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INVITED ARTICLE

Playing with discs

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The hierarchical self-assembly of disc-shaped molecules leads to the formation of discotic liquid crystals. These intriguing materials are of fundamental importance not only as models for the study of energy and charge migration in self-organised systems, but also as functional materials for various device applications. This has fostered numerous developments in this field. In this article, we have summarised the author's and the collaborators' research work on discotic liquid crystals.

Keywords: discotic liquid crystals; columnar phase; nematic phase; liquid crystal displays; organic semiconductors

1. Introduction

Shape anisotropy is the primary factor for any organic molecule to display mesomorphism. Until 1977, it was the belief that only rod-like molecules, having a much higher length than width, could show liquid crystalline properties, commonly known as calamitic liquid crystals (LCs). However, in 1977, Chandrasekhar *et al.* realised that not only rod-like molecules, but also compounds with a disc-like molecular shape are able to form mesophases (*1*). These are referred to as discotic liquid crystals (DLCs). Generally, these compounds have flat or nearly flat cores surrounded by a plural number of aliphatic chains (*2*). Mesophases formed by disc-shaped molecules are primarily of two types: nematic and columnar. In the discotic nematic phase, there is an orientationally ordered arrangement of discs with no long-range translational order. On the other hand, in the columnar phase, the discs are stacked one on top of another to form columns (Figure 1) (*2*). Over the past thirty years, the field of DLCs has grown rapidly, due to the realisation of their potential in various device applications, and to date about 3300 compounds of this category are known.

The synthetic work we have carried out in this area may be broadly divided into the following categories: (1) the discovery of new cores and ring structures; (2) the development of new reagents for the synthesis of DLCs; (3) the molecular engineering of the discotic nematic phase and room-temperature discotic nematic LCs; (4) new methodologies and new materials and (5) discotic-functionalised nanomaterials. These will be presented briefly in the following sections. Throughout the text, Cr stands for crystal, Col = columnar phase, $\mathrm{Col_h}$ = hexagonal columnar phase, $\mathrm{Col_r}$ = rectangular columnar phase, $\mathrm{Col_t}$ = tetragonal columnar phase, $\mathrm{Col_p}$ = columnar plastic phase, $\mathrm{N_D}$ = nematic discotic phase, g = glass transition and I = isotropic phase.

2. New cores and ring structures

2.1 Decacyclene core

Decacyclene (DC), a putative fullerene precursor, is a symmetric, large polycyclic aromatic molecule present in the carbonaceous mesophase. Since the discovery of the carbonaceous mesophase in the early 1960s, there has been a continuous search for a well-defined, chemically stable system that could serve as a model for this unstable phase and these efforts resulted in the discovery of DLCs in 1977. The common DLC has been characterised as a flat molecule comprised of a rigid polycyclic aromatic core surrounded by four to nine aliphatic side chains. It was a common belief that 'three elongated chains would insufficiently fill the space around the core and, therefore, could not allow the existence of columnar mesophase'. We anticipated that by increasing the size of the polycyclic aromatic core and keeping the minimal constraint around the core to avoid crystallisation, one could achieve liquid crystallinity regardless of the number, nature and size of the side chains. These mesophases could model the carbonaceous mesophase more closely than other known discotic systems.

Accordingly, trialkanoyl-DC based discotic mesogens **2** were designed and synthesised by a direct Friedel-Crafts acylation of commercially available parent hydrocarbon **1** (Scheme 1) (*3*). The reaction

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*Email: skumar@rri.res.in. Professor Kumar received the 2008 ILCS LG Display Mid-Career Award at ILCC 2008 for his work on the synthesis of discotic liquid crystals, including the first room temperature system, design of nematic discotic materials, innovative chemistry and the inclusion of nanomaterials in discotic systems.

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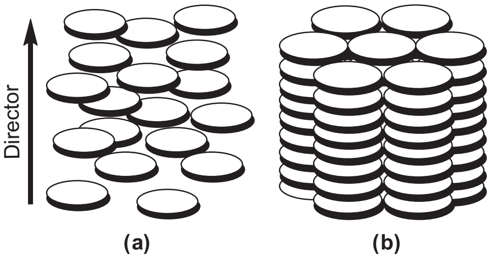


Figure 1. Schematic representation of: (a) discotic nematic; (b) columnar phase.

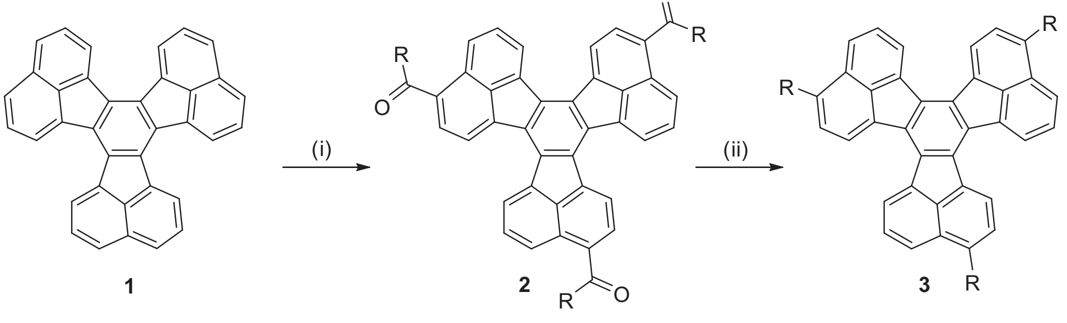
proceeds with very high regioselectivity and only the C_3 symmetric 1,7,13-trialkanoyl-DC could be isolated. Two liquid crystalline derivatives, triheptanoyloxy- **2a** and trioctanoyloxy-DC **2b**, have been prepared. Both compounds show a high tendency to aggregate, even at high dilution, as evident by nuclear magnetic resonance (NMR) studies. They display the following mesomorphism; **2a** (Cr 92.8 Col_t 115 Col_r 262 I) and **2b** (Cr 98 Col_t 108.5 Col 240.5 I). Hysteresis is observed on cooling. The deoxygenated hydrocarbons **3a** and **3b**, obtained by reduction of the keto groups, were found to be non-mesomorphic. Both compounds show double melting behaviour. 1,7,13-triheptyl-DC **3a** first melts at 90°C to give an isotropic liquid that crystallises immediately into fine needles and finally melts at 118°C. Similarly, 1,7,13-trioctyl-DC **3b** first melts at 92°C to give an isotropic liquid that crystallises at 95.7°C to another isomorph, which finally melts at 120°C.

The liquid crystalline triheptanoyloxy-DC **2a** has recently been studied for its electrochemical properties and a photovoltaic device using **2a** as an electron transport material has been prepared (*4*). Evidently, DC-based DLCs have huge potential. More LC derivatives of this core, particularly low temperature or room temperature DLCs, are required in order to investigate the intriguing properties of these materials and to find out their applications in industry.

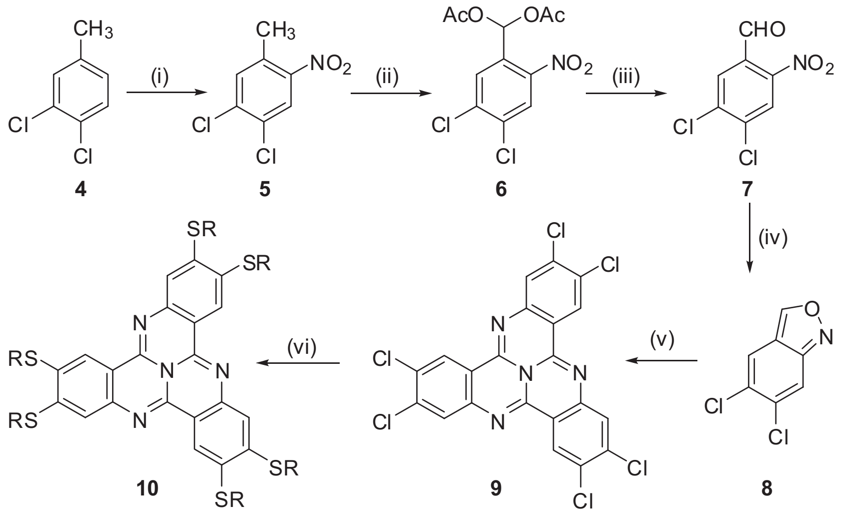
2.2 Tricycloquinazoline core

The tricycloquinazoline (TCQ) molecule is very attractive in materials science for a variety of reasons. It possesses C_3 symmetry, it displays extraordinary chemical and thermal stability, its derivatives are coloured, it exhibits low ionisation potential and interesting spectroscopic and electronic properties. Due to its electron deficient nature, it can be doped with a reducing agent and can be used as an n-type organic semiconductor. Because of these reasons, we focused our attention on this core and reported a wide spectrum of homologous 2,3,7,8,12,13-hexaalkoxy- and hexathioalkoxy-TCQ derivatives with alkyl side chain length varying from 1 to 18 carbon atoms (*5–7*). We have also used branched alkoxy chains to prepare the room temperature LC derivatives (*8*). The synthesis of these materials is shown in Schemes 2 and 3.

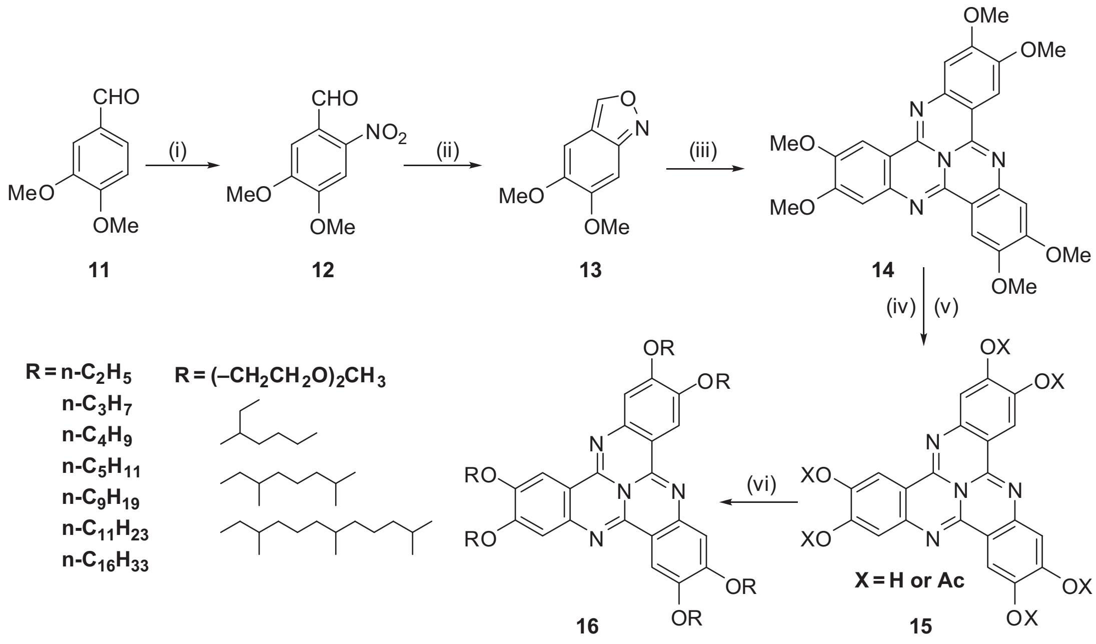
Polarising optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray investigations confirmed the presence of the Col_h phase in TCQ-derivatives having peripheral chains of 3–18 carbon atoms. In general, the phase transition and isotropic temperatures decrease gradually with increasing length of peripheral chains. The use of branched alkoxy chains (e.g. 3,7-dimethyloctyloxy and 3,7,11-trimethyldodecyloxy) reduces the clearing points significantly (<200°C). The 2,3,7,8,12,13-hexakis(3,7,11-trimethyldodecyloxy)-TCQ is of great importance as it does not crystallise up to −50°C and, thus, forms a stable Col_h phase at room temperature and goes to the isotropic phase at 143°C. The intercolumnar distance is dependent on the peripheral chain length, whereas the interdisc distance within the discotic molecules was estimated to be approximately 0.34 nm in normal alkyl chains substituted derivatives. The small angle X-ray scattering of the 2,3,7,8,12,13-hexakis(3,7,11-trimethyldodecyloxy)-TCQ displays a centre to centre distance of 0.329 nm, one of the lowest core–core separations known in DLCs and, therefore, making



Scheme 1. Synthesis of DC derivatives: (i) $RCOCl/AlCl_3/ClCH_2CH_2Cl$/reflux, 38%; (ii) $NH_2NH_2.H_2O/KOH$/reflux, 50%.



Scheme 2. Synthesis of 2,3,7,8,12,13-hexathioalkoxy-TCQ derivatives: (i) AcOH, H_2SO_4, HNO_3, 0–5°C, 90%; (ii) Ac_2O, H_2SO_4, CrO_3, 0–5°C, 3 hours, 20–60%; (iii) EtOH, H_2O, HCl, reflux 1 hour, 58%; (iv) AcOH, Sn, room temp. 20 hours, 15–55%; (v) Sulpholane, AcOH, NH_4OAc, 150°C, 7–24 hours, 10–40%; (vi) n-Thiol, potassium-*tert*-butoxide, NMP, 100°C, 10 minutes, 50%.



Scheme 3. Synthesis of 2,3,7,8,12,13-hexaalkoxy-TCQ derivatives: (i) HNO_3, 90%; (ii) AcOH, Sn, r.t. 50%; (iii) Sulpholane, AcOH, NH_4OAc, reflux, 25%; (iv) HCl, Py, 230 °C, 50%; (v) HCl, Py, 230°C, Py, Ac_2O, 90%; (vi) KOH, DMSO, RBr, 20–80%.

the molecule very attractive for one-dimensional charge migration.

Photo induced charge carrier mobility in the order of 10^{-3} cm^2 V^{-1} s^{-1} in the Col$_h$ phase of the hexathio-TCQ derivative has been observed, but because of its very high clearing temperature, full characterisation could not be done. We have recently carried out time of flight (TOF) measurements on 2,3,7,8,12,13-hexakis(3,7,11-trimethyldodecyloxy)-TCQ, using a pulsed N_2 laser as the light source for carrier generation. The mobilities for the positive and negative carriers were estimated to be 2×10^{-2} and 4×10^{-2} cm^2 V^{-1} s^{-1} at room temperature (20°C), respectively (*9*).

We have also studied the self-assembled monolayers (SAMs) of these materials on gold surfaces by scanning tunnelling microscopy, infrared spectroscopy, quartz crystal microbalance, and atomic force microscopy (AFM) (*10*, *11*). Cyclic voltammetry and NMR studies on 2,3,7,8,12,13-hexakis(2-(2'-methoxyethoxy)ethoxy-TCQ indicate its electron-deficient nature and its aggregation in acetonitrile solutions (*12*). Boden *et al.* prepared n-type one-dimensional conducting systems by doping alkali metals in hexahexylthio-TCQ and hexakis(2-(2'-methoxyethoxy)ethoxy-TCQ discotics (*13*, *14*).

Clearly, TCQ-discotics are very interesting for device applications. However, these materials have not been well explored, probably due to difficulties in synthesising these discotics. Yields, particularly in the trimerisation of anthranil (**8** or **13**) to TCQ (**9** or **14**), are generally poor and not reproducible. The addition of ammonium acetate periodically during the reaction improves the yield marginally. Efforts have to be made to develop new synthetic strategies to prepare known and new monomeric, oligomeric and polymeric TCQ discotics in large amounts to explore their full potential.

2.3 Dibenzo[g,p]chrysene core

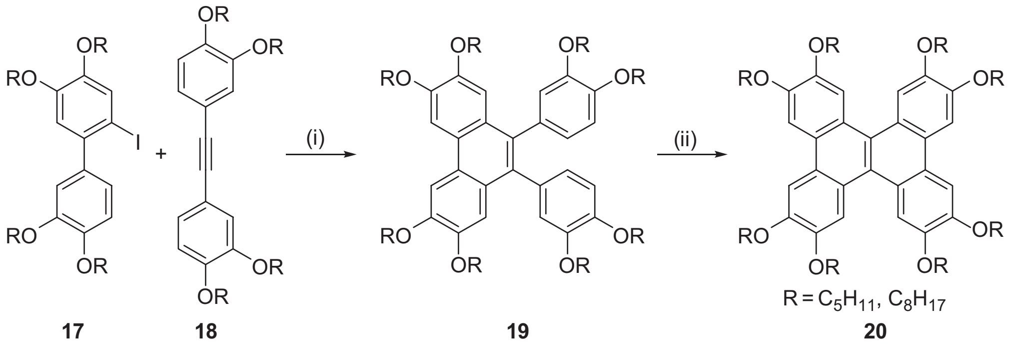
Dibenzo[g,p]chrysene (DBC) derivatives are interesting because of their notable fluorescent properties, such as good quantum yields, small Stoke shifts and long-lived exited states (*15*). Pyrolysis of bifluorenylidene has been reported to produce DBC via Stone-Wales rearrangement. Highly efficient blue–green emissive organic light-emitting diodes have been fabricated using bis(diphenylamino)chrysene derivatives, which were prepared from 2,7-dibromo-9-fluorenone via sequential reactions. Recently, Yamaguchi and Swager developed a novel oxidative acetylene cyclisation method to prepare DBC derivatives and incorporated these non-liquid crystalline chromophores into co-polymers for explosive detection (*15*).

As the DBC architecture is a flat, rigid and π-conjugated system, it is expected to form DLCs on peripherally long alkyl chains-substitution. Accordingly, molecules **20** were designed and the strategy followed to prepare these materials is outlined in Scheme 4 (*16*). A palladium-catalysed annulation reaction of diphenylacetylenes **18** with 2-iodobiaryls **17**, followed by oxidative coupling using $FeCl_3$, yields octaalkoxy-DBC **20**. Both the octapentyloxy- and octaoctyloxy-DBC derivatives do not display mesomorphism in their virgin state, but their charge-transfer (CT) complexes with trinitrofluorenone (TNF) exhibit columnar phases. Enantiotropic DLCs can be prepared by substituting the peripheral positions with dialkoxybenzoate groups (*17*).

2.4 Phenanathro[a]phenazine and phenanathro[b]phenazine derivatives

Polycyclic aromatic nitrogen heterocycles play an important role not only in biological science, but also in materials science. A large number of pharmaceuticals, pesticides, insecticides, dyestuffs, solvents, polymers and organic electronic materials are based on nitrogen heterocycles. Phenazine derivatives are well known for their antibacterial and insecticidal properties. Numerous phenazine-based dyes are used in the printing industry. The charge generating, transporting and photophysical properties of various phenazine derivatives have been realised (*18*). The incorporation of a phenazine unit into a triphenylene (TP)-based discotic architecture may result in novel materials with interesting material and biological properties. With this idea, we prepared some novel phenanthrophenazine derivatives.

