiimide (EPPTC) and electron-donor HBC improved the photovoltaic response with an external quantum efficiency up to 29.5% at 460 nm and an open circuit voltage of 0.70 V.²¹³ This was achieved by controlling the annealing of the HBC-EPPTC blend deposited on an elastomeric stamp of low-surface roughness.²¹³ The formation of “interpenetrating networks” between the electron-transport and hole-transport materials is crucial in preparing blend devices.²¹⁴

Furthermore, an OPV device formed of the ITO/triphenylene derivative/perylene/Al structure generated an external quantum efficiency of 3%, which was attributed to high exciton-diffusion lengths, high absorption coefficients, and optimized organic/inorganic interface.²¹⁵

An OFET device was constructed using aligned HBC-C₁₂ via the zone-casting technique with top contacts of $25 \mu\text{m}$ channel length with saturation mobility up to $5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, see Figure 23.¹²⁵ The on-off ratio was 10^4 and the turn-on voltage was $\sim 15 \text{ V}$.¹²⁵ Moreover, a solution processed OFET device made of magnetically aligned HBC-PhC₁₂ was fabricated with charge-carrier mobility of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$ along the perpendicular direction to the applied magnetic field, 10-fold higher than in the parallel direction or in the absence of magnetic field. The on-off ratio was 10^4 and the turn-on voltage was $\sim 5 \text{ V}$, see Figure 24.¹⁵⁵ Recently, bottom gold contact, bottom-gate ambipolar OFETs were fabricated by drop casting tetracarboxdiimide (SWQDI), see Figure 25,

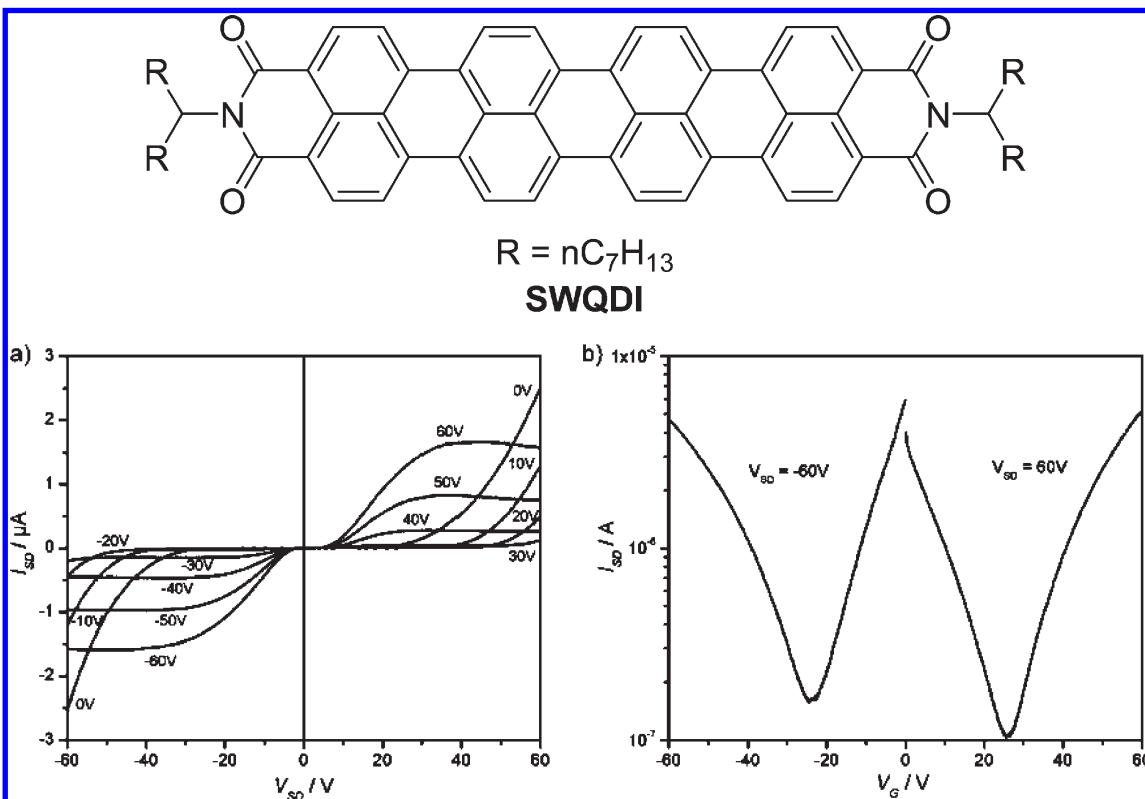


Figure 25. a) Output and b) transfer characteristics ($V_{SD} = 60 \text{ V}$) of an ambipolar SWQDI FET.²¹⁶ Tsao, H. N.; Pisula, W.; Liu, Z.; Osikowicz, W.; Salaneck, W. R.; Müllen, K. "From ambi- to unipolar behavior in discotic dye field-effect transistors", *Adv. Mater.* **2008**, *20*, 2715–2719. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

on hexamethyldisilazane (HMDS)-treated SiO_2 substrates.²¹⁶ The hole mobility was $1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while the electron mobility was $1.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.²¹⁶ OFETs using *N,N*-dialkyl-3,4,9,10-perylene tetracarboxylic diimides were also reported with an electron mobility up to $1.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (for $R = \text{octyl}$) with an on-off current ratio of 10^7 .²¹⁷ Moreover, solution-processed OFETs were fabricated using NIR-absorbing tetraoctyl-substituted vanadyl phthalocyanine, which exhibits a columnar rectangular mesophase, forming edge-on aligned molecules in a spin-cast film with mobility up to $0.017 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.²¹⁸ OFETs based on a triphenylene derivative were also reported.²¹⁹ Nuckolls' group reported the fabrication of stable high-performance photosensitive OFETs, produced from self-assembled HBC derivatives using single-walled carbon nanotubes (SWNTs) as point contacts, with resistance up to $8.99 \times 10^9 \Omega$.²²⁰ Furthermore, Fiji Photo Film Company showed the use of hybrid aligned DLCs to be effective in increasing the view angle of thin-film transistor liquid-crystal displays.^{221–223}

8. Conclusions and Future Outlook

Despite numerous reports on the synthesis and characterization of DLCs, the exploitation of DLCs in optoelectronic devices is still in its infancy. Only very few discotics have been reported in electronic devices in which the obtained results were truly encouraging. Though reports of DLCs with potentially attractive properties are extensive, optimization of their properties is far from

complete. The use of a suitable processing technique to align DLCs in the optimized arrangement is fundamental to achieve an efficient functioning device. It is conceivable that DLCs will have an excellent impact in opto-electronics in the near future.

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