

Electrohydrodynamic Jet Printing for Columnar Discotic Liquid Crystal Alignment and Applications in Organic Electronics

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Abstract

A review of the past and present work on discotic liquid crystals is presented paying particular attention to their use in organic electronics and uniaxial planar alignment. The use of electrohydrodynamic printing for micron and sub-micron resolution patterning is then investigated and the latest high resolution drop-on-demand techniques are reported. Finally, the use of the state of the art SIJ printer is demonstrated for its use in creating high resolution patterns of silver and SU8 photoresist for discotic liquid crystal alignment.

Discotic Liquid Crystals: Materials, Processing and Applications

The Many Phases of Liquid Crystals

It is often said that liquid crystals (LCs) lie in an intermediate state between liquid and solid. This is very much true when you look at the order of liquid crystalline phases, their viscosity is that between liquid and solid and they have a degree of alignment unlike the isotropic nature of a liquid. However, what makes liquid crystals so interesting, commercially, are their unique properties that aren't seen in either solid or liquids. This is most obvious when looking at the effect of electric and magnetic fields on liquid crystalline materials, with only small fields needed to orientate the molecules, some several orders of magnitude lower than needed for either liquids or solid crystals. Further, just small amounts of dopants and changes in temperature have huge effects on LC properties and they have the ability to self-organize, self-align and self-heal.

The order of a liquid crystal is easiest to understand by considering the degree of ordering within the system. A crystalline solid has its molecules fixed in position, at lattice sites, and their orientation is fixed around those sites, they have no rotational freedom and cannot move from where they sit. On melting, a single molecule cannot move or rotate without disturbing one of its neighboring molecules and will eventually cause the whole lattice to be destroyed and all degrees of order will be lost. However, there are molecules that possess a particular shape that are allowed some degree of disorder. For example, a spherical molecule is free to rotate in all directions on a crystal lattice site without disturbing its neighbors and this type of system is known as a plastic crystal. Further, highly asymmetric molecules such as rods and discs are able to have some translational as well as a rotational degree of freedom. These are the liquid crystals, rod like molecules are known as calamitics and disc like ones are called discotics (Figure 1).

In calamitic liquid crystals the rods lie with their long axis pointing in the general same direction where as in discotics the plane of the discs are all facing in the general same direction. The number of ways that these molecules can arrange themselves, states that have more or less order gives rise to the many phases of liquid crystalline systems. The most disordered phase is known as a nematic phase, here enough thermal energy allows the molecules to

move freely almost as individuals. In calamitics this is analogous to pencils in a tin and discotics can be imagined like coins stacked unevenly on top of one another. In most cases some level of aggregation and order is observed, in calamitics this comes in the form of layered smectic phases and for discotics they form stacks and columnar phases.

nematic

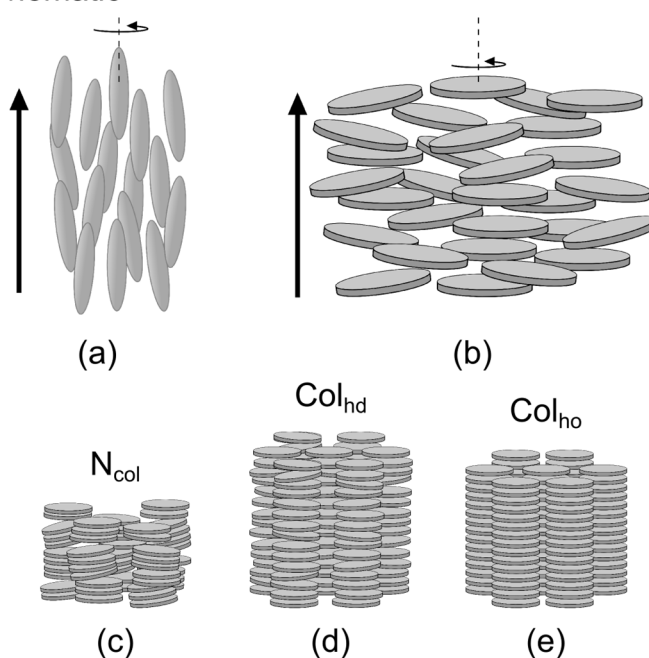


Figure 1. Nematic calamitic (a), nematic discotic (b), nematic columnar (c), columnar hexagonal disordered (d) and columnar hexagonal ordered (e).