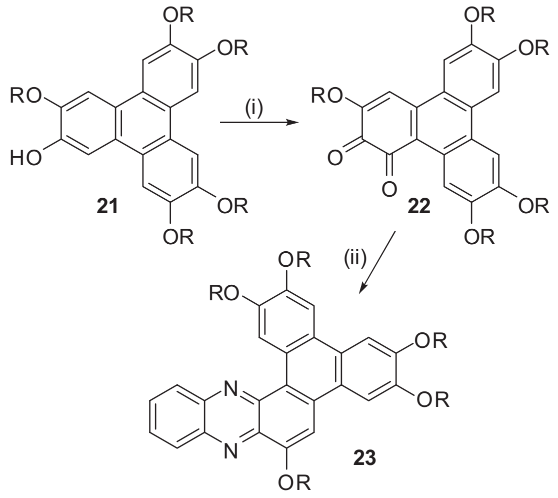
Phenazine derivatives are generally prepared by condensing a 1,2-diamino precursor with a 1,2-dione unit. During the course of our studies on TP-based DLCs, we realised that the ring oxidation of monohydroxy-pentaalkoxy-TP is extremely facile. Oxidation of 2-hydroxy-3,6,7,10,11-pentaalkoxy-TP **21** with ceric ammonium nitrate (CAN) gives a black 3,6,7,10,11-pentaalkoxy-TP-1,2-dione **22** in very high



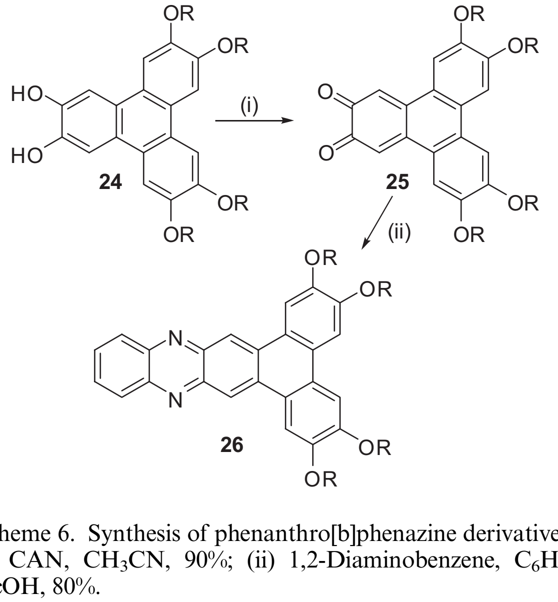
Scheme 4. Synthesis of octaalkoxy-DBC derivatives: (i) $Pd(OAc)_2$; 40%. (ii) $FeCl_3$, 20%.

yields (>90%). Reaction of this *o*-quinone with an equimolar amount of 1,2-phenylenediamine in benzene-acetic acid at room temperature for 2 hours furnished orange-red 2,3,6,7-tetrapentyloxy-phennanthro [a]phenazine **23** (Scheme 5). Two homologues with butyloxy- and pentyloxy-peripheral chains were prepared. Both display columnar mesophase over a wide temperature range (*19*).

Similarly, oxidation of 2,3-dihydroxy-6,7,10,11-tetrapentyloxy-TP **24** yields 6,7,10,11-tetrapentyloxy-TP-2,3-dione **25** (Scheme 6). Reaction of this *o*-quinone with an equimolar amount of 1,2-phenylenediamine yields 2,3,6,7-tetrapentyloxy-phennanthro[b]pheazine **26**, which exhibited a metastable monotropic columnar mesophase (*20*).



Scheme 5. Synthesis of phenanthro[a]phenazine derivatives: (i) CAN, CH_3CN, 94%; (ii) 1,2-Diaminobenzene, C_6H_6-AcOH, 80%.



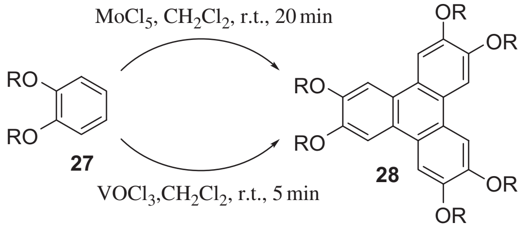
Scheme 6. Synthesis of phenanthro[b]phenazine derivatives: (i) CAN, CH_3CN, 90%; (ii) 1,2-Diaminobenzene, C_6H_6-AcOH, 80%.

The synthesis of these novel ring structures opens a route to prepare a variety of new materials using various alkyl and alkoxy-substituted 1,2-phenylenediamines. These unsymmetrical, coloured, polar, heteroaromatic supramolecular architectures could be potential candidates for various devices, such as photovoltaic solar cells, light-emitting diodes, etc. It would also be interesting to look at the medicinal properties of these novel phenazines.

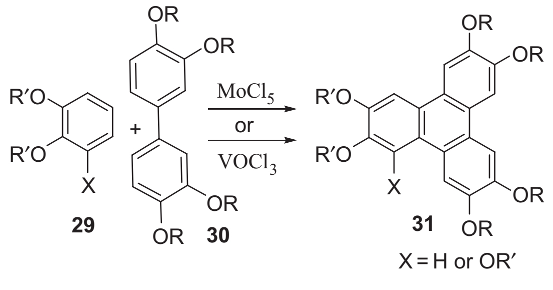
3. Development of new reagents for the synthesis of DLCs

3.1 $MoCl_5$ and $VOCl_3$: new reagents for the synthesis of hexaalkoxytriphenylenes

Hexasubstituted-TPs are the most widely synthesised and studied discotic mesogens and a number of methods have been developed for their synthesis (*2b*, *2c*). We have discovered that molybdenum(v) chloride is a novel reagent for the oxidative trimerisation of 1,2 dialkoxybenzenes to hexaalkoxy-TPs in high yield (*21*). The reaction occurs under very mild conditions with or without an acid catalyst and in a very short time at room temperature (Scheme 7). Synthesis of unsymmetrical TPs was achieved by coupling a 3,3',4,4'-tetraalkoxybiphenyl and an appropriate 1,2-dialkoxy- or 1,2,3-trialkoxybenzene (Scheme 8) under similar reaction conditions.



Scheme 7. Oxidative trimerisation of 1,2-dialkoxybenzene to hexaalkoxytriphenylene using $MoCl_5$ or $VOCl_3$.



Scheme 8. Synthesis of unsymmetrical and heptaalkoxy-triphenylenes using $MoCl_5$ or $VOCl_3$.

We have also discovered that vanadium oxytrichloride, a liquid oxidising agent, may be used as a novel reagent for the oxidative trimerisation of 1,2-dialkoxyloxybenzenes to hexaalkoxy-TP in high yields (Scheme 7) (*22*). Unlike other reagents, which are solid and insoluble in organic solvents, $VOCl_3$ can be readily handled using standard syringe techniques or by using an addition funnel. $VOCl_3$ has a high solubility in various organic solvents, which could be a reason for the almost spontaneous trimerisation of dialkoxy benzenes into hexaalkoxy-TPs. The handling of the reagent and work-up of the reaction are very easy; there is no need to use concentrated sulphuric acid, which is an obvious advantage, and the product yields were high. The effects of reagent concentration, solvent, and temperature have been studied in detail. Unsymmetrical and heptaalkoxy-TPs can also be prepared using $VOCl_3$ (Scheme 8). The reagent can also be used to prepare dibenzopyrene (dibenzo[*fg,op*]naphthacene – DBN) discotics (Scheme 9) (*23*).

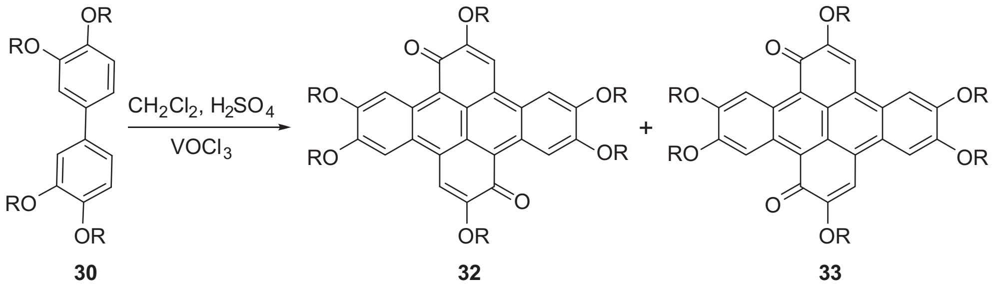
3.2 B-Bromocatecholborane for selective ether cleavage of hexaalkoxytriphenylenes

Hydroxy-functionalised TPs are required to prepare a variety of DLCs, such as unsymmetrical DLCs, mixed-tail derivatives, discotic dimers, oligomers and polymers. The physical properties of these non-conventional LCs are significantly different to those of conventional LCs (*24*). However, because of synthetic problems in obtaining functionalised TPs, the potential utility of these intriguing materials has not been fully explored. We have developed several methods to prepare various hydroxyl-alkoxy-TPs (*25–28*). Here, we present our results on the ether cleaving ability of *B*-bromocatecholborane (Cat-B-Br) to prepare various hydroxyl-alkoxy-TPs (*26*).

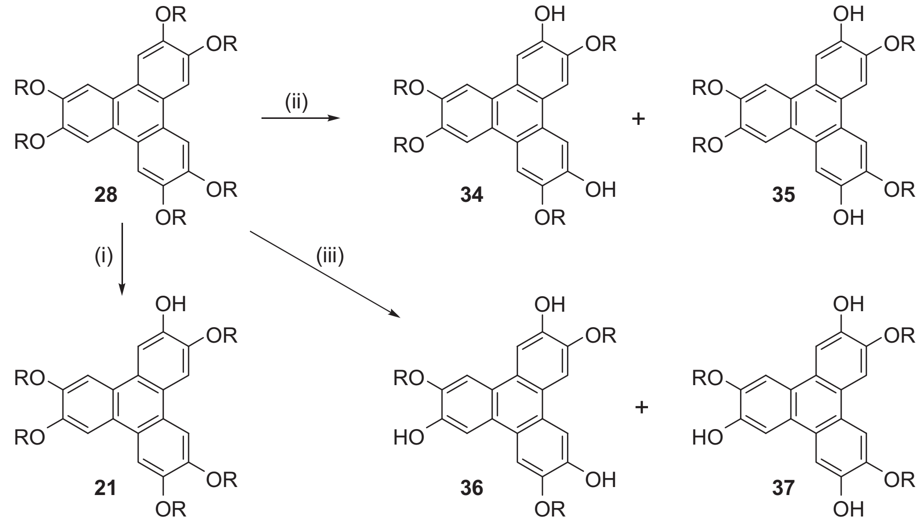
We anticipated that this monofunctionalised, bulky Lewis acid will have better regioselectivity than commonly used boron tribromide and may cleave selectively one, two and three alkoxy chains of hexaalkoxy-TP. The reagent can be readily prepared by reacting catechol with boron tribromide. The colourless solid is stable for months, but can be stored more easily as CH_2Cl_2 solutions. However, we observed that the freshly distilled product gives better results and very different reaction conditions are required for a commercial reagent.

When hexapentyloxy-TP (H5TP) **28** ($R = C_5H_{11}$) is treated with 1-1.2 equivalents of the reagent in dichloromethane at room temperature for 24–48 hours, it gives mainly the monohydroxy-H5TP **21** with a minor amount of unreacted H5TP (Scheme 10). An increase in reaction time and temperature does not change the yield of monohydroxy-H5TP significantly. An increase in the concentration of the reagent starts the cleaving of the other alkoxy chains and variable amounts of mono-, di-, and tri-functionalised-H5TP are obtained. The reaction of H5TP with 2-2.4 equivalents of Cat-B-Br at room temperature to prepare difunctionalised-H5TP always gives a mixture of mono- **21**, di- **33** + **35,** and trifunctionalised-H5TP **36** and **37**. However, the formation of trihydroxytriphenylenes can be checked by performing the reaction at 0°C and the dihydroxy derivatives can be isolated in reasonably good quantity, although the purification was tedious.

Out of the four possible isomers of dihydroxy-H5TP, we found that only 2,6- and 2,7-isomers, **34** and **35**, respectively, are the major products. These two isomers can be separated by a careful and repeated chromatography over basic alumina in a ratio of about 6:4. A trace (less than 1%) of the 2,11-isomer was also present in some cases, but the 2,3-isomer, as expected because of the bulkiness of the reagent, was completely absent. The real advantage of this monofunctionalised, bulky Lewis acid was found in the preparation of trifunctional TPs. Treatment of H5TP with 3.6 equivalents of Cat-B-Br in dichloromethane at room temperature for 36 hours gives exclusively two products, the symmetrical 2,6,10-trihydroxy-3,7,11-tris(pentyloxy)-TP **36** (61%) and the non-symmetrical 2,7,10-trihydroxy-3,6,11-tris(pentyloxy)-TP **37** (38%).



Scheme 9. Oxidative dimerisation of tetraalkoxybiphenyl using $VOCl_3$.



Scheme 10. Synthesis of mono-, di- and trihydroxy-TPs using *B*-bromocatecholborane: (i) Cat-B-Br, 1.2 eq.; (ii) Cat-B-Br, 2.5 eq.; (iii) Cat-B-Br, 3.6 eq.

4. Molecular engineering of discotic nematic phase and room temperature discotic nematic liquid crystals

Though there are several applications of LCs, such as temperature-sensing (medical thermometers), solvents in chemical reactions, in chromatography, in spectroscopy, in holography, etc., they have been extensively exploited in electro-optical display devices, such as watches, calculators, telephones, personal organisers, laptop computers, flat panel televisions, etc. The twisted nematic (TN) and supertwisted nematic (STN) display devices have dominated commercial displays since their invention. The LC layer in these devices is exclusively the calamitic LC. A vast number of calamitic nematic LCs having room temperature mesophases, such as cyanobiphenyls, phenylpyrimidines, phenylcyclohexanes, Schiffs' bases, etc., have been synthesised and used in practical displays. The major disadvantage with these types of devices is the narrow and non-uniform viewing cone, which is considered to be an unacceptable aspect of their performance. We have disclosed a novel approach to overcome this problem by utilising discotic nematic LCs instead of calamitic nematic LCs (*29*). The LC device prepared using hexalkynylbenzene-based discotic nematic LC shows a wide and symmetrical viewing angle and no reversal of contrast ratio in any direction.

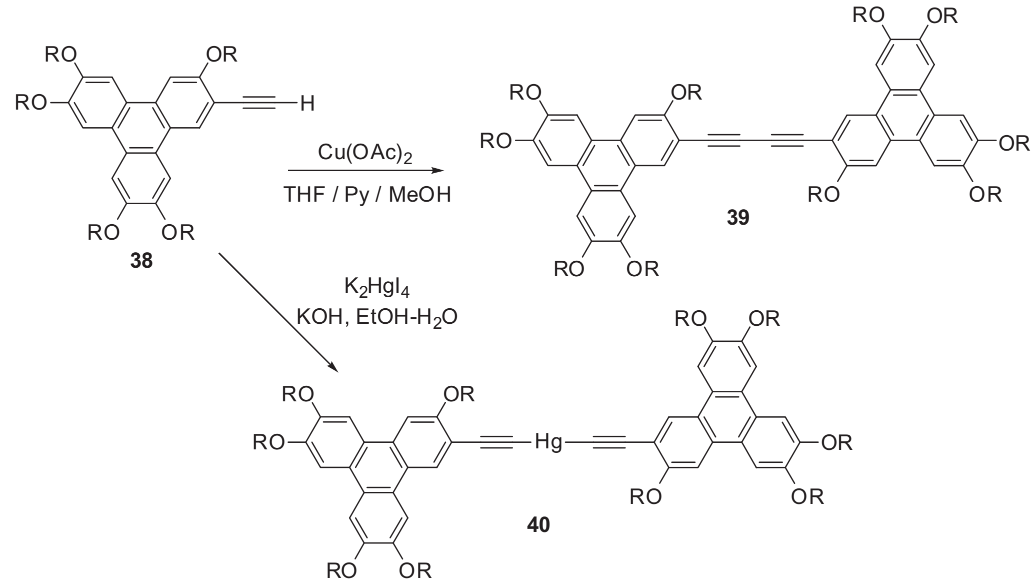
Compared to the large number of calamitic molecules showing a nematic phase, disk-shaped molecules showing the discotic nematic phase N_D are rare. Moreover, the N_D phase formed by these materials is high temperature with a narrow thermal range. For any LC device application, the temperature range of the mesophase and its stability well below and above room temperature are amongst the most important criteria. Therefore, it was desirable to find room-temperature discotic nematic materials.

The primary objectives of this research program were (a) the design and synthesis of organic molecules that can form a discotic nematic mesophase and, (b) synthetic modifications in known discotic nematic phase-forming materials to stabilise the nematic phase well below and above room temperature.

4.1 Design and synthesis of discotic nematic liquid crystals

The architectural design of DLCs is still in its infancy. While it is often easy to design DLCs forming columnar phases with basic structural features, flat or nearly flat aromatic cores surrounded by plural flexible side chains, it is rather difficult to design molecules that may form the N_D phase. This could be a reason why only a comparatively small number of nematic DLCs are known so far.

The majority of DLCs form columnar mesophases, probably due to the intense π–π interactions of polyaromatic cores. In order to get the nematic phase, sufficient steric hindrance around the core has to be introduced so that the rigid molecules may stay in a more or less parallel position, having only orientational order, but losing their long-range translational order. We anticipated that linking two discotic molecules via a short rigid spacer might create some steric hindrance due to overlapping or interdigitating aliphatic side chains and a weak distortion of the over all planarity of the molecule. This may reduce strong π–π interactions and, therefore, is likely to show a discotic nematic phase.



Scheme 11. Synthesis of diacetylene-bridged discotic dimers.

