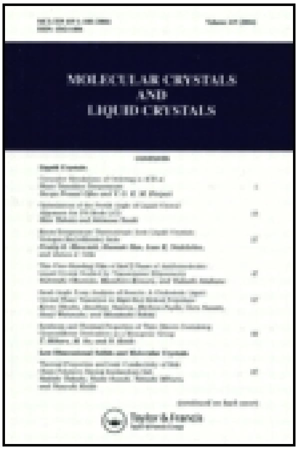

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Alignment of Discotic Liquid Crystals

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ALIGNMENT OF DISCOTIC LIQUID CRYSTALS

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Alignment techniques for calamitic liquid crystals are well developed and play a crucial role in liquid crystal devices. Comparatively little attention has been paid to the alignment of discotic liquid crystals. Only recently the integration of discotic liquid crystals into optical and electronic devices stimulated the development of new alignment techniques for discotic nematic and columnar mesophases. This mini-review attempts a brief summary of the challenges and recent success stories. Two new approaches to the alignment of discotic columnar mesophases will also be presented.

Keywords: discotic liquid crystals; columnar mesophases; nematic mesophases; alignment;, oligomers; electrostatic layer-by-layer deposition

Research on discotic liquid crystals (DCLs) has gone a long way since their liquid crystalline (LC) phases were discovered in 1977 [1]. Thousands of synthesised DLCs helped revealing the relationship between molecular structure and mesophase properties [2]. Physical measurements, most notably NMR [3] and X-ray diffraction [4], elucidated the subtle structural differences as well as the molecular dynamics of their mesophases. It is fair to say that our understanding of DLCs has matured and their further development will depend on their value as new materials.

Soon after the discovery of DLCs novel materials of commercial interest were envisioned based on their unconventional molecular structures, shape anisotropies, intermolecular interactions, and self-organization [5]. Application-directed efforts were particularly fuelled by their unique anisotropic optical and electronic properties [6]. Optical and electronic applications, however, require a perfect alignment of the self-organizing material, which

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is usually obtained by utilizing interfacial forces or by applying external fields.

Alignment of calamitic LCs on surfaces or in LC cells is an advanced technology but, unfortunately, few of the alignment methods developed for calamitic LCs affect the alignment of DLCs [7]. The Fuji Photo Film Company developed sophisticated alignment and fixation methods for the less ordered and more fluid nematic phase of DLCs. They achieved a precise control over the alignment of nematic DLCs in thin layers that function, after photo-polymerization, as optical compensation films for thin-film transistor LC displays (TFT-LCDs). The DLC based optical correction films are sold as "WV film" and greatly enhance the viewing angle of TFT-LCDs [8].

In another approach, amphiphilic nematic multy(arylethynyl)benzene derivatives aligned homogeneously on Langmuir-Blodget films [9]. Micropatterned films of similar compounds were obtained by photoalignment on p-cyanoazobenzene [10]. The alignment in micrometer-thick layers was shown to change from an orientation slightly tilted away from the photoalignment layer to a homogenous alignment at the air interface. The lateral alignment, however, was uniform and gave rise to linearly polarized photoluminescence.

The development of alignment methods for higher ordered and more viscous discotic columnar mesophases is in a comparatively early state, both theoretically and practically. A brief summary and discussion of different alignment methods that have been applied to discotic columnar mesophases is attempted in the following. The first part will deal with low molecular weight DLC while the second part focuses on oligomers of DLC. Each part ends with the presentation of a new concept that might overcome some of the shortcomings of the aforementioned methods.

ALIGNED COLUMNAR MESOPHASES OF LOW MOLECULAR WEIGHT DLCS

Bulk materials of DLCs have been aligned by mechanical and magnetic fields. Alignment in a magnetic field requires a transition from an isotropic, or a fluid nematic mesophase to the columnar mesophase. The alignment process takes place on cooling during the phase transition from the isotropic or nematic to the columnar mesophase. A magnetic field strength of 5 T or more is usually required for more viscous phases [11]. Thus, it is best conducted in an NMR magnet and, in fact, has been observed as very convenient side effect in 2D-NMR studies of DLCs. Nematic DLCs in sandwiched LC cells have also been aligned by a 5 T magnetic field and the quality of homogeniously aligned films was found to be depending on the type of alignment layer [12].