Discotics

The first discotic liquid crystals (DLCs), hexaalkyl benzenes (Figure 2a), were only discovered relatively recently by Chandrasekhar et al in 1977 [1]. An aromatic core surrounded by alkyl chains has since formed the basis for almost all thermotropic discotic liquid crystals (Figure 2). Demonstrating properties such as negative birefringence and large charge carrier mobilities, intensive research has since been afforded to DLCs over the past 30 years.

Discotics tend to exhibit two types of mesophase, the nematic and the columnar (Figure 1). In the nematic phase the DLCs can be aligned much in the same way as calamitics and as such have found a use in compensator films for LCDs, increasing the viewing angle [2]. However, the nematic DLC phase is quite rare and the columnar phases are favored. Further, these columns come in ordered and disordered states, much as in smectic calamitic phases, with the columns sitting on a hexagonal lattice (Col_h). Phases where the

molecules are tilted with respect to the column direction lead to well-ordered rectangular and oblique symmetries (Col_r , Col_{ob}) and phases where the molecules have some orientational order with respect to one another in a column are known as helical (H), and are the most highly ordered.

Discotic liquid crystal compounds being composed of large aromatic cores when aligned in a columnar phase demonstrate charge transport along the columns. Benefitting from being relatively easy to process, in comparison to crystalline and polycrystalline materials, their self-aligning and self-healing properties make them an interesting system for use in organic photovoltaics and field effect transistors.

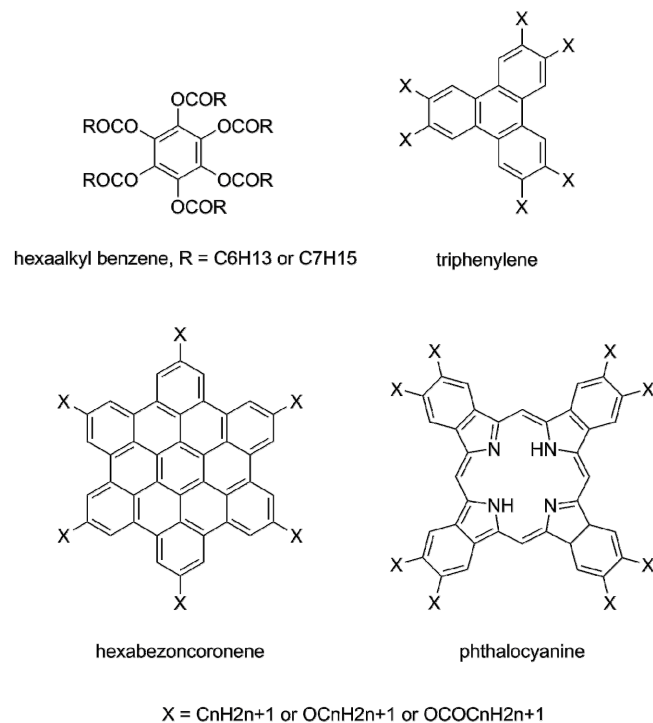


Figure 2. Examples of discotic mesogens. hexaalkyl benzene was the first discotic mesogen to be discovered, since then many other types based on the same system have been synthesized, three of the most common are shown here.

Charge Transport in Molecular Wires

For a long time charge transport in liquid crystalline materials was thought to be solely ionic due to the low observed mobilities [3], [4]. With the discovery of discotic liquid crystals and the extensive purification of calamitics the intrinsic conduction in these π -conjugated materials is now known to be electronic and ionic conduction is only observed due to impurities in the least ordered nematic phases [5], [6]. Charge transport in more ordered smectic and columnar phases where the charges move through layers or along columns is said to be quasi two- and one-dimensional respectively.

In DLCs the formation of columns allows good π -orbital overlap of the molecular cores leading to enhanced charge transport along these molecular wires. These wires are almost completely insulated from one another due to the liquid like alkyl chains that separate them and so large anisotropy is observed, with little or no electronic conduction perpendicular to the column direction [5], [7]–[11].