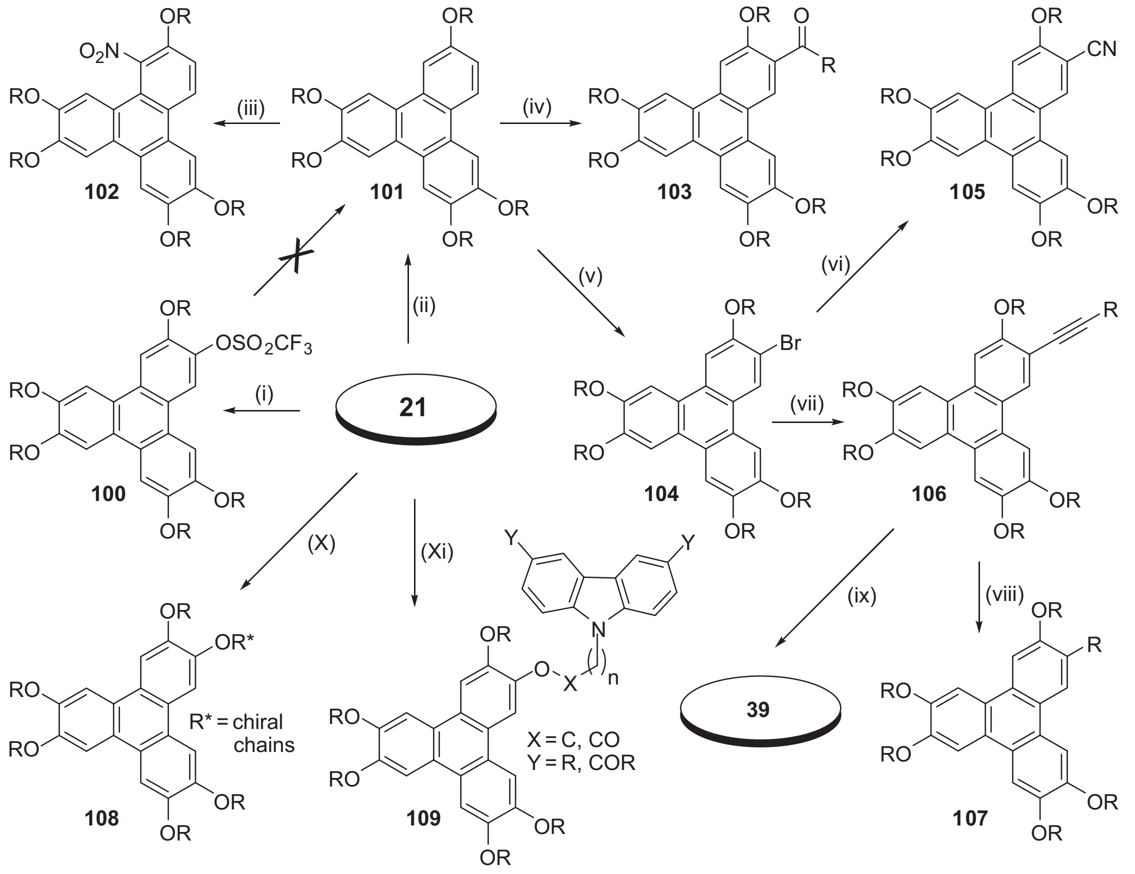
Accordingly, dimers **39** were designed to verify this idea (*30*). These twins were prepared by the dimerisation of free monoacetylenes **38** (Scheme 11), which in turn can be prepared from monobromo-pentaalkoxy-TP (Scheme 12). As predicted, all the dimers form discotic nematic phase over a wide temperature range. Replacing one of the alkoxy chains by thioalkoxy **99** (Scheme 13) does not change the nature of the mesophase, but displays a slightly lower isotropic transition temperature (*31*). Discotic dimers, obtained by linking two discotic units via a mercury atom **40** (Scheme 11), exhibit a metastable N_D phase (*32*). However, when the TP units were replaced by simple mono-, di- or trialkoxybenzene units, the dimers do not show any nematic phase. They exhibit smectic and columnar phases, observed in normal planar molecules (*33*).

4.2 Design and synthesis of room-temperature discotic nematic liquid crystals

To prepare room-temperature discotic nematic LCs, we focused our attention on discotic multiynes (hexa- and pentaalkynylbenzene-based molecules), primarily because a number of compounds of this class are already known to show stable N_D phases and, therefore, some minor structural modifications may lead to materials having room-temperature discotic nematic phases.

The use of branched chains in LCs often reduces melting and isotropic temperatures. The mesophase range is generally gets widened, but the type of mesophase formed is not affected by the introduction of branching in many cases. The decrease in the transition temperature could be due to the disorder caused by branched chains and stereoheterogeneity. This methodology has been successfully applied to reduce melting and isotropic temperatures of several DLCs forming columnar mesophases. From the reported thermal data of alkyl- and alkoxy-substituted hexalkynylbenzene derivatives, it was clear that when the peripheral alkyl chains are attached to the phenyl ring in the hexaalkynylbenzene via an oxygen atom, the melting and clearing temperatures are higher compared to when the alkyl chains are directly attached to the ring. Therefore, it was logically concluded that the replacement of normal alkyl chains by branched alkyl chains connected directly to the phenyl ring would reduce the melting point of alkynylbenzene derivatives and thus, stabilise the mesophase. Compound **46** (Scheme 14) was designed on this basis and it was indeed found to exhibit a nematic phase at ambient temperature. The compound exhibits the nematic phase between −12°C and 68°C (*34*).

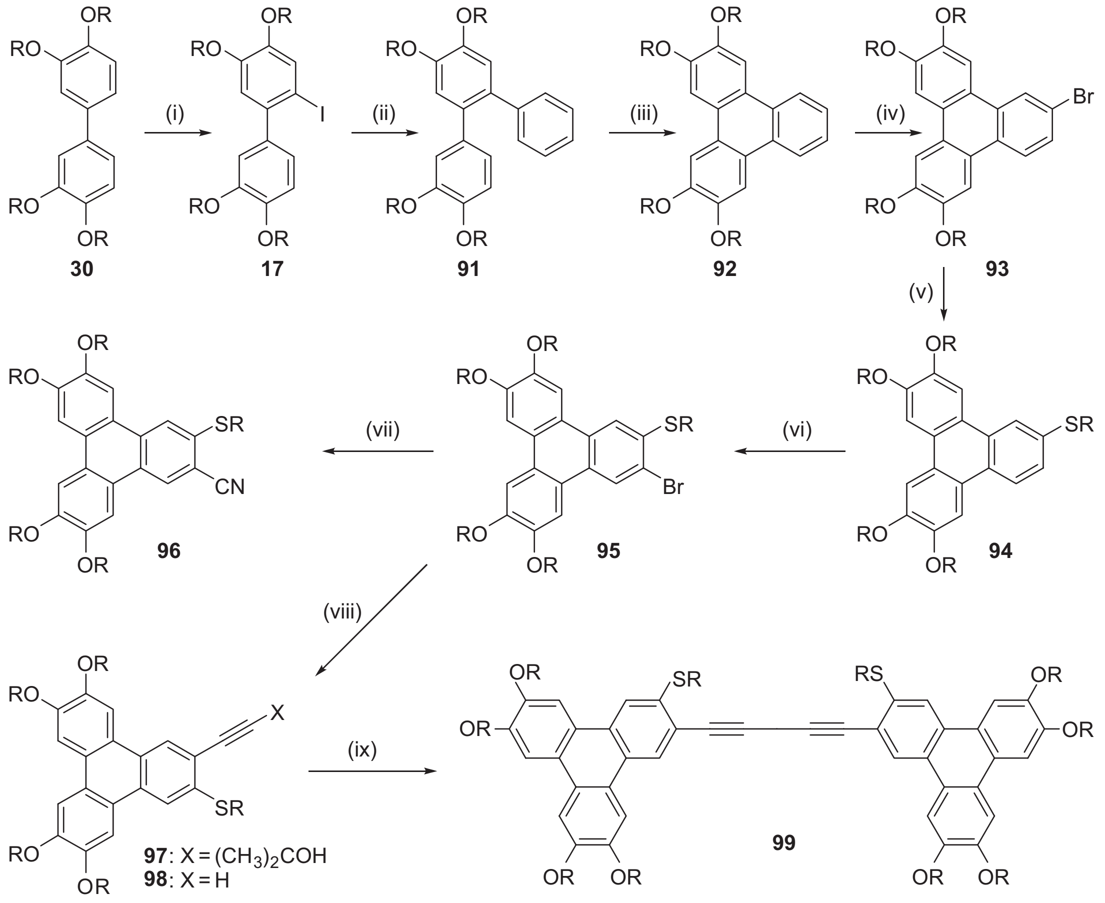
It has been observed that in the case of several TP-based discotic nematic LCs, a lateral methyl group substitution reduces the transition temperatures significantly. Accordingly, we designed several new hexa- and pentaalkynylbenzene based molecules (Figure 2) with a combination of normal and branched chains to look at room-temperature discotic nematics and to understand the structure–property relationship (*35*, *36*). Out of several molecules synthesised, two pentaalkynylbenzene derivatives (Structure **48**, X = H, R = 3,7-dimethyloctane (−35 N_D 40 I); X = CH_3, R = 3,7-dimethyloctane (−35 N_D 73 I)) displayed stable N_D phase at room temperature.



Scheme 12. TPs derived from mono-functionalised-TP (**21**): (i) CF_3SO_2Cl/Py; (ii) 5-chloro-1-phenyl-tetrazole/K_2CO_3; Pd/C, $EtOH/H_2$; (iii) HNO_3; (iv) $AlCl_3$/RCOCl; (v) Br_2/CH_2Cl_2; (vi) CuCN/NMP; (vii) $RC{\equiv}CH$/Pd/Cu/PPh_3/Et_3N; (viii) H_2/Pd/C; (ix) $Cu(OAc)_2$; (x) Py/R*COCl.

We prepared a novel LC display device employing discotic nematic material (*37*). This device exhibits many improvements over a conventional TN display device using a calamitic nematic material. The device is simple to fabricate, has excellent viewing angle characteristics showing a wide and symmetric viewing angle profile and has much less difference in the pixel capacitance between the ON and OFF states resulting in a reduced cross talk problem. However, the response time of the device was slower than conventional TN devices due to the high viscosity of the N_D material. To overcome this problem we have doped, in small concentrations, a long chain alkane compound to the parent room-temperature discotic nematic material. Systematic studies show that both the switch ON and switch OFF response times show a significant decrease, i.e. the device switches faster, in the case of the mixtures. It should be mentioned that wide and symmetric viewing angle characteristics remain unaffected by the addition of the dopant material. However, both the switch ON and switch OFF response times are still an order of magnitude slower compared to that of conventional TN devices. Considering the fact that these response times are not very different from those for the STN displays, the achievement of symmetric and wide viewing angle characteristics with a simple fabrication process makes this device quite interesting.

We have found that the discotic nematic LC, hexakis(4-nonylphenylethynyl)benzene (HNEB) (*38*), doped with the racemic chromium complex $Cr(Ocacac)_3$, shows a novel straight-needle texture with hexagonal columnar alignments, changing to a curved-needle texture under irradiation of circularly polarised light (CPL). This novel phenomenon is specific to the mixture of HNEB and $Cr(Ocacac)_3$. The formation of curved needles means that chiroselective photoinversion of racemic $Cr(Ocacac)_3$ by CPL irradiation induces a needle direction change in a DLC. The change in the chirality of $Cr(Ocacac)_3$ in HNEB induced by CPL irradiation, and the resulting nano-segregation of its enantiomers during cooling from the isotropic to mesophase of HNEB, are considered to influence changes in the alignment of columns and/or small domains of column aggregates in the DLC. This work



Scheme 13. Reagents and conditions: (i) iodine/iodic acid, CH_2Cl_2-AcOH, reflux, 45%; (ii) $C_6H_5B(OH)_2$, $[(C_6H_5)_3P]_4Pd$, Na_2CO_3, THF, reflux, 41%; (iii) CH_2Cl_2, $VOCl_3$, r.t., 80%; (iv) Br_2, CH_2Cl_2, 60%; (v) $C_5H_{11}SK$, NMP, $[(C_6H_5)_3P]_4Pd$, 73%; (vi) Br_2, CH_2Cl_2, 28%; (vii) CuCN, NMP, reflux, 35%; (viii) 2-methyl-3-butyn-2-ol, CuI, $PdCl_2(PPh_3)_2$, Et_3N, 60–70°C, 40%; (ix) KOH, toluene, reflux, 98%; (x) $Cu(Ac)_2$, THF–C_5H_5N–CH_3OH, reflux, 18%.

indicates the possibility of a nano-structure control by CPL, which could be applied to optical devices (*39*).

5. New methodologies and new materials

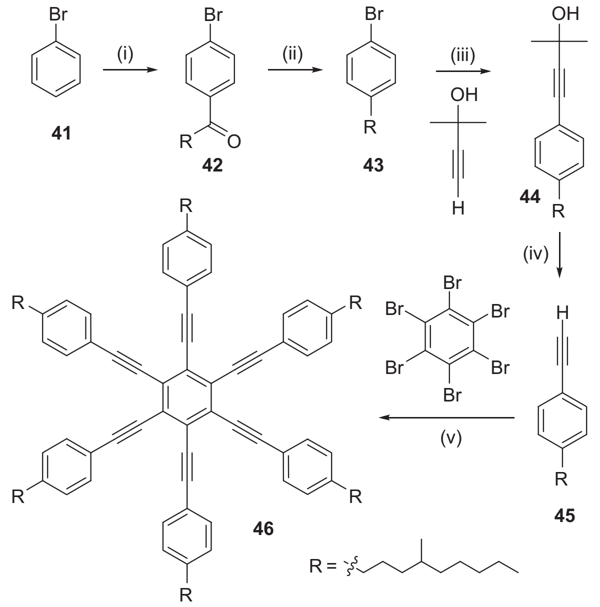
New materials are always required not only to understand the structure–property relationship, but also to find their application in devices. We have prepared a variety of novel DLCs and also developed several new methodologies to prepare them. Some of these are presented in the following sections.

5.1 Microwave-assisted facile synthesis of LCs

Microwave (MW)-assisted high-speed chemical synthesis has attracted a considerable amount of attention in the past decade. Almost all types of organic reactions have been performed using the efficiency of MW-flash heating. This is not only due to the fact that reactions proceed significantly faster and more selectively than under conventional thermal conditions, but also because of the operational simplicity, high yield of products and cleaner reactions with easier work-up. Surprisingly, this technology has not been much exploited for the synthesis of LC materials. We looked at the potential of MW dielectric heating to quickly prepare a variety of LC samples (*28*, *40–47*). We realised that some molecules, which are difficult to prepare under classical conditions, could be easily synthesised using MWs.

5.1.1 Microwave-assisted easy synthesis of rufigallol and its derivatives

Rufigallol is a molecule of both biological and materials science interest. It has been found to function as the core fragment for a remarkable family of DLCs. Rufigallol-based DLCs are interesting materials, as these molecules have an elongated core with a two-fold symmetry axis, they are coloured and exhibit



Scheme 14. Synthesis of hexaalkynylbenzene derivatives having a room-temperature N_D phase: (i) $RCOCl/AlCl_3$; (ii) NH_2NH_2/KOH; (iii) Pd^{II}, triphenylphosphine (TPP), CuI, Et_3N; (iv) KOH/toluene; (v) Pd^{II}, TPP, CuI, Et_3N.

important polymorphism, the core is electron-deficient in nature, they are thermally stable and their chemistry is fairly easy. The first discotic liquid crystalline hexaesters of rufigallol were prepared in 1980 and since then about 100 different discotic liquid crystalline derivatives of this molecule have been prepared and studied (*48*).

The synthesis of rufigallol in very poor yields was reported as early as 1836 by Robiquet, by the action of sulphuric acid on gallic acid and Grimshaw and Haworth reported the purification of rufigallol in 1956 (*48*). Since then, little further work has appeared and no new efficient method to prepare rufigallol was reported. We have observed (*42*) that the self-condensation of gallic acid in the presence of sulphuric acid can be achieved in high yield in about one minute using MW heating (Scheme 15). The resultant rufigallol was converted to several novel DLC derivatives by substitution with straight and branched-alkyl chains. We were particularly interested in preparing room temperature DLCs. In order to prepare novel room-temperature rufigallol discotics, we initially replaced all six peripheral *n*-alkyl chains with 3,7-dimethyloctyl chains. The reaction of rufigallol with 1-bromo-3,7-dimethyloctane in the presence of cesium carbonate under MW heating produced **52** (R = R’ = 3,7-dimethyloctyl) within three minutes. However, it was found to be a non-LC viscous oil. The synthesis of the unsymmetrical hexaethers was achieved by a two-step alkylation process. The unequal reactivity of the six phenolic groups, two of which are less reactive by virtue of being intra molecularly hydrogen bonded to the adjacent quinone carbonyls, was exploited. Etherification of rufigallol **50** under mild conditions produced 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone (**51** and **53**) without alkylating the hydrogen bonded C–1 and C–5 positions. These tetraalkoxy derivatives were further alkylated with the help of MW dielectric heating, as shown in the Scheme 15, under mild basic conditions to give the unsymmetrical hexaethers in very good yield within 3–4 minutes. It should be noted that under classical reaction conditions no product could be obtained in such a short reaction time. In this way, we prepared 20 different novel rufigallol derivatives. Out of these, 13 displayed stable columnar mesophase at room temperature. The compound **53** is particularly interesting as it has only four branched alkoxy chains and exhibited a very