DLCs usually show negative magnetic susceptibility so that the disc-shaped cores align parallel to the magnetic field while the orientation of the director is confined to the plane perpendicular to the magnetic field. Thus, a monodomain can only be obtained if the sample is spun in a magnetic field to control the in-plane orientation of the director (Fig. 1). Only one specific in-plane orientation remains parallel to the magnetic field throughout a full revolution and slow spinning of the sample will allow all cores to reorient in plane and adopt a single orientation.

Very viscous columnar mesophases that do not clear below the decomposition temperature of the compound can be aligned in magnetic

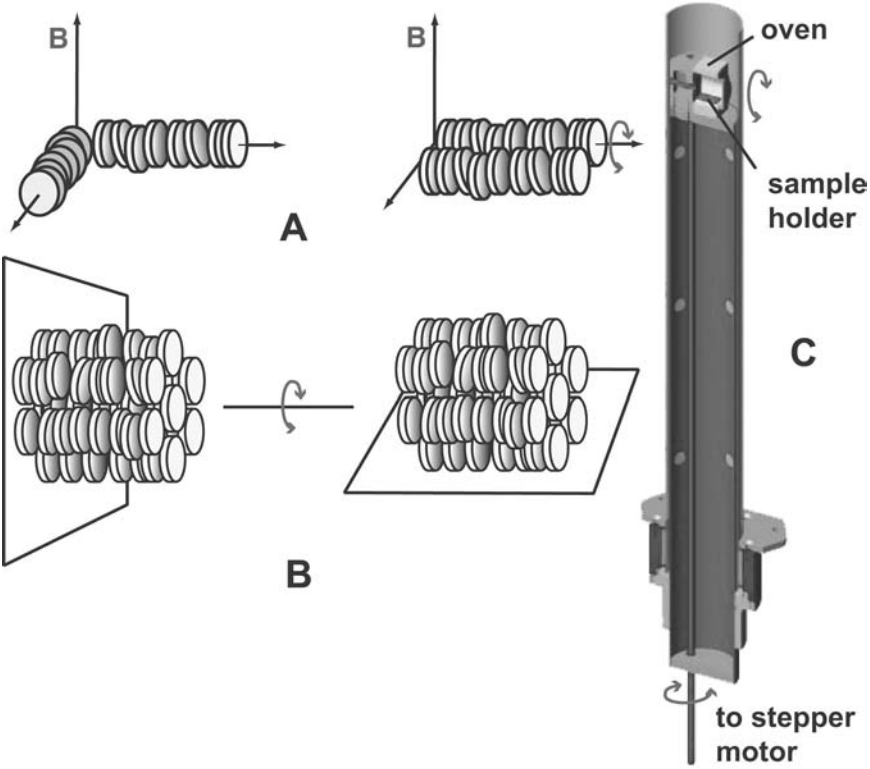

FIGURE 1 A) Illustrates the formation of a monodomain with the director along the X-axis upon spinning about the X-axis; B) Illustrates the formation of homotropically and homogeneously orientated monodomains depending on the orientation of the spinning substrate with regard to the magnetic field; C) Shows a cartoon of an alignment apparatus that allows heating and spinning of samples in an NMR magnet.

fields if they show lyotropic mesomorphism in certain solvents. Here, the phase transition from the fluid isotropic or lyotropic nematic solution to the thermotropic columnar mesophase is achieved by a controlled evaporation of the solvent. Figure 1 shows a special alignment apparatus that was designed for NMR magnets. A shortcoming of this approach is the huge shrinkage of volume that causes the formation of defects. Finding optimum conditions has been proven difficult and LC cells can not be used if the solvent needs to be evaporated [13].

Simple mechanical forces were found to align bulk materials of some highly viscous columnar mesophases. Aligned columnar hexagonal mesophases of phthalocyanines were obtained by rolling the waxy material into a stick [14]. The mechanical shear field aligned the columns perpendicular to the applied field, parallel to the long axis of the stick. Similarly, fibres of DLCs were carefully elongated while in the temperature range of the columnar mesophase and gave monodomain samples that could be studied by X-ray diffraction [15].

A very unusual approach was taken by Okabe *et al.* who incorporated charge transfer complexes of DLCs into mesoporous silica films [16]. Highly aligned films of lamellar and hexagonal architectures were obtained by casting, spin- and dip-coating solutions of partially polymerized mixtures onto substrates.

Technologically more important is the alignment of DLCs in thin films and sandwiched devices. Columnar π,π-stacks of aromatic DLCs provide quasi one-dimensional charge-carrier conduction along their stacks, which makes them attractive as materials in organic light emitting devices. Generally, DLCs make available an alternative approach to conducting organic materials fundamentally different to conducting polymers, and the self-organizing properties of DLCs promise low-cost solution techniques for the preparation of organic electronic devices [17].