Molecular Order, Orbital Overlap and Mobility Measurements

To achieve a high charge carrier mobility (a measure of the ability for charges to move in a material in an electric field) the molecular wires require a high degree of order and good π -orbital overlap. Perhaps the most important parameter is the molecules positional order within a column. This is clear when looking at certain triphenylene derivatives. On increasing side chain length there is only a negligible change in disc separation but a change in the disc order is observed. For shorter chain lengths a Col_p phase is observed, here the correlation length, a measure of spatial disorder, is longer than in the Col_h phase seen for longer chain length derivatives [12]. A decrease in correlation length and hence increase in disorder, is observed as you increase chain length and a reduction in mobility is seen. Further, the lower temperature and more ordered Col_r , Col_{ob} , and H phases in other discotic systems always show higher mobilities. Increasing the coherence length has been demonstrated by creating hydrogen bonding molecules, adding gelling agents and utilizing complementary polytropic interactions (CPI) all of which show an increase in charge transport properties [13]–[16].

The degree of overlap between neighboring molecules is a key factor in achieving high charge carrier mobility in all organic semiconducting systems. This is equally true in discotic liquid crystals. Creating more diffuse orbitals by replacing oxygen atoms with sulphur or selenium has been shown to increase mobility in triphenylene discotics [17]. Better overlap is also achieved by decreasing the inter-disc separation which has been seen in tri-indole molecules where replacing nonylphenyl with octylethynyl side chains reduces the stacking distance from 4.4 to 3.9 Å increasing the mobility by four orders of magnitude [18].

Intrinsic mobility measured by time resolved microwave conductivity (TRMC) has shown certain discotic mesogens with mobilities as high as 1 cm²V⁻¹s⁻¹ [19]. However, TRMC measurements do not take into account defects, impurities or processing conditions that would be observed in real life devices such as photovoltaics or field effect transistors. Time of flight (TOF) experiments which probe at longer length scales have shown mobilities as high as 0.1–0.3 cm²V⁻¹s⁻¹ for highly ordered triphenylenes and phthalocyanines [17], [20], [21]. Interestingly, there are very few examples of field effect transistor measurements of discotic liquid crystal mesogens. This is in part due to the difficulty of forming uniaxial planar alignment on substrate surfaces, where the columns are all directed from source to drain electrode.

Alignment of the Discotic Mesophase

From a technological stand point aligning the columnar structures is very important. Generally, homeotropic alignment is observed for thick films sandwiched between two substrates, here the columns are aligned with the director pointing normal to the substrates with the columns running from one surface to the other. However, planar alignment, with the columns running parallel to the substrate, has been observed for thinner samples open to the air [22]. These general observations are due to the competition between the air-liquid crystal interface and the solid-liquid crystal interface where homeotropic alignment is favored at the solid surface and planar at the air [23]. Even though this simple rule applies to most systems, uniaxial and large area, monodomain alignment is challenging and can only be achieved with clever molecular design and processing conditions.

Thermal treatments by melting and cooling allows for the alignment of discotic molecules between two substrates. It has been shown that the surface and molecular chemistry effect the quality of this alignment [24], [25]. However, homeotropic alignment on single substrates, open to the air is more challenging. There is a large array of possible outcomes which depend on the choice of molecule and the choice of substrate, with reports of only planar or only homeotropic alignment in different cases. Although the choice of system has shown to be important, uniform alignment can only be guaranteed using external stimuli or processing techniques. For homeotropic alignment reports using electric fields, photo-switching with IR radiation and sacrificial layers have all shown promising results [26]–[28]. For certain device applications such as field effect transistors, however, planar alignment is required. And, although planar alignment is generally favored on a single substrate a distribution of column directors is normally observed. The challenge in this instance is to align all the columns so that directors all face in the same direction in a uniaxial planar alignment. Successful techniques include spin coating, magnetic field alignment, rubbed PTFE layers, Langmuir Blodgett deposition, zone casting and zone melting [9]–[11], [29]–[42].

Using chemically patterned surfaces with hydrophilic and hydrophobic regions, uniaxial planar alignment has been achieved. On heating triphenylene and phthalocyanine DLCs into their isotropic phase they spontaneously dewet from the hydrophobic regions creating hemi-cylindrical liquid droplets [43]. Dependent on the type of DLC and width of the hemi-cylindrical droplet, different order was observed.

Controlled planar alignment can also be achieved by containing the liquid crystal within microchannels. The microchannels are created using SU8 photoresist, a negative resist which crosslinks under UV irradiation. These SU8 microchannels are filled using capillary action of the liquid crystal in the isotropic phase [44]. As with the phase dewetting experiments all the investigated DLCs show planar alignment, however the preferential homeotropic alignment enforced at the SU8 interface means that all the DLCs are forced to align with their columns perpendicular to the channel direction.