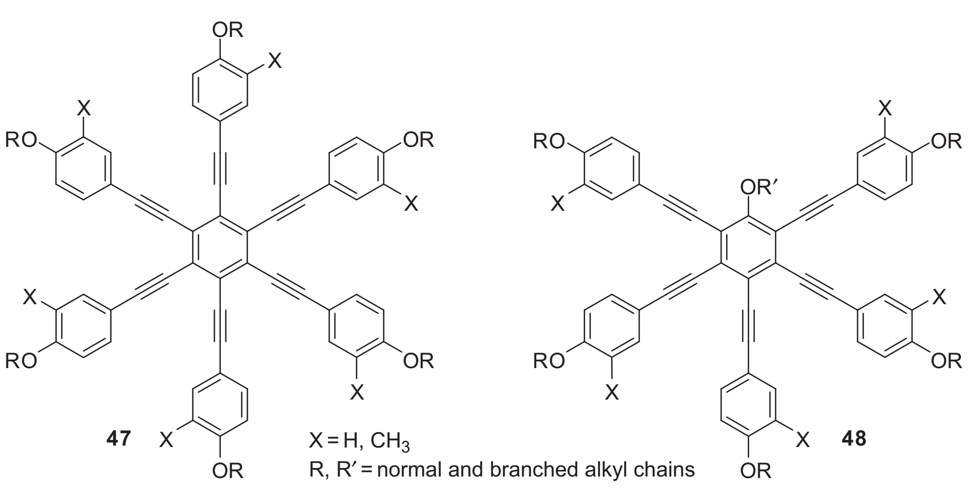
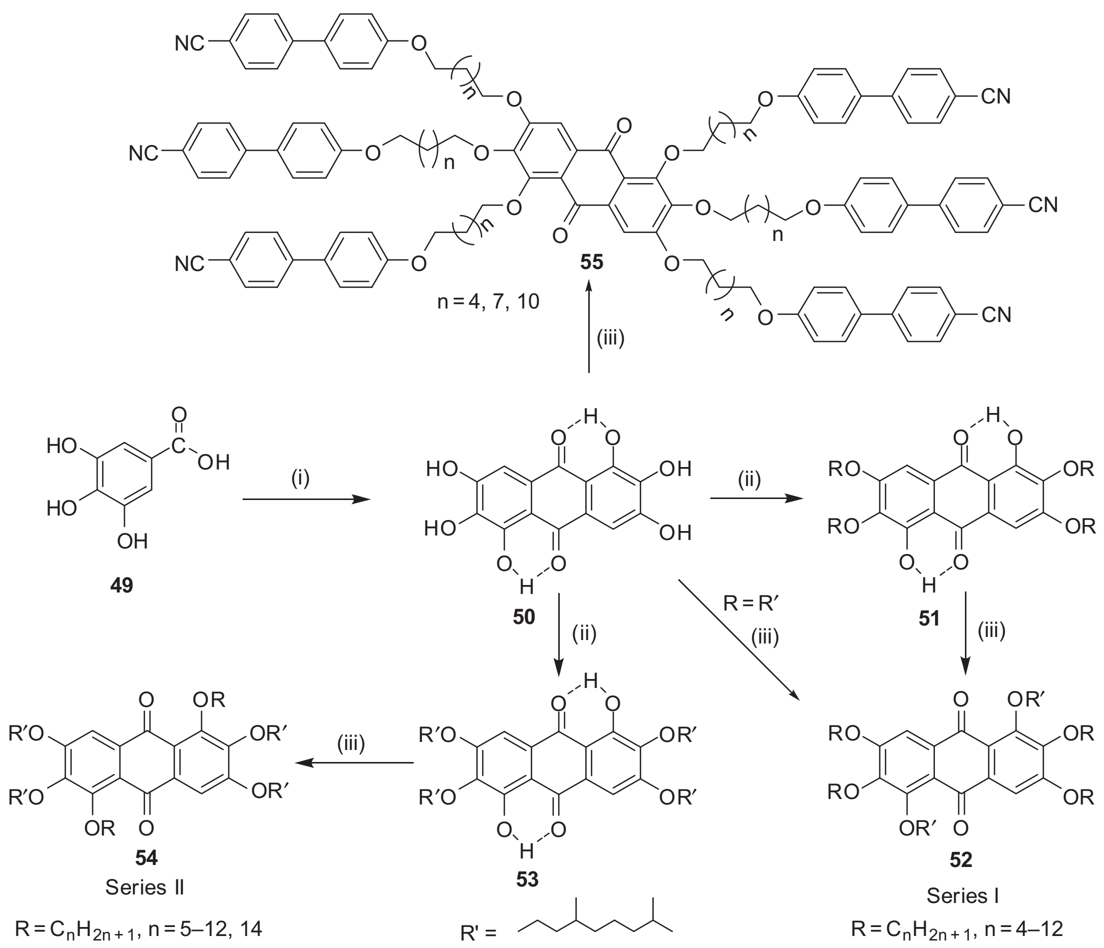


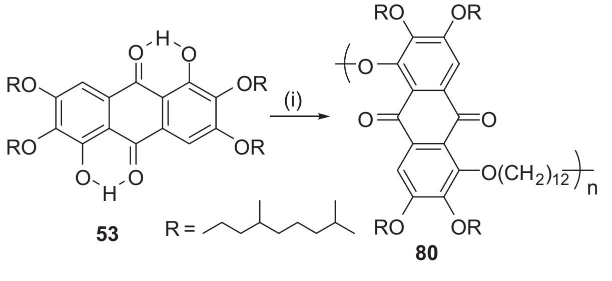
Figure 2. Structure of multiynes designed for room-temperature discotic nematics.



Scheme 15. Synthesis of novel liquid crystalline rufigallol derivatives: (i) H_2SO_4, MW, 90 sec., 80%; (ii) RBr or R'Br, DMSO, NaOH, 90°C 20h; (iii) RBr or R'Br, Cs_2CO_3, NMP, MW, 3–10 min.

broad mesophase stable at room temperature (Col_h132 I). The two free hydroxyl groups can be used to prepare main chain polymeric LCs (Scheme 16).

Novel liquid crystalline oligomers **55**, containing six rod-like cyanobiphenyl moieties connected to the rufigallol core via flexible alkyl spacers, were prepared by reacting rufigallol with terminally bromo-substituted alkoxycyanobiphenyls (*45*). The synthesis of the target compounds was challenging as classical reactions failed to produce these oligomers. DSC and POM analysis revealed the existence of a nematic phase with a shorter spacer and a smectic A (SmA) phase with the longer spacer. The compound with medium alkyl spacer shows both nematic and SmA phases at a higher temperature and a reentrant nematic phase at a lower temperature.



Scheme 16. Synthesis of rufigallol-based main chain polymers: (i) 1,12-dibromododecane/ Cs_2CO_3/*o*-dichlorobenzene/90°C/ 10 days.

5.1.2 Synthesis of monohydroxy-functionalised triphenylenes

The mono-functionalised TPs are valuable precursor molecules for the synthesis of a variety of discotic dimers, oligomers, polymers, networks and mixed tail derivatives. The synthesis of mono-functionalised TPs can be achieved in different ways. Most of the reagents used to prepare these materials are expensive, hazardous and difficult to handle. We were interested in finding an inexpensive and less hazardous method to produce these materials quickly. We have found that ionic reagents can be used to prepare mono-functionalised TPs in moderate yield (*28*). This methodology avoids all types of toxic, volatile and hazardous reagents. Developing green chemistry methodologies is one of the main themes of modern synthetic chemistry. In this context, the use of ionic liquids and MWs are powerful tools.

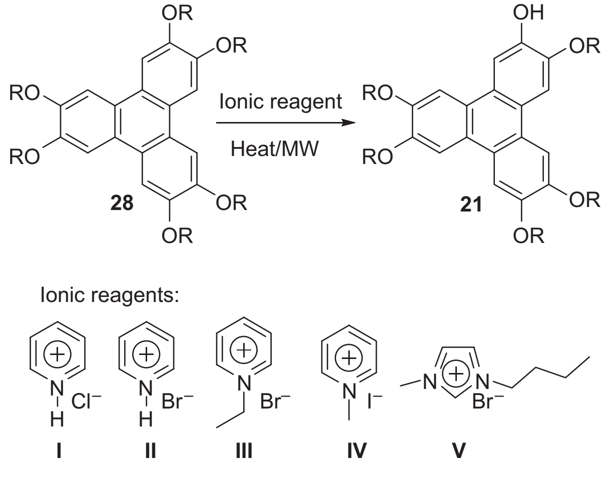
We have applied several pyridinium and imidazolium salts to examine the possibility of selective ether dealkylation in hexaalkoxy-TP under classical as well as MW heating conditions (Scheme 17). When different hexaalkoxy-TPs [R = -C_4H_9 (H4TP), -C_5H_{11} (H5TP), -C_6H_{13} (H6TP)] were treated with various ionic reagents (**I-V**) (Scheme 17), mono-functionalised-TP formed in moderate yields. For example, when hexabutyloxy-TP was heated with pyridine hydrochloride (no solvent) for 48 hours, about 35–40% of monohydroxy-pentabutyloxy-TP is formed. Other reagents afforded slightly lower yields. We looked at the potential of these reagents (**I-V**) to prepare mono-functionalised TP derivatives under MW irradiation. While reagents **I**, **III** and **IV** did not give any mono-functionalised TP under MW heating up to 10 minutes, reagents **II** and **V** produced the desired product. Thus, when a mixture of hexabutyloxy-TP and pyridine hydrobromide (3 equivalent) was irradiated at 360 W for 3 minutes, monohydroxy-pentabutyloxy-TP is formed in about a 36% yield. Enhancing the MW power to 600 W or 800 W did not increase the yield significantly. Compared to thermal heating, the yield of monohydroxy-TP was low under MW heating conditions, but the reaction can be finished in a very short time.

Although this method is not the best, yield-wise, it is an economic and green synthesis method for the preparation of monohydroxy-hexaalkoxy-TP derivatives. In all cases, no side reaction occurred and the unreacted starting material can be isolated easily, and can be recycled.

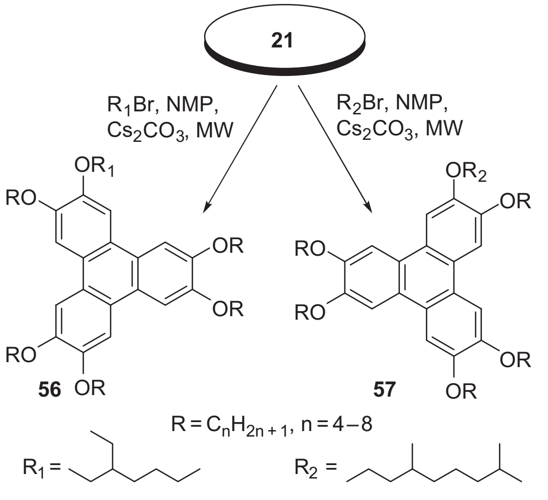
5.1.3 Microwave-assisted facile synthesis of liquid crystalline non-symmetrical hexaalkoxytriphenylenes

Two novel series of liquid crystalline non-symmetrical hexaalkoxy-TPs containing a branched alkyl chain have been prepared using MW dielectric heating (Scheme 18) (*44*). Thus, a few drops of n-methylpyrrolidinone (NMP) (0.2 ml) were added to a mixture of monohydroxy-pentaalkoxy-TP (0.15 mmol), cesium carbonate (0.3 mmol) and appropriate branched chain alkyl bromide (0.3 mmol) in a small glass vial. The vial was loosely covered with a rubber septum and then irradiated under MW for 30 seconds. The vial was taken out and again kept back after about one minute. The process was continued six to eight times until the reaction was completed (monitored by thin layer chromatography (TLC)). The reaction mixture was cooled and worked up by adding water, followed by extraction with dichloromethane. The crude product was purified by column chromatography and crystallised from methanol in about 79–87% yield.

Series-1 (**56**) contains the 2-ethyl hexyloxy group as the branched chain, whereas series-2 (**57**) contains 3,7-dimethyl octyloxy as the branched chain along with five normal alkoxy chains. The number of carbon atoms varies from four to eight in the normal alkoxy chains. The mesophase behaviour of the compounds has been characterised by POM, DSC and the mesophase structure has been characterised by X-ray diffractometry. All the compounds show enantiotropic mesophase transitions with Col_h structure. In series-1 the mesophase range and transition temperatures of all the compounds are lowered as compared to the parent compounds, whereas in series-2 the transition



Scheme 17. Synthesis of monohydroxy-TP using ionic reagents.



Scheme 18. Synthetic route of asymmetric hexaalkoxy TPs.

temperatures of all the compounds are lowered, the mesophase range for the lower members is decreased, however, the higher members show greater mesophase stability. Both melting and clearing temperatures of series-2 show a strong odd–even effect. The intercolumnar distance increases, as expected for compounds of both of the series, with an increase in alkyl chain length with some degree of interdigitation of the alkyl chains. The intercolumnar distances for the compounds of the series-2 are slightly higher than the compounds of the series-1. Some of these compounds display homeotropic alignment without using any special technique for the alignment of the columnar phase or the application of any external force.

5.1.4 Microwave-assisted synthesis of ionic discotic liquid crystals

We efficiently utilised MW dielectric heating to synthesise a number of ionic LCs (*41*, *43*). It is noteworthy that many of these compounds could not be prepared under classical heating conditions. Please see Section 5.7 for more detailed discussion.

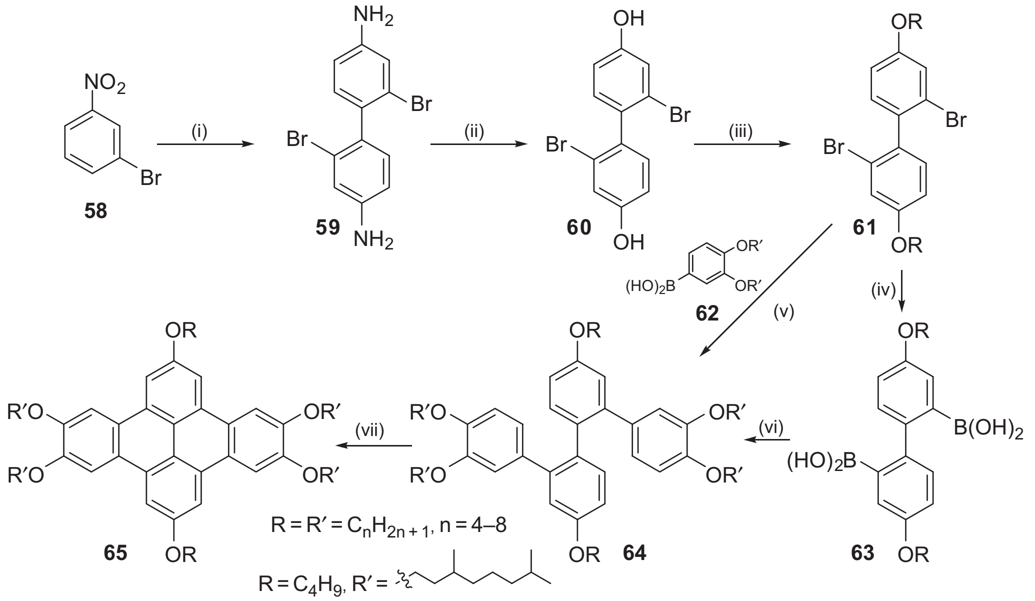
5.1.5 Microwave-assisted facile synthesis of discotic donor–acceptor oligomers

Many discotic donor–acceptor–donor (D–A–D) oligomers, which were difficult to prepare by conventional methods, were easily prepared using MW dielectric heating. For further discussion, please see Section 5.8

5.2 A rational synthesis of dibenzo[fg,op]naphthacene DLCs

DLCs based on 1,2,5,6,8,9,12,13-octaalkoxy-DBN have been the subject of many publications. Because of the larger core having more delocalised π electrons than TP, a greater degree of π–π interaction and hence higher charge carrier mobility was expected in these derivatives. However, the charge carrier mobility in the octaalkoxy-DBN derivatives was found to be one order of magnitude lower than in the columnar phase of hexaalkoxy-TP. This could be because of less ordered columnar packing due to the steric hindrance caused by the 'bay region' alkoxy chains and this results in lower charge carrier mobility.

We anticipated that the removal of these alkoxy chains from the 1 and 8 positions will give a better core–core interaction and, therefore, high charge carrier mobility. Energy minimised structures of an octa-substituted-DBN and hexasubstituted-DBN clearly suggested that hexasubstituted-DBN derivatives should form a more ordered columnar mesophase due to less steric hindrance of the bay region side chains. Accordingly, various 2,5,6,9,12,13-hexaalkoxy-DBN derivatives (Scheme 19) were designed. While the synthesis of octaalkoxy-DBN is very easy and well known, no synthetic route was available for hexaalkoxy-DBN derivatives. We developed a novel, versatile and



Scheme 19. Synthetic route to hexaalkoxy-DBN derivatives: (i) Zn/NaOH, HCl; (ii) $NaNO_2$/HCl; (iii) DMSO/KOH/RBr; (iv) n-BuLi/$B(OMe)_3$/HCl; (v) $Pd(PPh_3)_4$/Na_2CO_3; (vi) $h\upsilon$/I_2 or $FeCl_3$.

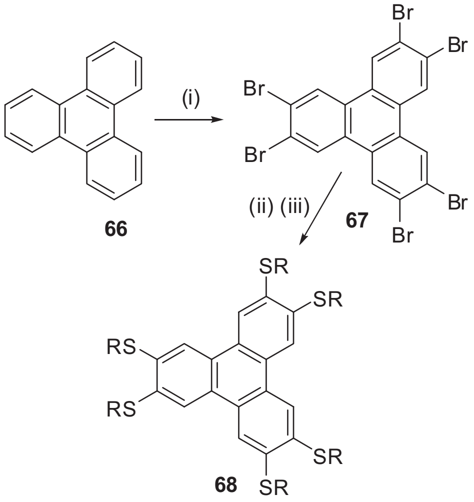
regiospecific synthesis of variable degree substituted DBN derivatives **65** (*49*, *50*). The methodology involves the preparation of a quaterphenyl **64** using a palladium-catalysed cross coupling of arylboronic acids, followed by chemical or photochemical cyclisation. All the DBN derivatives exhibit a single mesophase, which has been identified by X-ray diffractometry and optical microscopy as a hexagonal columnar phase. X-Ray results confirm that hexasubstituted DBN are more ordered than octasubstituted derivatives.

5.3 An improved synthesis of hexaalkylthiotriphenylenes

Interest in hexaalkylthio-TPs, and particularly in 2,3,6,7,10,11-hexahexylthiotriphenylene (HHTT), arises from the fact that this material displays a very high photoconductivity. HHTT forms a self-organised helical columnar phase at low temperatures with nearly crystalline order, in addition to the normal columnar phase. The photo-induced charge carrier mobilities up to 0.1 $cm^2 V s^{-1}$ were achieved in the H phase. With the exception of organic single crystals, these were the highest electronic mobility values reported until recently. However, now much higher mobilities have been achieved in some DLCs.

The synthesis of hexaalkylthio-TPs involves the thiolate anion substitution of 2,3,6,7,10,11-hexabromo-TP with an excess of sodium alkylthiolate in a polar aprotic solvent DMEU at 100°C for 1–2 hours in 40–55% yield. An improvement in this process was reported by generating the thiolates with sodium hydride in dry ether, instead of sodium ethoxide in ethanol, and subsequently heating with hexabromo-TP in DMEU at 70°C for 30 minutes. This enhanced the yield was 78–84% and the product was less contaminated with side products. We anticipated that the poor yield and contamination could be due to the nucleophilic dealkylation reactions, where the initially formed hexaarylalkyl sulphide may be attacked by excess thiolate anion to produce dialkyl sulphide and thiophenolate. In order to re-alkylate these exposed thiophenolate groups, we worked up the reaction mixture with the appropriate l-bromo- or 1-iodoalkane. This modification not only improved the yield substantially (>95%) but also afforded very high purity (>99.9%). Thus, thiolates were generated with potassium-t-butoxide in NMP and subsequently heated with hexabromo-TP at 70°C for 25 minutes in the same solvent, followed by quenching the reaction with an appropriate 1-bromoalkane (Scheme 20) to afford the desired products (*51*).