A homogeneous alignment of the columnar mesophase is required for devices such as organic field effect transistors (OFETs), while organic light emitting diodes (OLEDs) and photovoltaic cells dictate a homeotropic alignment. Phenomenologically, the homogeneous alignment of the columnar mesophase, or edge-on alignment of the DLCs, is the preferred alignment of viscous columnar mesophases. More fluid columnar mesophases of DLCs have the tendency of self-aligning homeotropically at a solid interface [18]. A homeotropically aligned film always is a monodomain but homogeneous alignment does not necessarily result in a macroscopic in-plane alignment (unidirectional) of the columns, which is essential for the formation of a monodomain.

Monodomains of homogeneously aligned discotic columnar mesophases were obtained by the Langmuir-Blodgett (LB) technique [19]. This approach preferentially works with non-symmetrically substituted DLCs that have polar and non-polar edges (side-chains). The in-plane alignment is obtained during the dip-coating process and is purely based on difficult to control flow fields. Macroscopic monodomains have been obtained but the method is rather tedious and integration in industrial production processes is not feasible. Also, non-symmetrically substituted DLCs are more difficult to synthesise. Liquid crystallinity, however, is not a requirement for the formation of aligned π,π-stacks in LB films [20].

Self-assembling monolayers on gold surfaces displayed properties similar to LB films. The cores of triphenylene derivatives with 1-2 thiols attached to their side-chains align homogeneously and form domains of columnar stacks with different in-plane orientation [21]. The domain size increased with decreasing spacer length between the thiol end groups and the core. A face-on, homeotropic, alignment was found for derivatives with thioethers attached to the core whereas terminal thiols attached to more than two side-chains per molecule resulted in the formation of non-uniform layers.

Other techniques that usually generate a homogeneous alignment of the columnar mesophase involve the application of mechanical shear fields or flow fields. A shear field is most easily applied to a columnar mesophase sandwiched between two substrates by moving the top substrate with respect to the bottom substrate. Alignment by flow coating works particularly well with lyotropic columnar mesophases [22]. The alignment is not disturbed upon evaporation of the solvent as long as any crystallization of the DLC is suppressed. Both techniques produce highly aligned discotic columnar mesophases of thicknesses between several nanometers and micrometers. They might also be scaled up and integrated in production processes.

Polymer dispersed DLCs gave homogeneous alignment when mechanically sheared. This alignment was locally disturbed by a laser beam and produced homeotropic domains. Long lasting patterns could be written into the layer and make them potentially useful for optical storage applications [23]. In a related attempt, homeotropically aligned triphenylene derivatives were locally reoriented by vibrational excitation with a free electron laser [24].

In liquid crystal displays calamitic LCs are predominantly aligned by interactions with specially treated or prepared surfaces [25]. Surface treatments developed for calamitic LCs, however, have surprisingly little affect on the alignment of DLCs. In fact, hexaalkoxy triphenylene aligns homeotropically when cooled down from its isotropic phase, independent of the type of alignment layer [26]. More viscous DLCs, such as compounds based on phthalocyanines, show small domains of more homogeneously aligned columns, again mostly unaffected by the type of surface.

Obviously, alignment layers made for calamitic LCs do not provide specific interactions with most DLCs and it is the property of the discotic columnar mesophases that defines the alignment. To our knowledge, very little work has been invested in designing alignment layers for a discotic columnar mesophase and very few systematic investigations on their surface alignment have been published.

The first and most comprehensive paper dates back more than 20 years [27]. Several hexaesters and hexaethers of hexahydroxy triphenylene displaying nematic and columnar discotic mesophases were tested on a variety of different surfaces. Glass surfaces and glass surfaces coated with disc-shaped aromatic molecules such as hexaphenol, mellitic acid, hexahydroxytriphenylene, and rufigallol promoted a homeotropic alignment of both, the nematic and the columnar discotic mesophases. Similarly, freshly cleaved surfaces of apophyllite and muscovite aligned the mesophases homeotropically or had no observable effect on the alignment. Uniform homogeneous alignment was achieved only for some of the nematic discotic mesophases on slides coated with obliquely deposited silicon oxide.

Polarized IR measurements elucidated the alignment of a truxene hexaester and hexapentyloxy triphenylene on silicon and ZnSe wafers. Both derivatives align homeotropically between silicon and are tilted by 57° on ZnSe [28].