Discotic Devices

The combination of semiconductor and self-assembling properties make DLCs an attractive candidate for their use in organic electronic devices. Indeed, DLCs have found themselves used in many device architectures including organic light emitting diodes (OLEDs), organic photovoltaics (OPVs) and organic field effect transistors (OFETs). The capacity to self-heal structural defects such as grain boundaries and the formation of millimeter domains combined with ease of processing and high charge carrier mobilities is very desirable.

Although the use of discotic-like semiconductors, such as copper phthalocyanine derivatives have been investigated for field effect transistors [45], the use of self-aligning discotic liquid crystals for OFETs has only been fully realized in a few cases. Hexabenzocoronenes (HBCs) are probably the most investigated DLCs for field effect transistors, planar alignment and devices have been demonstrated by spin coating, zone casting, using PTFE alignment layers, magnetic fields and the transfer of molecular fibers and mobilities in the range of $0.001 - 0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ have been reported [10], [29], [34], [36], [37]. Guo et al reported HBC liquid crystals deposited between two carbon nanotube electrodes having a mobility of $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [39]. As well as HBC discotic transistors, equal hole and electron transport was reported for an

ambipolar discotic liquid crystal with mobilities in the range of $0.001 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [38] and finally, triphenylene derivatives have been used in OFETs but with only relatively low mobilities in the range of $10^{-6} - 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [41], [42].

Interestingly, although many of these examples benefit from the self-assembling nature of discotic mesogens all of them rely on solvent crystallization into solid columnar like fibers. Some reports do benefit from annealing above the liquid crystalline temperature, demonstrating improvements in the charge transport properties and the self-ordering ability that these molecules possess. However, methods for creating high mobility FETs from DLCs, further, ones benefitting from all of their unique properties is still an ongoing quest.

Non-Contact, High-resolution Printing

The role of organic electronics is to create a disruptive technology, one that allows cheap, solution based electronics that can be fabricated on substrates ranging from plastic to paper and textiles. Printing has been heralded as the go-to technology for realizing the potential of organic electronics. It affords the ability to create large area patterns, roll-to-roll and, with the use of drop-on-demand inkjet technologies, the design and implementation of patterns on the fly to meet the needs of the end user.

Conventional piezo, thermal and electrostatic inkjet printers have had significant commercial success over the years, however, new printing techniques which can combine fine feature sizes and large area patterning are required for the future of printed electronics. Here we will discuss several of those emerging technologies for patterning at micron and sub-micron resolutions.

Electrohydrodynamic

Electrohydrodynamic jet (e-jet) printing uses fine capillary nozzles and high electric fields to jet femtolitre droplets for micron to sub-micron resolution. When a voltage is applied between the conductive micro-capillary and the substrate, the electric field creates an electrohydrodynamic phenomena that drives the flow of inks out of the nozzle. Mobile ions in the ink accumulate near the surface of the meniscus at the end of the nozzle. The columbic repulsion of the ions causes the meniscus to form a conical shape, known as a Taylor cone, once the electrostatic stress overcomes the capillary force droplets are ejected from the apex of the cone. This phenomena creates drop sizes that are smaller than the size of the nozzle orifice. Dependent on the size of the electric field three jetting modes are seen; pulsating mode at low fields, followed by a stable jet mode, where a continuous deposition is observed and e-spray and atomization at higher field strengths. Ultimately, high resolution printing with this technology was demonstrated using very fine capillaries with inner diameters of less than $1 \mu\text{m}$ using pulsed DC voltages. E-jet printing has demonstrated the patterning of conductive polymers, biological samples, metals and polymer brushes [46]–[49].

Dielectrophoretic

In a similar manner to e-jet a metal coated micro-capillary nozzle is used to create patterns at sub-micron resolution. Unlike e-jet, uncharged colloidal suspensions are jetted using dielectrophoresis (DEP). When the nozzle is within $1 \mu\text{m}$ of the substrate the electric field, set up between the nozzle tip and the stage, causes particles in the liquid to move by dielectrophoresis toward the region of highest electric field, finally exiting the nozzle and dragging with them some of the liquid. In this mechanism, no Taylor-cone is observed as the medium (liquid suspension) is not

being charged and drop sizes are approximately the size of the orifice diameter [50].