We have studied the electrical conductivity of well-aligned samples of HHTT in the pure as well as doped states (*52*). The dopant used was a small concentration (0.62 mol%) of the electron acceptor TNF. In the columnar phases, doping causes the AC (1 kHz) conductivity along the columnar axis ($\sigma_{||}$) to increase by a factor of 10^7 or, more relative to that in undoped samples ($\sigma_{||}$), attains a value of 10^{-2} S m^{-1}, which was the maximum measurable limit of our experimental set up. On the other hand, in the isotropic phase, doping makes hardly any difference to the conductivity. The frequency dependence of the conductivity has been investigated. The DC conductivity of doped samples exhibits an enormous anisotropy, $\sigma_{||}/\sigma_{\perp} \geq 10^{10}$, which is seven orders higher than that reported for any liquid crystalline system, and, to our knowledge, the largest observed in an organic conductor. We have also reported the first thermoelectric power studies on these ‘molecular wires’. The sign of the thermoelectric power is in conformity with the expected nature of the charge carriers, namely, holes.



Scheme 20. Synthesis of hexaalkylthiotriphenylenes: (i) Br_2; (ii) RSK/NMP; (iii) RBr.

We have also studied the dispersion of electron-deficient ferrocenium ions in HHTT as well as in hexaalkoxy-TPs (*53*). These composites were characterised using POM, DSC, X-ray, UV-vis, and dc and ac conductivity measurements. It was found that these composites form donor–acceptor systems that enhance the quasi-one-dimensional conductivity of the discotic system without altering the hexagonal columnar mesophase. The absorbance spectra confirm the formation of a CT complex between the electron-rich discotic molecules and the electron-deficient ferrocenium ions.

We have prepared SAMs of HHTT and other discoid molecules on gold (*54*). Monolayers are formed owing to the known strong interaction of these functional groups with the gold. The assembly of the compounds onto gold was monitored by quartz crystal microbalance measurements and the final structure of the monolayers was investigated by the contact angle, the grazing incidence Fourier transform infrared (FTIR), and AFM measurements. The discotic hexaalkylthioethers assemble essentially face-on and without detectable lateral order onto the gold substrate. The alkyl chains do not lie flat on the gold, but cover the aromatic cores.

We have studied orientational transition in HHTT as well as in hexaalkoxy-TPs by polarised FTIR spectroscopy (*55–57*). It has been observed that for the clean substrates (amorphous Si and polycrystalline ZnSe) the alignment achieved is planar. However, whether this alignment has a heterogeneous or homogeneous character depends on whether or not a substrate has one or more than one easy axis of orientation or a strong surface topology.

We have investigated the phase behaviour of HHTT and other TP discotics under hydrostatic pressure (*58–61*). HHTT displayed the normal enantiotropic phase transitions, i.e. Cr–helical phase (H), H–Col_h and Col_h–I up to 32 M Pa. The application of hydrostatic pressures above 32 M Pa results in the H and Col_h phases becoming monotropic, depending upon the applied pressure. The H phase was observed as a monotropic phase in the pressure region between 32 and about 180 M Pa. Thus, the I–Col_h–H–Cr transition sequence appeared only on cooling under these pressures, while the Cr–Col_h–I transition occurred on heating. Further increases in pressure above a second limiting value leads to the Col_h phase becoming monotropic. Thus the I–Col_h–Cr transition sequence appeared on cooling, while the Cr–I transition was observed on heating. The T vs. P phase diagram, based on the data obtained in the heating mode, contains two triple points; one is estimated as 40 M Pa, 77.2°C for the Cr–H–Col_h triple point and the other is extrapolated as 285 M Pa, 118.3°C for the Cr–Col_h–I triple point. These triple points define the upper limits for the appearance of the stable H and Col_h phases, respectively.

We have also carried out experimental and numerical studies on HHTT and other TP discotics to understand the influence of disorder on electronic excited states (*62–64*). We have determined the strength of dipolar/multipolar coupling and coupling due to orbital overlap for excitation transport in TP columnar LCs using time-resolved fluorescence spectroscopy and computer simulations. The fit of the experimental and simulated fluorescence decay reveals that the transfer process is dominated by short-range interactions (multipolar and orbital overlap), but the contribution of long-range dipolar interactions cannot be neglected. Triplet excitation transport occurring in the columnar liquid crystalline phase of a TP derivative at room temperature is studied by transient absorption spectroscopy with nanosecond resolution. We found that interactions due to intermolecular orbital overlap, responsible for energy transport in the triplet state, are also the main driving force for singlet excitation transport. The migration length of the triplet exciton is limited by structural defects to a few hundreds of TP cores.

We have carried out ^{13}C and ^{1}H NMR investigations on HHTT under both static and magic-angle spinning conditions (*65*). NMR spectroscopy is a powerful experimental tool for studies of solid and liquid crystalline phases. The motivation was to characterise the molecular order and dynamics and to investigate differences at the molecular level between the two mesophases: H and Col_h. It is shown that Col_h is a conventional columnar LC, where the molecular core undergoes fast rotation about the symmetry axis. The orientational order in this mesophase is lower and the temperature dependence of the order parameter is steeper than in other TP-based compounds. On the other hand, in the helical phase the core, similarly to the solid phase, is essentially rigid. The difference between the solid and helical phases is mainly manifested in an increased mobility of the aliphatic chains observed in the latter phase.

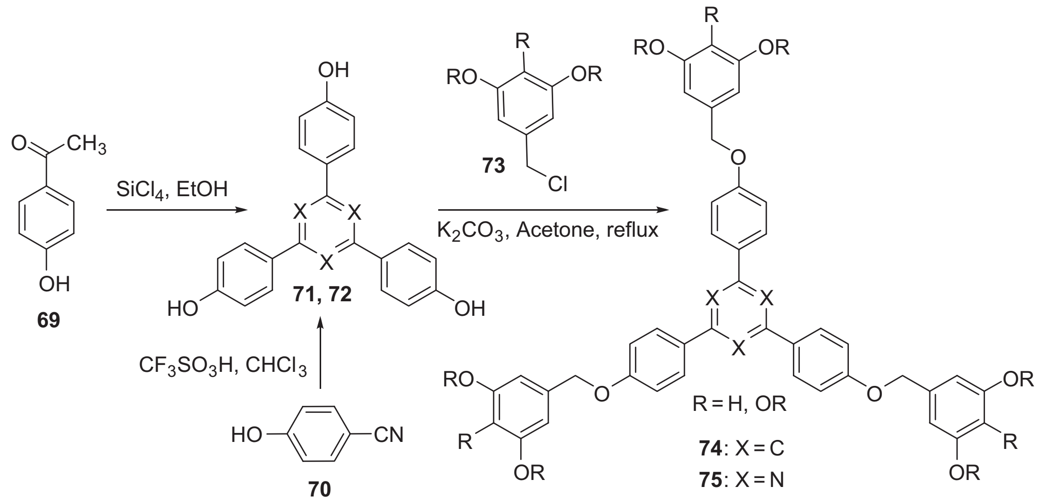
5.4 DLCs derived from 1,3,5-triphenylbenzene and 2,4,6-triphenyl-1,3,5-s-triazine

Polyether dendrimers with 1,3,5-triphenylbenzene and 2,4,6-triphenyl-1,3,5-s-triazine central cores with long alkyl chains at the peripheries were prepared as shown in Scheme 21. A number of hexaalkoxy- and nonaalkoxy-derivatives with different chain length were prepared and characterised. C_3-symmetric derivatives with n-hexyl and n-dodecyl chains at the periphery show mesophase properties when they are complexed with TNF at different temperatures (*66*).

5.5 Rufigallol-based DLCs

In Section 5.1.1 we described MW-assisted synthesis of rufigallol and its derivatives. Here we present the synthesis of some novel rufigallol discotics prepared by conventional methods. We were primarily interested in the synthesis of 1-hydroxy-2,3,5,6,7-pentaalkoxyanthra-9,10-quinones (hereafter written as monofunctionalised rufigallol), so that rufigallol-based novel electron-deficient dimers, oligomers, polymers, mixed-tails derivatives and discotic donor–acceptor systems can be prepared.

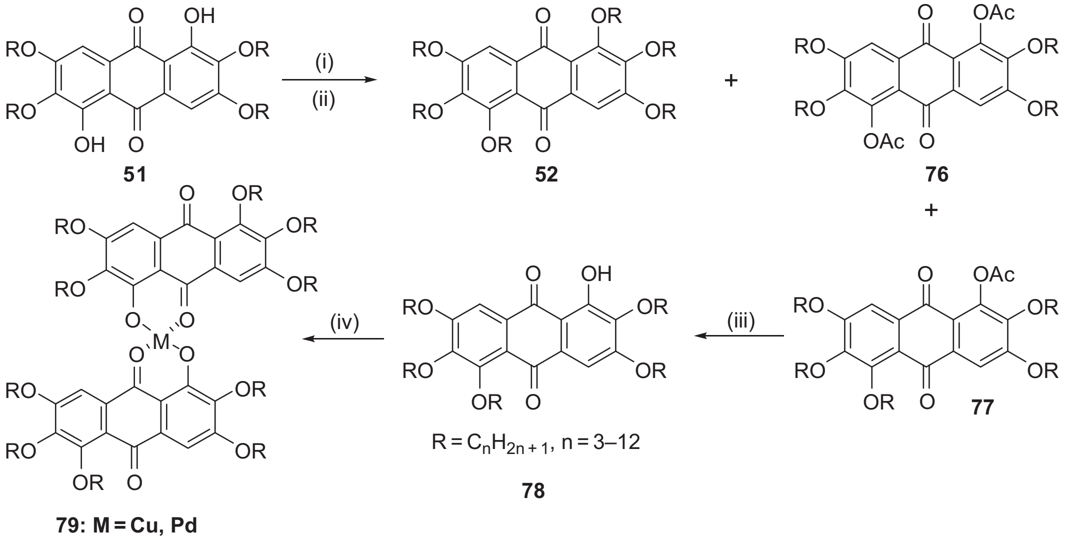
As mentioned earlier, in rufigallol, the hydroxyl groups at 1- and 5-positions are hydrogen bonded and, therefore, are less reactive. Under milder etherification conditions, the hydrogen bonded 1- and 5-positions do not get alkylated and thus 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone **51** (Scheme 15) (hereafter



Scheme 21. Synthesis of 1,3,5-triphenylbenzene and 2,4,6-triphenyl-1,3,5-s-triazine derivatives.

written as di-functionalised rufigallol) forms. In principle, partial alkylation of this material should give a mixture of unreacted (tetraalkylated), pentaalkylated and hexaalkylated products from which the desired mono-functionalised rufigallol can be isolated, but all efforts to isolate it in pure form from this mixture were met with failure. However, we realised that acetylation of the crude product furnished tetraalkoxydiacetoxy-rufigallol **76** (Scheme 22), pentaalkoxymonoacetoxy-rufigallol **77** and hexaalkoxy-rufigallol **52** (Scheme 15), having significant difference in R_f values on a chromatographic column, and thus all three products could be separated readily by column chromatography. Pure monoacetoxy-pentaalkoxy-rufigallol on hydrolysis afforded the desired mono-functionalised rufigallol **78**. The unreacted material can be recycled and the hexaalkylated by-product can be used for various physical studies. All the mono-hydroxy-pentaalkoxy-rufigallols **78** (Scheme 22) display hexagonal columnar phases over a wide temperature range (*67*).

We studied the phase behaviour of three hexaalkoxy-rufigallols under hydrostatic pressure using a high-pressure differential thermal analyser (*68*). Under pressure, on the one hand, the induction of the Col_r phase in hexaoctyloxy-rufigallol was observed. On the other hand, the stable Col_r phase of hexahexyloxy-rufigallol has a decreased temperature



Scheme 22. Synthesis of mono-functionalised rufigallol and derived metallomesogens: (i) DMSO/KOH/RBr; (ii) Ac_2O/Py; (iii) Aq. NaOH/EtOH; (iv) metal acetate/CH_3CN-Py.

range with increasing pressure and then the $\mathrm{Col_r}$ phase disappears under higher pressure.

We have looked at the temperature dependent dielectric spectroscopy of four homologous hexaalkoxy-rufigallols in the frequency range between 10 Hz and 10 MHz (*69*, *70*). The dielectric anisotropy ($\Delta\varepsilon' = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$) has been found to be positive throughout the entire range of the $\mathrm{Col_h}$ phase for all of the four compounds of this series. No relaxation phenomenon is found in the frequency range of the measurement, i.e. 10 Hz to 10 MHz.

5.5.1 DLCs derived from mono- and di-functionalised rufigallol

5.5.1.1 Rufigallol-based discotic metallomesogens

Metal complexes of β-diketonates were the first disc-like complexes reported to exhibit mesomorphism in the pure state. They are amongst the most widely synthesised and studied metallomesogens. They exhibit either calamitic or discotic mesomorphism, depending on subtle differences in the molecular structure. A comparison of the structure of the β-diketone molecule with that of a 1-hydroxyanthraquinone derivative clearly demonstrates a similarity between the two systems. Therefore, similar to the β-diketone system, a large number of metallomesogens can be prepared from monofunctionalised rufigallols. Refluxing monohydroxy-pentaalkoxy-rufigallols with metal acetate in acetonitrile-pyridine easily furnished metal-bridged rufigallol dimers **79** (Scheme 22). Two series of complexes, one with copper and the other with Pd, were prepared in this way (*71–73*). While the Pd complexes were found to be thermally unstable at higher temperatures, the Cu complexes of the same ligand were stable. Lower members of both the series are not liquid crystalline, but columnar mesophase can be induced by doping them with an electron acceptor, TNF.

5.5.1.2 Rufigallol-based discotic main chain polymers

The branched chain substituted tetraalkoxy compound **53** (Scheme 16) was very interesting as it exhibits liquid crystalline behaviour at room temperature contrary to its straight chain analogous, which do not show any liquid crystalline property. The columnar phase was stable below –30°C and clear at 115°C. The two unreacted hydroxyl groups of this tetramer can be utilised to prepare main chain polymers simply by reacting with α, ω-dibromoalkanes (Scheme 16). The polymer so prepared displayed a $\mathrm{Col_r}$ phase at room temperature, which clears at 56.3°C. The mesophase structure was confirmed by X-ray studies (*74*).

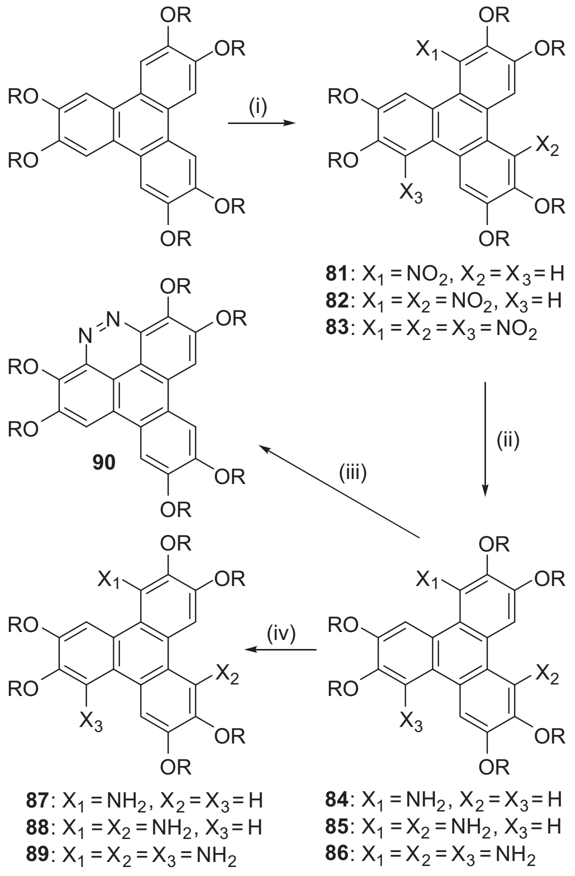
5.6 Synthetic modifications of TP discotics

5.6.1 Electrophilic aromatic substitution in triphenylene discotics

Electrophilic aromatic substitution in unsubstituted TP is directed by steric and electronic effects. Substitution at the β- or 2-position is favoured compared with the α- or 1-position, presumably owing to a steric hindrance effect. However, the electronic effect plays a major role in the nitration of TP and results in a mixture of 1-nitro and 2-nitro-TP. During the course of low symmetry, when we nitrated pentapentyloxy-TP, fluorescent TP synthesis (Scheme 12) nitration occurred preferentially in the sterically hindered α-position. Evidently, electronic effects dominate in the nitration of alkoxy-TP. This prompted us to examine the nitration of TP discotics more carefully (*75*, *76*). The functionalisation of the nucleus at the α-position is important not only to induce colour, molecular dipole, enhanced liquid crystalline properties and a chemical reaction site, but also to helically deform the normally planar TP core.

In hexaalkoxy-TP, only the α-positions, ('bay regions',1, 4, 5, 8, 9 and 12 positions) are free for further substitution. The nitration of 2,3,6,7,10,11-hexaalkoxy-TP provides a α-nitrated product in very high yields. Solvents play an important role in the nitration of hexaalkoxy-TP. In a mixture of ether-acetic acid the α-nitro product is formed almost exclusively. Even under exhaustive conditions, in this solvent system, only a small amount of trinitro-hexaalkoxy-TP forms. Changing the solvent system from ether-acetic acid to dichloromethane-nitromethane imparts a dramatic effect and all the three rings of TP can be successively nitrated under very mild conditions. The trinitration proceeds with high regioselectivity to give exclusively one isomer having C_3 symmetry, i.e. 1,5,9-trinitro-2,3,6,7,10,11-hexaalkoxy-TP. Alkoxynitro-TPs are valuable precursors to several other derivatives, such as amino, mono- and di-alkylamino, acylamino-, azo- etc., and thus a number of new TP derivatives can be prepared (Scheme 23).