Face-on self-assembled monolayers were studied on highly oriented pyrolitic graphite (HOPG) [29]. Graphite surfaces generally promote homeotropic alignment of columnar mesophases. An interesting dependence on the film thickness, however, was observed for thin layers of non-discotic self-assembling columnar LCs on HOPG [30]. Thin, only a few columnar diameter thick films displayed a homogeneous alignment but thicker films gave a homeotropic alignment.

Other alignment studies involved homeotropically aligned hexaalkoxy triphenylenes coated on substrates with interdigitated electrodes for sensor studies. The changes in lateral conductivity suggested a more homogeneous, disordered orientation of the molecules at the air interface while the orientation at the solid interface remains homeotropic throughout the measurements [31]. Selective conductivity responses were reported for different absorbed small organic molecules. Presumably, the orientation of triphenylene molecules at the free surface layer, and therefore the lateral conductivity of the surface layer, is affected by the absorbed organic gas molecules.

Highly viscous discotic columnar mesophases do not easily form monodomains and prefer a homogeneous alignment, as stated earlier. This is a dilemma since the highly ordered viscous mesophases display the highest charge carrier mobility and would be the best suited candidates for organic electronic devices. Some DLCs have been shown to gradually change from a very fluid columnar mesophase to a highly ordered solid like mesophase, such as hexaalkylthiotriphenylene and alkoxytriphenylene derivatives containing one group that sterically and/or electronically interacts with neighbouring molecules in the same column [32]. Those compounds self-align homeotropically in their fluid mesophase and remain aligned upon cooling into the solid like discotic columnar mesophase. The higher ordered mesophases were obtained mainly because crystallisation occurred at much lower temperature or was fully suppressed.

Increasing the size of the discotic cores was shown to be even more beneficial to the charge carrier mobility but those compounds, such as substituted phthalocyanines and hexabenzocoronenes [33], do not display fluid mesophases or an isotropic liquid phase at temperatures below their decomposition temperatures. Alignment and monodomain formation are notoriously difficult to obtain if possible at all.

We currently investigate a new approach that aims for a homeotropic self-alignment of discotic columnar mesophases as required for devices such as OLEDs and photovoltaic cells. The approach makes use of strong electrostatic interactions between charged DLCs and oppositely charged surfaces. Electrostatic layer-by-layer assembly is a very recent approach to surface coating based on electrostatic forces and was developed for notoriously difficult to process polyelectrolytes. The preparation of these robust films is simple but the obtained multilayer films are disordered and have poorly developed interfaces between each layer [34]. Our objective is to combine the advantages of electrostatic layer-by-layer assembly with the self-organizing properties of DLCs to allow an electrostatic layer-by-layer self-assembling of ordered multilayer films.

Our first set of polyionic DLCs is based on tetraazaporphyrines and is of the general structure shown in Figure 2. The compounds do not display thermotropic mesomorphism and their lyotropic mesomorphism is currently under investigation. Gel phases were formed by the short chain carboxylic acids. Their adsorption onto hydrophilic (anionic) glass substrates is being investigated by alternating dip-coating from dilute solutions

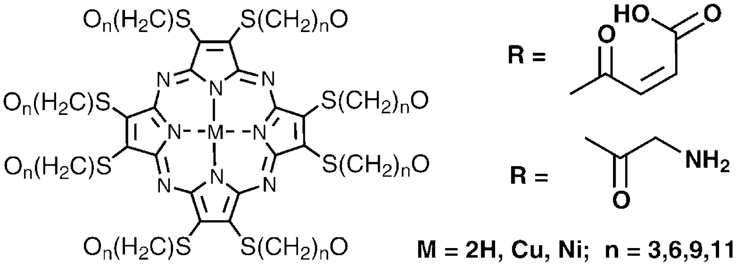

FIGURE 2 Octaacids and amines of octaalkylthio tetraazaporphyrins.

of an anionic and a cationic tetraazaporphyrin, first starting with the cationic derivative. The layer build-up and the average orientation of the DLCs are monitored by polarized UV/VIS-spectroscopy.

ALIGNMENT OF OLIGOMERIC DLCS

Principally, aligned networks of DLCs can be obtained in two different ways. A low molecular weight DLC containing polymerizable groups is aligned first and then polymerized or, alternatively, DLCs are linked together to an oligomer or polymer and the columnar mesophase of the oligomer is aligned.