Super-Fine Inkjet

The super-fine inkjet (SIJ) system developed at AIST also uses micro-capillaries and electric fields to create micrometer resolution patterns. Unlike e-jet and DEP printing the SIJ printer creates electrostatic discharge by applying a voltage between a grounded substrate stage and a fine metal wire which is immersed in the solution inside the capillary nozzle. Sub-femto liter droplets with accurate placement and patterning have been demonstrated with silver inks for organic transistors, terahertz metamaterials and copper wiring [51]–[54].

Pyroelectrodynamic

Attoliter drops are created using the pyroelectric effect resulting in drop sizes of approximately 300 nm without the need for a nozzle. Two plates, separated by 1 mm are placed together. One, a glass slide acts as a reservoir for the ink, either as a thin film or a sessile drop, the other substrate is a lithium niobate (LN) film which is both the active component and the deposition substrate. Using a laser or a hot tip as a heat source, changes in temperature to the LN crystal film causes a pyroelectric effect which in turn set up an electric field exerting an attractive force on the liquid, much the same as other electrohydrodynamic techniques. A cone is formed in the liquid and at high enough fields droplets can be created. This technique benefits from being nozzle-less with no complications arising from cross contamination or complicated nozzle designs [55].

Laser-Induced Forward Transfer

Laser-induced forward transfer (LIFT) is another nozzle-less technique consisting of focusing a laser onto the backside of a film supported on a transparent substrate. A tiny amount of the film material can be transferred to a substrate that is placed just a short distance away. This technique has been used to pattern metals, inorganics, pastes, liquids and DNA microarrays, and droplet sizes of less than 5 μm have been achieved by LIFT [56], [57].

Other, Unconventional Micro/Nano-Patterning Techniques

Self-aligned inkjet printing demonstrated by Sele et al produced sub hundred nanometer gaps between two printed lines of PEDOT:PSS using a dewetting method. When one drop is deposited onto a hydrophobic pre pattern, dewetting occurs, leaving a sub hundred nanometer gap between the two conductive electrodes [58].

Dip-pen nanolithography has been used to create very high resolution patterns by employing the use of an atomic force microscope. A liquid meniscus formed between a solution coated AFM tip and the substrate leaves a pattern on the surface, this has been used to deposit DNA, organic molecules, polymers and proteins [59].

The nano-fountain pen technique also makes use of the scanning probe microscope, this time using very fine, near field optical microscope style glass fibers with inner diameters as small as 3 nm to write metal nanoparticles and DNA with high resolution [60], [61].

High Resolution Photoresist Printing and HAT6 Alignment

Controlled Printing of SU8 Microchannels using SIJ

The SIJ-050 e-jet printer utilizes the super-fine inkjet technology. The printing process is controlled with a pulsating DC voltage,

either in square, triangle or sinusoidal wave format. Typical maximum voltages are in the range of 200–400 V. With the manipulation of amplitude, wave bias, working distance and frequency influencing drop size and, combination of ink formulation, solvent boiling points, vapor pressures, viscosity and surface tension dictating the quality of the printed patterns and the ease at which an ink can be printed at high resolution. For example, water based inks must be manipulated to lower the surface tension. For such fine capillary nozzles the large surface tension of water requires very high voltages to be ejected and higher voltages tend to be more difficult to control often

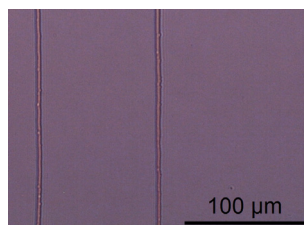


Figure 3. 5 μm silver tracks printed with the SIJ

leading to solid build up at the nozzle tip.

Silver tracks have been printed using this system. Silver nanoparticle inks (Harima NPS-JL) are jetted on to UV-Ozone cleaned silicon substrates with 300 nm of thermally grown oxide. Voltages in the range of 200–300 V, at a frequency of 1 kHz enabled patterning of fine lines with line widths less than 5 μm , see Figure 3, in the range reported by the literature [53] and demonstrates the applicability of the SIJ printing system for fine patterning of conductive tracks.