Nitro-TPs **81**, **82** and **83** were easily reduced to the corresponding amino derivatives **84**, **85** and **86** with hydrazine and palladium, or with nickel chloride and sodium borohydride (Scheme 23). The reduction of mononitro-TP **81** also works well with tin and acetic acid, but this method gives very poor results with di- and tri-nitro derivatives. The amino derivative **84** was readily converted to an α, α-diazo compound **90** by diazotisation of the amine with nitrous acid followed by cyclisation. Acylation of amines **84**, **85** and **86** with



Scheme 23. Synthesis of nitrotriphenylenes and their derivatives: (i) HNO_3/CH_3NO_2; (ii) NH_2NH_2/Pd or $NiCl_2/NaBH_4$; (iii) Ac_2O/Py.

acetic anhydride in pyridine converted them into their *N*-acyl derivatives **87**, **88** and **89**. Many of these derivatives exhibited columnar mesophases.

We have studied the dielectric properties of two mononitro-hexaalkoxy-TPs (*77*). Both hexabutyloxy and hexapentyloxy derivates exhibited a Col_h mesophase, but the hexabutyloxy derivative shows, in addition, a more ordered mesophase at lower temperatures. The dielectric constants observed are high compared to the values observed in other discotic materials. In the frequency range studied (1 Hz–1 MHz) one relaxation mode is observed in the Col_h phase, which can perhaps be correlated with a glass transition. A strong reduction in the magnitude of the relaxation frequency and an associated increase in the dielectric strength of the mode are observed at the transition from Col_h to the lower temperature phase. We have also carried out detailed X-ray studies on mono- and dinitro-derivatives as well as on several other TP discotics (*78*). Analysis of the X-ray patterns yields, apart from information on the structural symmetry in terms of the planar space groups, quantitative data on (i) the ordering of the chains and the cores of the mesogens, (ii) the core–core correlation length along the column axis and (iii) the intercolumnar spacing. In particular, it is seen that the extent of ordering of the discs within the columns has significant temperature dependence.

5.6.2 *Triphenylene discotics having three different types of peripheral substituent*

The nature of peripheral substituents around the core has a great influence on the mesophase structure and its stability. For example, hexaesters of TP form Col_r and Col_h mesophases, TP hexabenzoates form N_D and Col phases, hexaphenylacetylene derivatives of TP exhibit N_D phases, symmetrically-substituted hexaether derivatives of TP having 5–13 carbon atoms in the aliphatic chains form a single Col_h mesophase, while hexabutyloxy-TP displays a more ordered Col_p phase and hexahexylthio-TP exhibits a highly ordered helical phase, in addition to a Col_h phase. Numerous rod-like molecules with a variety of peripheral substitutions are known to exhibit various types of mesophases. However, probably because of synthesis problems, such a rich variety of peripheral substitutions are uncommon in DLCs. Almost all the TP derivatives reported in the literature have either a single type of peripheral substitution pattern, or two types of peripheral substitution. Efforts have not been made to prepare DLCs having more than two types of peripheral substituent. We looked at this challenging problem and prepared a variety of novel TP derivatives having three different types of peripheral substitution (Scheme 13) (*31*).

Monobromination of 2,3,6,7-tetrakis(pentyloxy)-TP **92**, prepared by Suzuki coupling of 2-iodo-3',4,4',5-tetrakis(pentyloxy)biphenyl **17** and phenylboronic acid followed by cyclisation, yields 10-bromo-2,3,6,7-tetrakis(pentyloxy)-TP **93**. Nucleophilic aromatic displacement of the bromine with the potassium salt of pentanethiol, followed by bromination, yields 2-bromo-6,7,10,11-tetrakis(pentyloxy)-3-(pentylsulphanyl)-TP **95** having a bromo, thioalkyl and alkoxy-substituted periphery of the TP nucleus. The reaction of **95** with copper(I) cyanide gives the cyano-TP derivative **96**, while palladium-copper catalysed alkynylation of **95** results in the synthesis of the substituted alkyne derivative **97**. The deprotected alkyne **98** was converted to dimer **99**, where two molecules of a monothioalkyl-tetra-alkoxy-TP are connected via a rigid π-conjugated diacetylene bridge. Compounds **95**, **96**, **97** and **98** form hexagonal columnar phases, while the dimer **99** shows a discotic nematic phase.

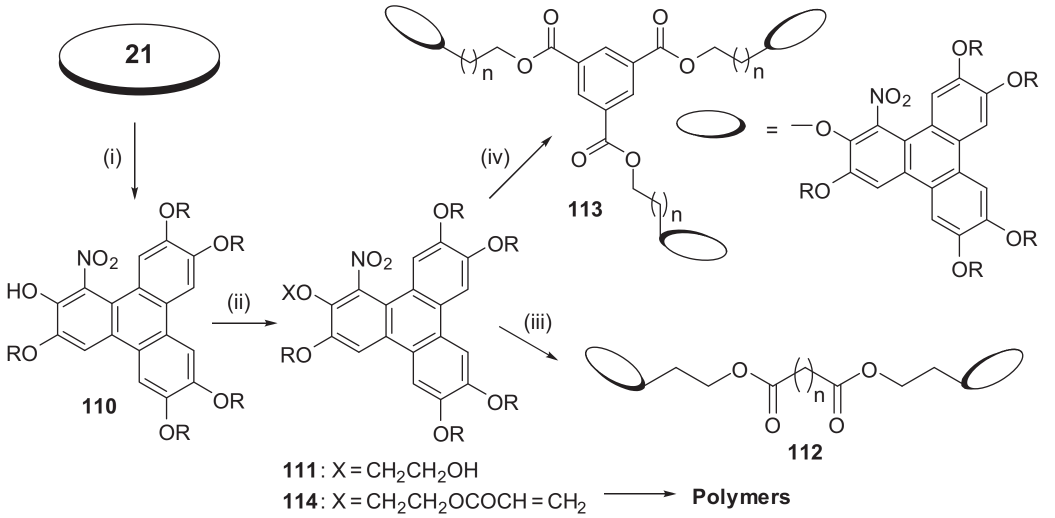
5.6.3 Discotics derived from hydroxy-functionalised triphenylenes

The hydroxy-functionalised TPs are very valuable precursors for the synthesis of dimers, oligomers, polymers, networks, mixed tails and lower and higher degree substituted derivatives. Although a number of different alkoxy-hydroxy-TPs are possible, seven different types of alkoxy-hydroxy-TP derivatives: monohydroxy; 2,3-dihydroxy; 2,6-dihydroxy; 2,7-dihydroxy; 2,11-dihydroxy; 2,6,10-trihydroxy; and 2,6,11-trihydroxy, have been prepared using selective or non-selective chemical methods (*2c*). These derivates have been used to prepare a number of TP discotics. Here we present some of the derivatives prepared by us using these precursors.

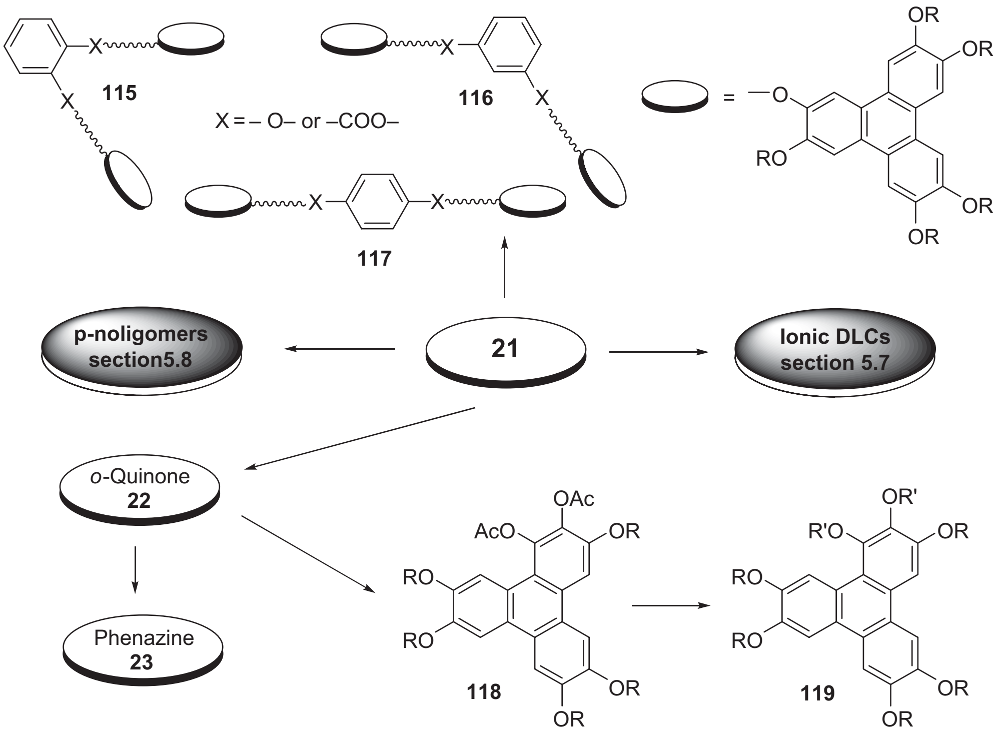
5.6.3.1 Discotics derived from monohydroxy-pentaalkoxy-triphenylenes Given a readily available supply of monohydroxy-pentaalkoxy-TPs, it was not difficult for us to prepare a variety of novel discotics. The synthesis of some of these derivatives is shown in Schemes 12, Scheme 24 and Scheme 25.

Our initial interest was in synthesising fluorescent, low-symmetry TP DLCs having a single electron-withdrawing group (and consequently a large dipole moment), connected directly to the polyaromatic core. To have such materials, we required a pentaalkoxy-TP **101**. We first attempted its synthesis via triflate **100** reduction, which can be easily prepared from hydroxyalkoxy-TP **21.** Although the reduction was not successful, we discovered that triflate **100** is mesogenic over a broad temperature range, with an unidentified phase occurring below the hexagonal discotic phase (*79*). Reduction of the phenolic groups of hydroxyalkoxy-TP has ultimately been accomplished by activation with a tetrazole unit followed by catalytic hydrogenation.

Compounds **101** now possess reactive sites capable of derivatisation via classical aromatic substitution chemistry. Thus, the bromination of **101** with Br_2 in methylene chloride affords the mesogenic bromoalkoxy-TP **104** in 98% yield (*79*). Friedel–Crafts acylation of **101** with acetyl chloride and aluminium trichloride proceeds in high yield with acylation occurring in the 2-position (**103**). Somewhat surprisingly, classical nitration of **101** with nitric acid in acetic acid occurs preferentially in the sterically hindered α-position (**102**), as unambiguously indicated in the ^1H NMR. The reaction of **104** with copper cyanide gives the cyanotriphenylene **105** in excellent yield. Palladium/copper-catalysed alkynylation of **104** can be accomplished in excellent-to-quantitative yields with a variety of substituted alkynes as demonstrated with compounds **106** (R = (a) TMS, (b) $(CH_3)_2COH$, (c) C_4H_9). In addition, TPs **106a** and **106b** can be deprotected to yield free phenylacetylenes for further elaboration or potential polymerisation. Compound **106c** on hydrogenation with catalytic palladium yields the alkyl/alkoxy-TP derivative **107**. All the new LCs show a significantly broader range of mesogenicity relative to the parent compound 2,3,6,7,10,11-hexakis(pentyloxy)-TP. Moreover, some of the new mesogens exhibit a more ordered mesophase relative to the hexagonal columnar phase at lower temperatures (*80*). The free acetylene compound can be easily dimerised to **39** (Scheme 11) to generate the N_D phase. On the other hand, the monohydroxy-TP can be directly



Scheme 24. Synthesis of double functionalised TP discotics: (i) HNO_3/CH_2Cl_2; (ii) $BrCH_2CH_2OH/K_2CO_3$; (iii) $ClCO(CH_2)_nCOCl$/Py; (iv) 1,3,5-benzenetricarboxylicacid chloride/Py.



Scheme 25. Synthesis of hepta-substituted TPs and benzene-bridged TP dimers.

converted to chiral esters **108** by reacting with (S)-2-chloro-4-methylpentanoic acid chloride or (2S, 3S)-2-chloro-3-methylpentanoic acid chloride. Induction of the cholesteric phase in a nematic-discotic phase was observed by doping with these chiral DLCs (*81*). We have prepared several derivatives **109** incorporating a carbazole unit in TP to get added physical properties (*82–84*). These modifications have been achieved by the alkylation or esterification of monohydroxy-TP derivatives, with alkyl bromides and carboxylic acids incorporating the carbazole moiety. The pure compounds are not liquid crystalline in nature, but when doped with TNF the Col_h phase was induced. These mesophases exist below room temperature. The mesophase clearing temperatures are dependent on several factors, including the chain length separating the carbazole moiety from the TP core, and the nature of the ether or ester linkage, and the degree of TNF doping. The corresponding 3,6-bisalkylated or 3,6-bisacylated carbazole derivatives do not show mesomorphism either in pure form or when doped with TNF (*84*).

The monohydroxypentaalkoxy-TP can be nitrated at the α-position, but this reaction is complicated and often only the oxidised products, the 3,6,7,10,11-pentaalkoxytriphenylene-1,2-diones, can be isolated. Under very careful conditions, we prepared 1-nitro-2-hydroxy-3,6,7,10,11-pentaalkoxy-TPs **110** (Scheme 24). These double functionalised TP derivatives are extremely important precursors, as the functional group, such as nitro, amino, azo, etc., can be utilised to modify the electronic nature of the core and at the same time the hydroxy functional group may be converted to a polymerisable group. Thus, processable oligomers and polymers can be synthesised. The 1-nitro-2-hydroxy-3,6,7,10,11-pentaalkoxy-TP was alkylated with 2-bromoethanol and the resultant alcohol **111** was coupled with various diacids to afford a number of functionalised dimers **112** (Scheme 24). These yellow coloured materials with a polar nitro group have a broad mesophase range and in many cases they are stable at room temperature (*85*). Similarly, condensation of this alcohol **111** with 1,3,5-benzenetricarboxylicacid chloride easily furnished a trimer **113**. POM and DSC measurements reveal the existence of a monotropic columnar mesophase in this novel functionalised oligomer. The product does not crystallise at room temperature over a long period or on cooling to a very low temperature. The corresponding unfunctionalised trimer was not liquid crystalline. The dipolar interaction of nitro groups is probably responsible for the induction of mesogenicity (*86*). The acrylate **114** derived from the alcohol also exhibited a very broad room temperature columnar phase. We performed an AFM study on the surface morphology of the quenched mesophase of the novel polymerisable

2-[(3,6,7,10,11-pentabutoxy-1-nitro-2-triphenylenyl)oxy] ethyl acrylate **114** in 50–100 nm thin films on highly ordered pyrolytic graphite (HOPG) (*87*). The material was also polymerised, but because of the paucity of the material, full characterisation could not be done.

Recently, we examined the outcome of the variation of the relative orientation of two discotic mesogenic moieties around the benzene ring **115**, **116**, **117** (Scheme 25) (*88*). Two series of novel TP-based benzene-bridged symmetric discotic dimers were prepared and characterised. Two TP discotics were been connected to a rigid benzene ring via flexible methylene spacers. In one series, TP moiety was tethered with benzene via ester linkage, while in the second series it was tethered via ether linkage. Within each series, the orientation of the linkage of the TP core around the benzene core has been changed by substituting the benzene ring at the *o, m* and *p*-positions. All of the virgin compounds do not display mesomorphism, however, their CT complexes with TNF exhibited columnar mesophases.

As mentioned earlier, oxidation of monohydroxy-TP furnished the 3,6,7,10,11-pentaalkoxytriphenylene-1,2-diones **22** in high yield. We utilised these diones in order to prepare novel discotic phenazine ring structure **23** (Scheme 5). The reductive acetylation of these *o*-quinones furnished the diacetate **118**, which can be directly alkylated to various 1,2,3,6,7,10,11-heptaalkoxy-TP derivatives **119** (Scheme 25) (*89*). These unsymmetrically substituted TP derivatives are of three varieties: i) with seven identical peripheral alkoxy chains; ii) two or three out of the seven alkoxy chains have different chain lengths; and iii) the mode of the attachment of two of the peripheral chains is different, i.e. via ester linkages. Unsymmetrical substitution has a large effect on the thermal behaviour, but the type of mesophase formed does not change. All of the 21 liquid crystalline compounds prepared show a very broad $\mathrm{Col_h}$ phase. Mixed ether–ester derivatives have smaller core–core separations and higher correlation length, therefore, they are better candidates for charge transport studies (*90*).

A variety of ionic liquid crystalline monomers, dimers and polymers can be prepared from monofunctionalised-TPs (Section 5.7) . We have also utilised the monofunctionalised-TPs to prepare a number of donor–acceptor dimers, trimers, oligomers and polymers (Section 5.8).

5.6.3.2 Discotics derived from trihydroxy-trialkoxy-triphenylenes Both symmetric **36** and unsymmetric **37** trihydroxy-trialkoxy-TPs are relatively easy to prepare and purify (Section 3.2). Following the chemistry developed for the synthesis of TP derivatives derived from monohydroxy-pentalkoxy-TPs (Scheme 12), we have prepared a number of new materials from symmetric as well as from unsymmetric trihydroxy-trialkoxy-TPs (*54*, *81*, *83*, *91*). Some of these derivatives obtained from symmetrical trifunctionalised-TPs are shown in Scheme 26.