A subsequent polymerization of aligned monomolecular DLCs requires polymerizable groups to be attached to the DLC [35]. This is particularly problematic for sterically demanding polymerizable groups [36] or relatively weak discogens such as triphenylenes [37] because the mesophase temperature ranges are drastically reduced or the mesomorphism is lost altogether. Also, the polymerization process of those compounds results in shrinkage of the material which can cause defects in thin films. Well aligned monodomains were obtained by partial crosslinking of substituted triphenylenes and subsequent elongation of the elastic material. The improved alignment in the elongated material could be fixed by completing the crosslinking of the polymer [38].

Oligomers of DLCs have certain advantages over low molecular weight DLCs. They are known to increase the temperature range of discotic columnar mesophases [39], and disc-shaped aromatic molecules that do not form columnar mesophases on their own may display columnar liquid crystalline phases when linked together. Oligomers do not crystallize on cooling but rather form an anisotropic glass of the preceding mesophase structure [40]. Finally, the oligomeric approach provides a wide flexibility in molecular design.

Unfortunately, linear oligomers do not align homeotropically and the domain sizes of homogeneously aligned films are usually very small. An explanation for this behaviour is based on intrinsic strain that is due to the many different ways the discotic monomers of the oligomer can be positioned within the same or different columns. The critical length at which the monomer dominated alignment is lost was shown to be three monomers [41].

In contrast, a single example of a star-branched oligomer has been described and formed macroscopic monodomains of columnar stacks that self-aligned homeotropically on a glass substrate [42]. The difference in behaviour might be due to the identical symmetry of the star-heptamers and the hexagonal columnar mesophase.

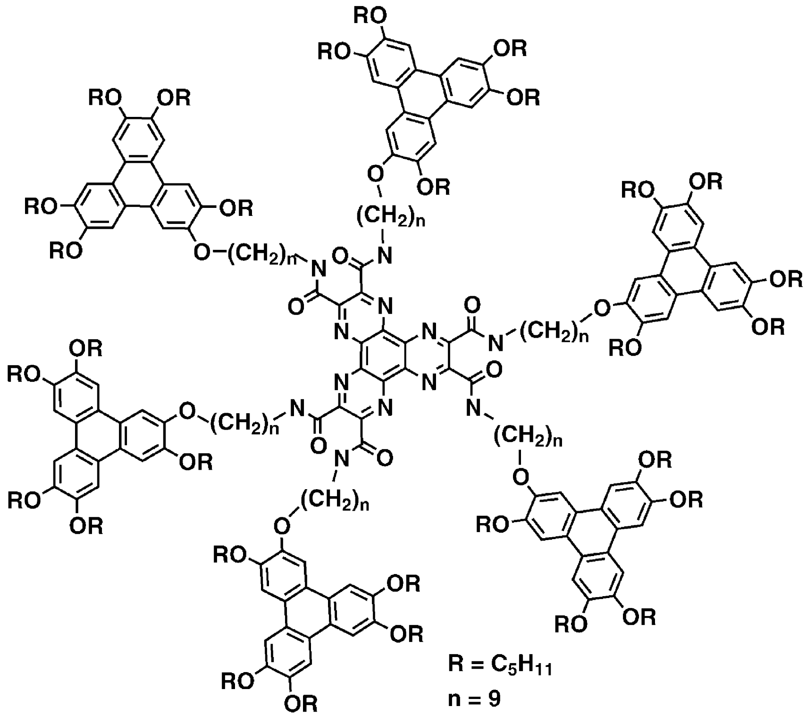

FIGURE 3 Hetero-heptamer with n-type semiconducting hexaamido hexaazatriphenylene as central molecule and p-type semiconducting hexaalkoxytriphenylenes as ligand.

We have started synthesising new star-shaped oligomers of n-type [43] and p-type semiconducting DLCs to demonstrate the generality of this observation. The chosen star-branched structure of the oligomers also allows for the design of hetero-heptamers containing two different molecular entities that self-assemble into nanophase-segregated π,π-stacks of identical entities. Examples of a star-shaped homo- and hetero-heptamers with electron rich triphenylene based DLCs and electron deficient hexaazatriphenylene based DLCs are shown in Figure 3. Nano-patterned arrays of electron- and hole-semiconducting stacks can be envisioned if one of the entities is easily reduced and the other easily (photo)oxidized, respectively. Such a material would have the highest possible interface area (heterojunction) between the n-type and p-type semiconducting columns of discotic liquid crystals. Organic photovoltaic cells of unprecedented efficiency should be obtainable from these materials if the charge carrier mobility along the columns is sufficiently high.

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