Patterning of microchannels is accomplished using SU8 (Microchem). SU8 is a negative photoresist epoxy and comes dissolved in cyclopentanone. Cyclopentanone is a good solvent for jetting from an SIJ nozzle, however, its relatively low boiling point and high vapor pressure allows buildup of SU8 at the nozzle tip under certain conditions. Very fine control over line width and line height are possible and, due to the speed at which a femtoliter drop dries, well defined features are deposited. The best resolution so far attained for this system is approximately 10 μm in line width (Figure 4). No coffee staining is observed as SU8 remains liquid after solvent evaporation, before UV curing and, with careful control of parameters it is possible to create 10 μm lines with separations of less than 5 μm over large areas (Figure 5). This is 5 – 10 times finer detail than has been reported in the literature for inkjet printing of SU8 (50–200 μm), to the best of our knowledge.[62]–[65]

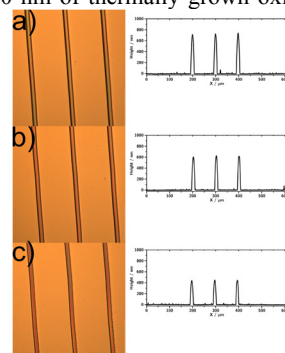


Figure 4. SIJ printed lines of SU8 showing the control over the line height for lines with a lateral resolution of 10 μm and a pitch of

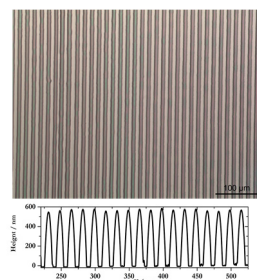


Figure 5. SU8 microchannel patterns printed with the SIJ. Optical image (top) and profilometry (bottom) Line widths of 10 μm with channel widths of less approximately 8 μm . Scale bar 100 μm .

Alignment of HAT6 in SU8 Microchannels

Nominally HAT6 is deposited using capillary fill action, where a small amount of the compound is deposited near the channel

entrance in the isotropic phase. The quality of the filling, i.e. the distance that a liquid can fill the channel is dependent on the width and height of that channel and, intuitively, narrower channels with higher side walls will fill further due to smaller volumes and larger capillary forces.

Figure 6 displays the alignment of HAT6 DLC in microchannels of SU8 Printed using the SIJ under a polarized optical microscope. When the channels are orientated at $\pm 45^\circ$ to the crossed polarizers the DLC is light and at 0° the lines are dark (not pictured), this suggests that the DLC has aligned in a planar manner on the substrate, with the director either pointing perpendicular or parallel to the channel direction. To elucidate the direction of the alignment a lambda plate can be inserted at 45° angle to the crossed polarizers. Dependent on the observed colors and whether they are shifted positively or negatively the orientation of the fast and slow axis of the discotic can be found. In **Figure 6** the colors switch from a blue green at $+45^\circ$ to a yellow at -45° , due to the thickness of the liquid crystal and without going in to too much detail, it is evident that the columns are aligned perpendicular to the channel.

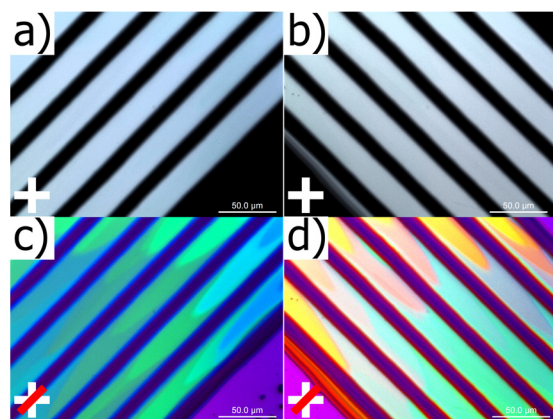


Figure 6. HAT6 alignment in printed SU8 microchannels viewed under crossed polarizers (a) and (b) and with the inclusion of a λ plate (c) and (d) at 45° angle to the polarizers. Scale bar is 50 μm .

The field of discotic liquid crystals is broad and fascinating. Here we have presented just one line of inquiry into the properties and applications of thermotropic DLCs for organic electronics and field effect transistors. High charge carrier mobilities, self-aligning, self-healing, easy processability of large area monodomains, electronic anisotropy are all properties that can be harnessed, but, only if proper care and attention is applied to the processing conditions of discotic materials onto substrate surfaces. Uniaxial planar alignment is paramount for the performance of DLC organic field effect transistors, with the discovery of planar alignment in microchannels and the ability to pattern fine features using the state of the art electrohydrodynamic techniques the next stage for discotic devices might just be around the corner.

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