5.7 Ionic discotic liquid crystals

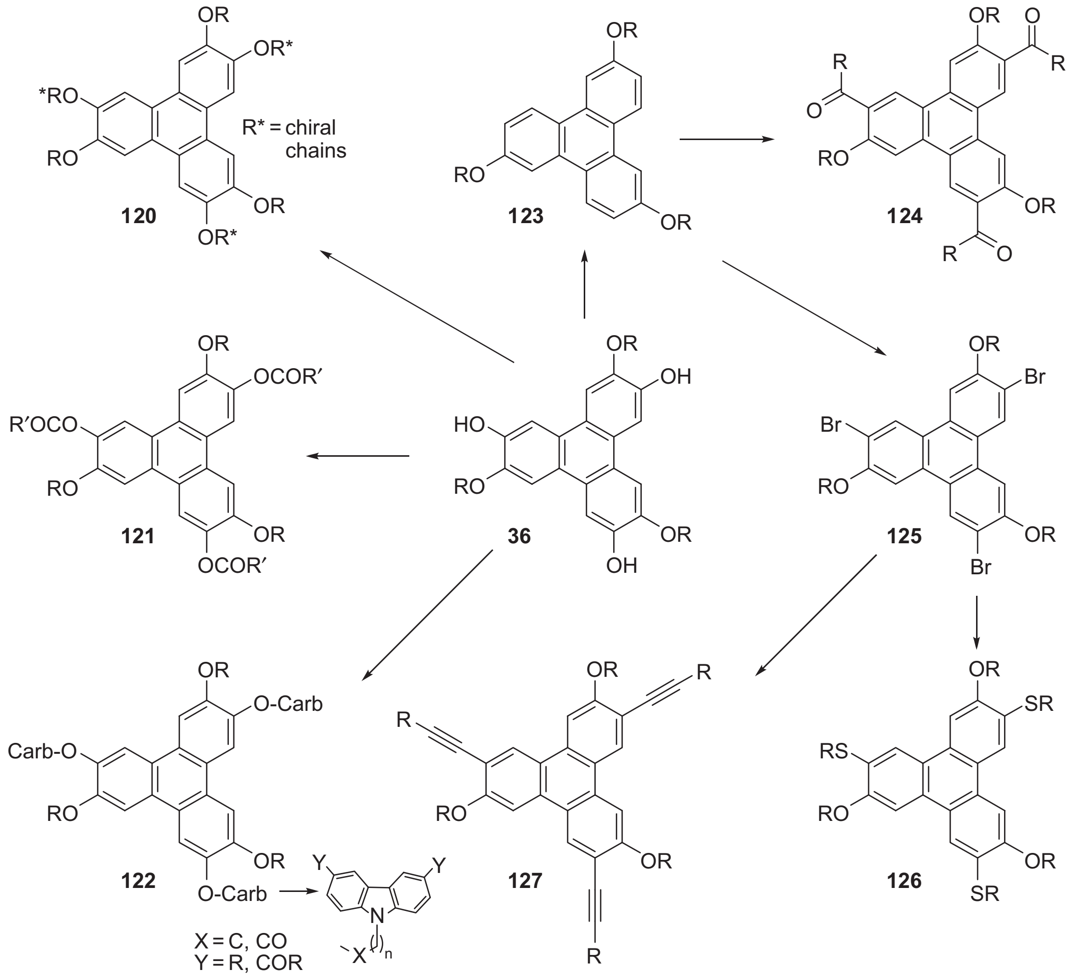
5.7.1 Monomeric ionic discotic liquid crystals

Ionic liquids are currently attracting considerable attention as 'green' solvents for various chemical reactions. Additionally, it is well known that ionic molecules form amphotropic LCs. They have great potential as ordered reaction media that can impart selectivity in reactions by ordering reactants. The formation of supramolecular assemblies containing ionic liquids may find applications as heat carriers in solar–thermal energy generators and as electrolytes for batteries and capacitors. Therefore, we focused our attention on TP-tethered imidazolium and pyridinium ionic LCs (*41*, *43*, *91–93*).

Imidazolium-based ionic liquids are interesting as environmentally benign solvents for various chemical reactions due to their interesting properties, such as thermal stability, non-flammability, very low vapour pressure and reusability. Hybridisation of self-organising TP discotics with imidazolium ionic liquids may lead to novel materials with interesting properties that are useful for many applications. With this in mind, we have initiated a research program to incorporate imidazolium-based ionic liquids in the supramolecular order of DLCs by attaching TP discotics covalently to the imidazolium salts and we study the effects of counterions, spacers and peripheral substitution in these materials.

Two novel TP-tethered imidazolium salts **130** were synthesised, either by the quaternisation of 1-methylimidazole with an ω-bromo-substituted TP or by the quaternisation of a TP-substituted imidazole with methyl iodide (Scheme 27) (*91*). These TP-based imidazolium salts with bromide or iodide as the counterion show columnar mesophase properties over a wide temperature range. The iodide salt exhibited a slightly lower isotropic transition temperature than the bromide salt. This could be due to the bulky nature of the counterion. Interestingly, the non-ionic imidazole-substituted TP derivative **129** was found to be non-liquid crystalline. Therefore, the mesomorphism in ionic salts is induced due to ionic self-assembly.

Pyridinium salts **131** were obtained by reacting the bromo-substituted compounds **128** with pyridine (Scheme 27). In this way, several members with different peripheral chains and spacers were prepared and



Scheme 26. Discotics derived from trifunctionalised-TP. Reagents and conditions, as given in Scheme 23.

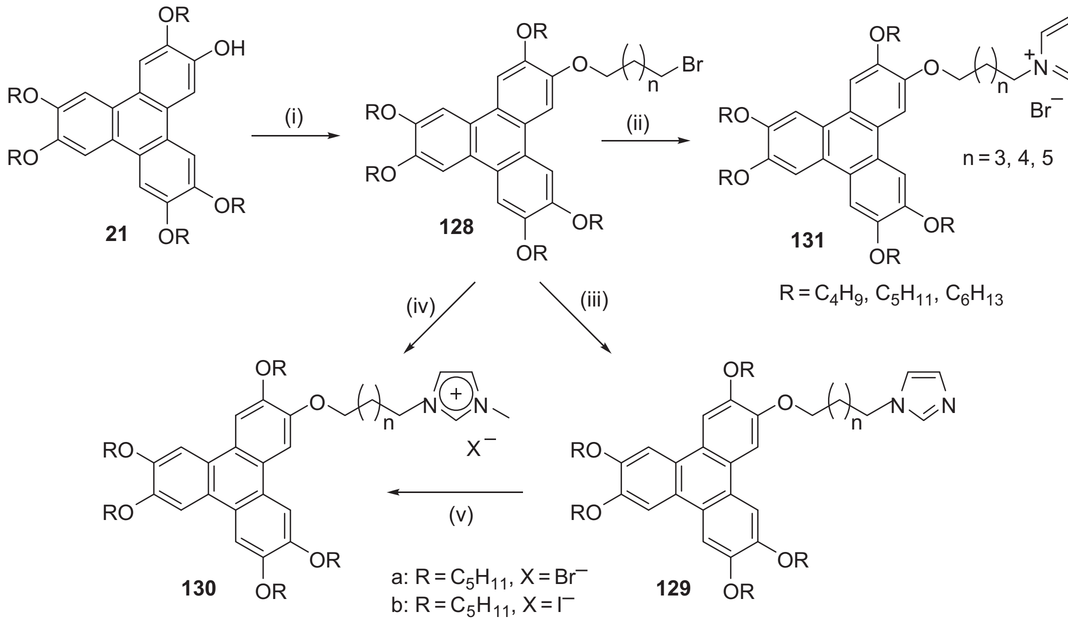
characterised. Increasing the number of carbon atoms on the peripheral chains of the TP core stabilised the columnar phase, while increasing the spacer length connecting the TP unit with the pyridine moiety destabilised the mesophase (*92*).

We have studied these imidazolium and pyridinium salts at air-water and air–solid interfaces (*94*). The monolayer phases were investigated at the air–water interface, employing surface manometry and Brewster angle microscopy techniques. They indicate a uniform monolayer phase, which shows negligible hysteresis on expanding and compressing. In both the systems the collapsed state completely reverts to the monolayer state. These monolayer films, transferred at different surface pressures by the Langmuir–Blodgett technique, were studied by employing AFM. The topographies of these films, transferred at the low and high surface pressure region of the isotherm, indicate a transformation of the monolayer from face-on to edge-on structure.

5.7.2 Imidazolium-based ionic liquid crystalline dimers

Compared to the large number of calamitic and discotic ionic molecules, only a few ionic liquid crystalline dimers and polymers are known. Hybridisation of two different types of mesogens with imidazolium moieties may lead to novel materials with interesting properties. With this in mind, we have initiated this research program to incorporate imidazolium-based ionic liquids in the supramolecular order of calamitic and DLCs by attaching two calamitic, two discotic and a hybrid of both the moieties to imidazole (Figure 3). The most widely studied alkoxycyanobiphenyl and TP units were chosen as the calamitic and discotic parts, respectively.

The synthesis of imidazolium-based calamitic–calamitic ionic dimers is outlined in Scheme 28. Commercially available 4′-hydroxy-4-biphenylcarbonitrile was alkylated under classical conditions with an excess of the appropriate α,ω-dibromoalkanes to



Scheme 27. Synthesis of imidazolium and pyridinium-based DLCs: (i) $Br(CH_2)_nBr$, Cs_2CO_3; (ii) Py/toluene/reflux; (iii) imidazole/THF/NaH/reflux; (iv) 1-methylimidazole, toluene, reflux; (v) CH_3I, r.t.

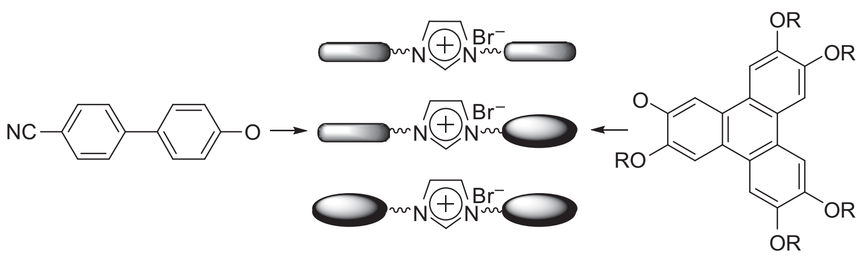
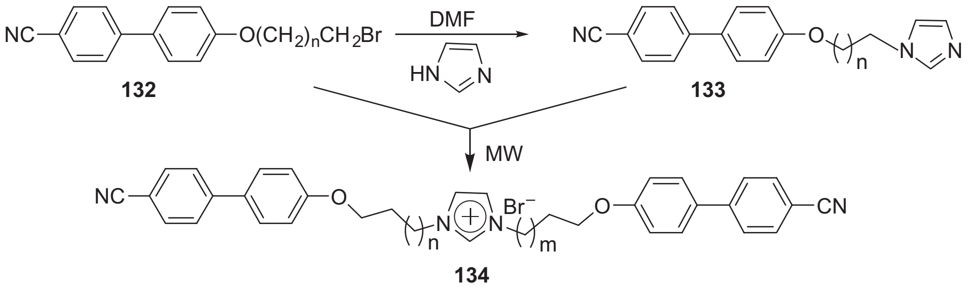
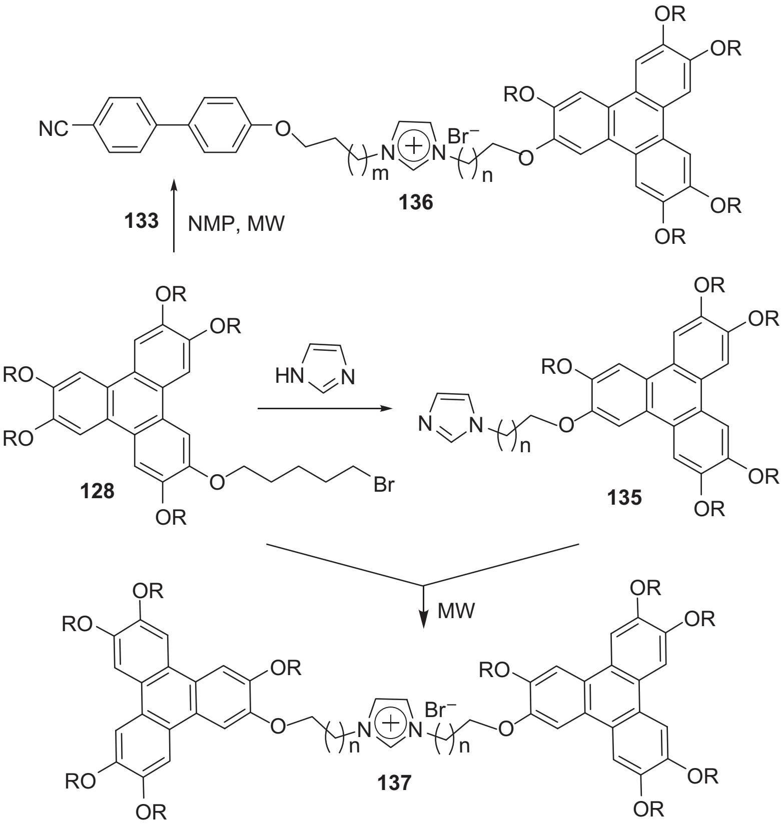


Figure 3. Imidazole-based calamitic–calamitic, calamitic–discotic and discotic–discotic ionic dimers.



Scheme 28. Synthesis of imidazole-based calamitic–calamitic dimers.

obtain the ω-brominated products **132**. Imidazole-substituted alkoxycyanobiphenyls **133** was obtained by reacting **132** with imidazole in the presence of NaH. Ionic liquid crystalline calamitic–calamitic dimers **134** were obtained by attaching one more molecule of ω-brominated cyanobiphenyl to the imidazoles **133**. Thus quaternisation of **133** with ω-bromo-terminated cyanobiphenyl under MW irradiation furnished the dimers **134** in about 1 minute. Similarly, calamitic-discotic **136** and discotic–discotic **137** salts were prepared as shown in Scheme 29 (*41*). POM and X-ray diffraction experiments showed smectic and columnar



Scheme 29. Synthesis of imidazole-based calamitic–discotic and discotic–discotic dimers.

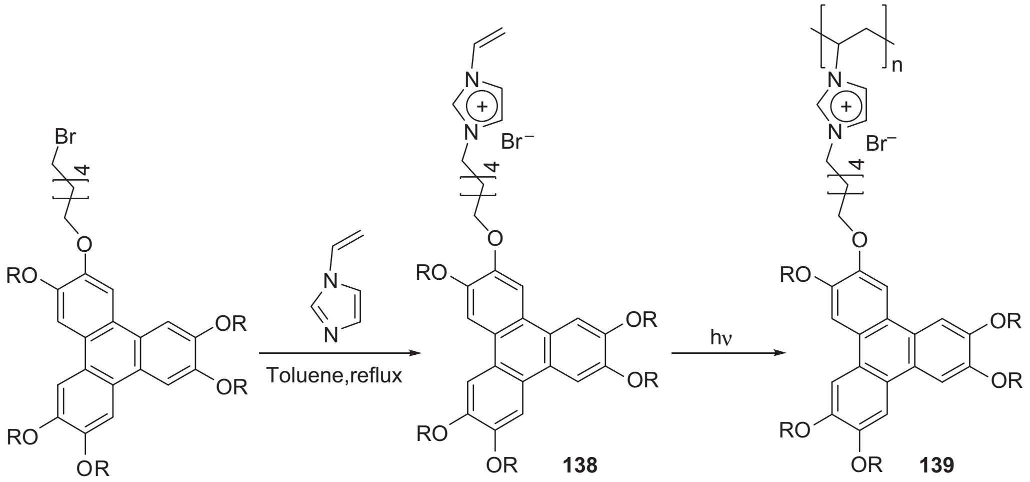
phases of the calamitic–calamitic and discotic–discotic hybrids, respectively. The calamitic–discotic hybrid **136** was found to be non-liquid crystalline, probably due to the non-compatibility of two different types of cores.

5.7.3 Ionic discotic liquid crystalline polymers

For many years, ionic liquid crystalline polymers with the mesogen in the main chain or in the side group have been investigated intensively for their scientific and technological potential. We were interested in looking at the self-organising supramolecular properties of ionic polymers composed of the well-known discotic core, TP, and an ionic liquid, imidazole. Accordingly, the polymer **139** was designed and synthesised (Scheme 30) (*93*). The photopolymerisation of TP-substituted 1-vinylimidazole **138** yielded a novel ionic discotic liquid crystalline polymer **139**. The thermotropic liquid crystalline properties of both the monomer and the polymer were investigated by POM and DSC. The calculated weight-average molecular weight of the polymer was around 5352 and the number-average molecular weight was nearly 1192, with respect to the polystyrene standard. Thus, the polymer is actually a mixture of low molecular weight oligomers. This is probably due to steric hindrance of TP units into the side chain. The mesophase structure has been characterised by X-ray diffractometry. Both the monomer and the polymer displayed a $\mathrm{Col_r}$ phase over a wide temperature range. However, the columnar order in the polymer was found to be small compared to the monomer. These materials are not only important for new possibilities of polymeric molten salts in materials science, but also contribute to the development of novel anisotropic soft materials for directional ion conductivity and charge transport at the nanoscale.

5.8 Novel discotic p–n systems

Recently there have been tremendous efforts to achieve both p-type (hole conducting) and n-type (electron conducting) properties in organic semiconducting materials, which are crucial for molecular electronics. One elegant approach for such materials is to covalently link electron donor and electron acceptor components at the molecular level. These kinds of materials are expected to behave as intrinsic, non-composite p/n-type semiconductors. Such chemical



Scheme 30. Synthesis of imidazole-based ionic polymer with pendent TP discotic.

tailoring could lead to the development of other molecular architectures and it is envisaged that the combination of covalent chemistry and self-assembly will be crucial for the development of nano-engineered functional materials for electronic applications. In this context we are interested in the design and synthesis of novel functional discotic oligomeric materials and their mesophase behaviour. Our molecular design is such that it contains the well-studied electron rich TP moiety and electron deficient anthraquinone as the hole and electron transporting components, respectively. These molecular double-cables may stack one on top of the other in the columns, which could eventually provide side-by-side percolation pathways for electrons and holes in solar cells. Thus, we designed various discotic donor–acceptor dimers and oligomers as shown in Figure 4.

Having access to a mono-functionalised donor and an acceptor, it was not difficult to assemble these materials. The dimer **140** was prepared in two steps (Scheme 31). Alkylation of monohydroxy-pentahexyloxy-TP with an excess of 1,12-dibromododecane furnished the triphenylenedodecylbromide **128**, carrying one terminal bromine substituent. The desired dimer **140** was prepared by reacting **128** with monohydroxyanthraquinone under classical alkylation reaction conditions. The dimer displayed a Col mesophase over a wide temperature range. It exhibited one weak broad peak, probably a glass transition, in the DSC at about 40°C, and the mesophase to isotropic

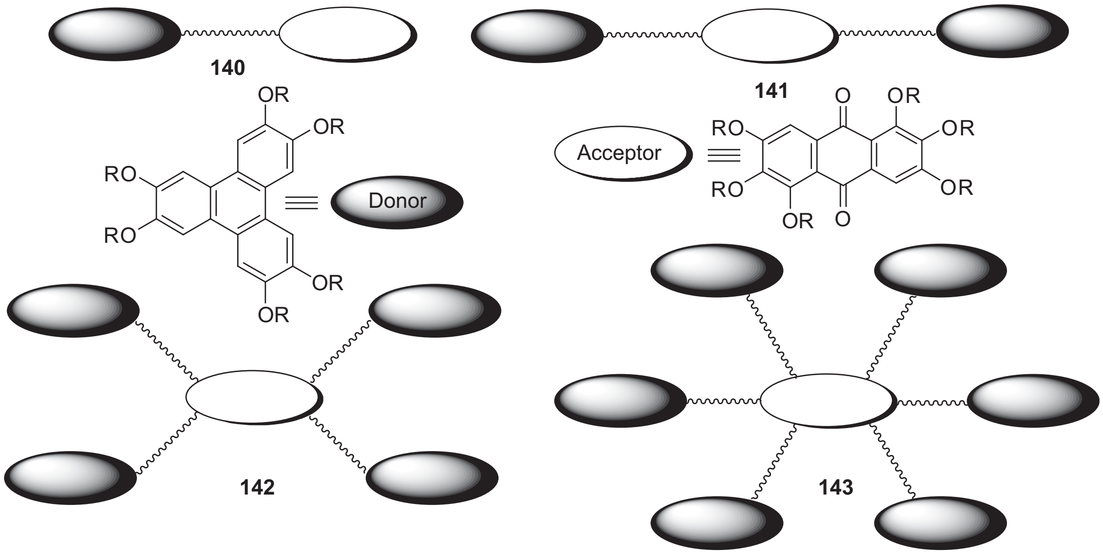
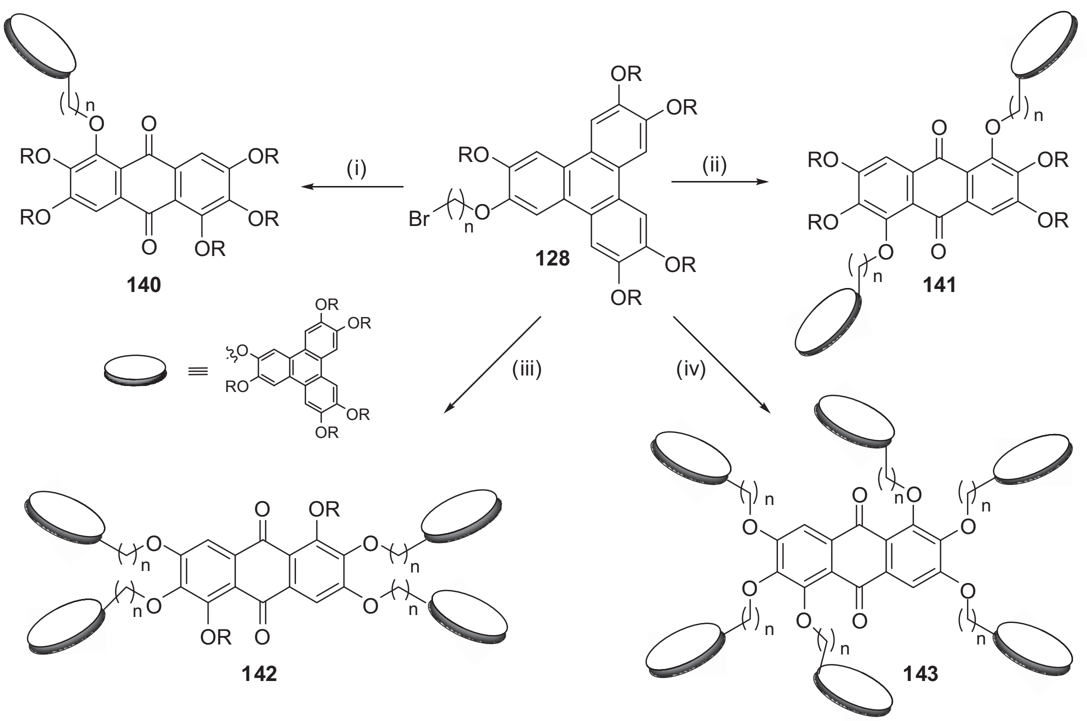


Figure 4. Discotic donor–acceptor systems.



Scheme 31. Synthesis of discotic donor–acceptor oligomers: (1) K_2CO_3/DMF/monofunctionalised rufigallol; (ii) Cs_2CO_3/NMP/difunctionalised rufigallol/MW; (iii) DMSO/NaOH/ rufigallol/90°C; (iv) Cs_2CO_3/NMP/rufigallol/MW.

phase transition at 96.9°C. Upon cooling, the isotropic to columnar phase transition appears at 94.3°C. The DSC does not show any crystallisation or glass transition peak down to room temperature. On subsequent heating, the DSC shows only a mesophase to isotropic transition and the weak transition at 40°C was not discernible (*95*).

Similarly, TP-anthraquinone-based symmetric discotic liquid crystalline trimers **141** can be prepared. Thus, two series of donor–acceptor–donor (D–A–D) triads with different spacer length and peripheral chains were prepared (*47*). These triads were synthesised using MW dielectric heating. The etherification of H-bonded hydroxyl groups of tetraalkoxy anthraquinone with bulky ω-bromo-substituted TP failed to produce the desired triads under classical reaction conditions. Mesophase behaviour of the symmetrical trimers was studied by POM and DSC. They exhibit a columnar mesophase over a wide range of temperatures. The hexagonal columnar structure of the mesophase of these D–A–D triads was established by X-ray diffraction studies. Longer spacer length, smaller peripheral alkyl chain length and branching in the peripheral alkyl chain of the anthraquinone are in favour of liquid crystalline properties in these symmetrical trimers.

Alkylation of rufigallol with ω-bromo-substituted TP under mild etherification conditions furnished novel pentamer **142**, leaving the less reactive intramolecular hydrogen-bonded hydroxyl groups at the 1- and 5-positions unreacted (*96*). The dihydroxyl-functionalised pentamer **142** was acetylated to its corresponding diacetate (**142diAc**) with acetic anhydride and sulphuric acid under classical conditions. DSC measurements of both the pentamers revealed only one first order transition for cooling and heating runs, corresponding to the mesophase to isotropic transition as observed by POM. The pentamer **142** showed the transition from columnar to isotropic at 143.6°C. On cooling it exhibited an isotropic to columnar transition at 139°C. There was no other detectable transition down to –40°C. Upon heating, the pentamer **142diAc** showed a transition at 112.5°C, while on cooling the transition is at 106°C. In subsequent heating and cooling cycles the transitions were highly reproducible. No actual glass transition could be detected in the range between –40°C and the clearing points for both of the pentamers. The mesophase structure was established by preliminary X-ray diffraction studies.

On the other hand, alkylation of rufigallol with ω-bromo-substituted TP under MW irradiation furnished a novel star-shaped oligomer **143** (*97*). The compound exhibited a very broad col$_h$ phase between –40°C and 123°C. Full characterisation of the material is in process. We are now interested in synthesising various discotic donor–acceptor polymers. These dimers, oligomers and polymers certainly hold immense potential for device applications.

6. Discotic-functionalised nanomaterials

In the past two decades, the field of nanoscience and nanotechnology has made enormous growth because of its potential industrial applications. The properties of the materials change drastically when their dimensions scale down to nanometer length scale. For instance, the conductivity of bulk gold is very high ($4.3\times10^{7}\ \Omega^{-1}\ \mathrm{m}^{-1}$), while gold nanoparticles (GNPs) of 1–2 nm are only semiconducting ($1.4\times10^{-3}\ \Omega^{-1}\ \mathrm{m}^{-1}$). The incorporation of nanoparticles in the supramolecular order of DLCs would provide materials that possess the properties of the nanoparticles as well as the processing, handling and self-assembling properties of LCs and, therefore, is likely to lead to novel materials for many device applications. With this view, we have initiated a research program to insert nanomaterials, such as GNPs and carbon nanotubes (CNTs) into the supramolecular order of DLCs (*74*, *98–102*).

6.1 Inclusion of gold nanoparticles into a discotic liquid crystalline matrix

GNPs are the most stable metal nanoparticles and they present fascinating aspects, such as their self-assembly, the behaviour of individual particles, size related electronic, magnetic and optical properties, and their applications as a catalysis and in the bottom-up approach of nanotechnology. Monolayer-protected GNPs can be handled as simple organic materials and a variety of chemical reactions can be performed on functionalised GNPs. By providing metal nanoclusters with liquid crystalline properties, one could introduce the self-assembling ability and the reversible control of morphology of their aggregates by external stimuli, as well as the control of their properties by a simple and solvent free method. The reversible control of the properties of metal nanocluster aggregates will cultivate their potential as functional nanomaterials. The basic objective of this work was to incorporate GNPs into liquid crystalline systems.

We prepared four types of monolayer-protected GNPs (Figure 5): (a) alkanethiol-capped GNPs; (b) alkanethiol and discotic mixed monolayer-protected GNPs; (c) GNPs fully covered with TP-based DLCs; and (d) alkoxycyanobiphenyl-covered GNPs. These GNPs were prepared by reducing gold salt in the presence of an appropriate thiol. The ligand exchange reaction was used to prepare mixed monolayer-covered GNPs. All of the virgin monolayer-protected GNPs were found to be non-LC. Binary mixtures of GNPs with DLCs were prepared by mixing the two components in dichloromethane, followed by removal of the solvent and drying in a vacuum. Several compositions were prepared by mixing alkanethiol-covered GNPs (a) and TP-covered GNPs (c) in HHTT and H6TP and characterised for their mesomorphic properties (*98–101*).

The thermophysical properties of these nanocomposites, studied using POM, DSC and small angle X-ray diffraction studies, confirm their insertion into the columnar matrix. The presence of the GNPs in the TP-based DLCs does not disturb their mesomorphic behaviour, other than altering the transition

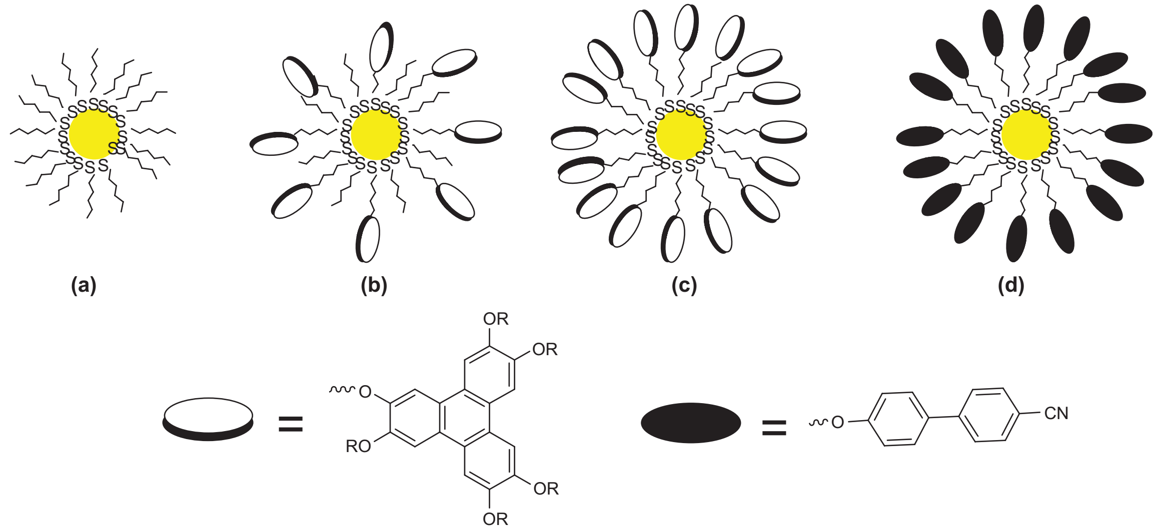


Figure 5. Schematic representation of monolayer-protected GNPs.

temperatures. Increasing the amount of GNPs increases the tendency of phase segregation and decreases the isotropic temperature. The DC conductivity measurements show an enhancement of electrical conductivity by more than a million times upon doping of the DLCs with the TP-capped nanoparticles under ambient conditions (*100*). The dispersion of discotic-capped nanoparticles in the liquid crystalline matrix can provide a route for synthesising similar composites of varying properties that may find applications in many device developments.

The reduction of gold salts in the presence of novel terminally thiol-functionalised cyanobiphenyls (*103–105*) yields alkoxycyanobiphenyl-covered GNPs (Figure 5d). Recently these materials were claimed to display LC properties (*106*), but our alkoxy-cyanobiphenyl-covered GNPs failed to exhibit any mesomorphism. However, these thiol-functionalised cyanobiphenyls forms stable SAMs on a gold surface, which we have been studied using cyclic voltammetry and electrochemical impedance spectroscopy (*107*). The barrier property of the SAM-modified surface was evaluated using two different redox probes, mainly potassium ferro/ferri cyanide and hexaammineruthenium (III) chloride. It was found that, for a short length alkyl chain thiol (C5), the electron transfer reaction of hexaammineruthenium (III) chloride takes place through a tunnelling mechanism. In contrast, the redox reaction of potassium ferro/ferri cyanide is almost completely blocked by the SAM-modified Au surface.

We have also studied the SAMs of alkoxycyanobiphenyl thiols on gold prepared in a lyotropic liquid crystalline medium using electrochemical techniques (*108*, *109*). Alkoxycyanobiphenyl-thiols of different alkyl chain lengths were dispersed in a hexagonal lyotropic liquid crystalline phase, consisting of a non-ionic surfactant, Triton X-100 and water. This medium provides a highly hydrophobic environment in which to solubilise the thiols and later facilitate their delivery to the gold surface to form a monolayer. The electrochemical techniques, such as cyclic voltammetry and electrochemical impedance spectroscopy, were used to evaluate the barrier property and ionic permeability of these monolayers on the gold surface. We have compared our results with those of the corresponding monolayers prepared using dichloromethane as a solvent. We find from our studies that the monolayers prepared using the hexagonal liquid crystalline phase show a better electrochemical blocking ability towards the redox reactions and exhibit very low ionic permeability. From the impedance studies, we have determined a surface coverage value of greater than 99.9% for the monolayer on Au surface for all the thiol molecules studied in this work.

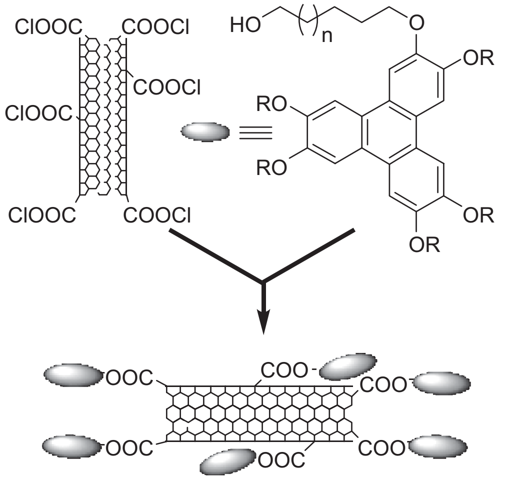
We have also synthesised amphiphilic GNPs functionalised with hydroxy-terminated alkyl-thiol and studied the Langmuir film of the particles by surface manometry and microscopy techniques (*110*). We find a stable Langmuir monolayer of the GNPs at the air–water interface. The monolayer exhibits the gas, low-ordered liquid (L_1), high-ordered liquid (L_2) and collapsed states. The first-order phase transition between L_1 and L_2 is accompanied by a coexistence of the two phases. The coexisting region of L_1 and L_2 vanishes above a critical temperature of 28.4°C. For a range of higher temperatures ($\geq$29.4°C and 36.3°C), the L_1 phase undergoes a transition to a bilayer of the L_2 phase before entering into the collapsed state.

6.2 Single-wall carbon nanotubes in discotic liquid crystals

CNTs, the one-dimensional carbon allotropes, are well ordered all-carbon hollow cylinders of graphite with a high aspect ratio. The combination of superlative mechanical, thermal and electronic properties displayed by CNTs make them ideal for a wide range of applications, such as conductive and high-strength composites, catalyst supports in heterogeneous catalysis, energy-storage and energy-conversion devices, field emitters, transistors, sensors, gas storage media, tips for scanning probe microscopy and molecular wires.

There has been growing interest in the field of dispersion of CNTs in both thermotropic and lyotropic LCs. The insertion (dispersion) of CNTs in the supramolecular order of discotic liquid crystalline monomers and polymers, particularly those having a stable columnar phase at room temperature, may lead to novel materials with interesting properties that are useful for device applications. With this in mind, we have initiated a research program to disperse functionalised CNTs into the matrix of liquid crystalline discotic monomers and polymers. TP-functionalised single-wall carbon nanotubes (SWNTs) and commercially available octadecylamine (ODA)-functionalised SWNTs were used to disperse in hexaalkoxy-TP discotics as well as in rufigallol and TP-based room-temperature monomeric and polymeric DLCs (*74*, *102*).

As prepared grade SWNTs were purchased from Carbolex Inc., (USA) and purified as reported. The resultant carboxylic acid groups-terminated SWNTs were converted into acid chloride groups (SWNT-COCl) by treatment with thionylchloride. The hydroxyl-terminated TP was prepared by the etherification of monohydroxy-pentabutyloxy-TP with 1-bromohexanol under classical reaction conditions. Discotic-functionalised SWNTs were prepared by mixing SWNT-COCl with hydroxyl-terminated TP and heating at 80°C for



Scheme 32. Synthesis of discotic-decorated SWNTs.

48 hours under anhydrous reaction conditions (Scheme 32). These functionalised SWNTs were highly soluble in common organic solvents, such as dichloromethane, chloroform, THF, etc. The formation of discotic-functionalised SWNTs was confirmed by infrared, ^{1}H NMR, ^{13}C NMR, thermogravimetric analysis (TGA) and scanning tunnelling microscopy studies.

The insertion of either discotic-functionalised SWNTs or commercially available ODA-functionalised SWNTs does not affect the mesophase structure of the pure compounds, but brings down the isotropic transition temperatures. With an increase in the amount of CNTs, the isotropic transition temperature decreases in all of the composites. Commercial ODA-functionalised SWNTs can be dispersed in DLCs only in small amounts (~1%) while a large amount (10%) of discotic-functionalised SWNTs can be dispersed in a columnar matrix. X-ray studies indicate that SWNTs align in the hexagonal columnar phase along the director (Figure 6). The room temperature liquid crystalline nanocomposites with broad mesophase ranges and different electronic properties may be important for many device applications.

We have also doped SWNTs in the nematic matrix of a room temperature liquid crystalline material 4-(trans-4'-n-hexylcyclohexyl)isothiocyanatobenzene. The effect of SWNTs doping on various display parameters, namely, threshold voltage, dielectric anisotropy and the splay elastic constant, has been studied using electro-optical and dielectric spectroscopy. The nematic phase supports alignment of SWNTs parallel to the nematic director. On the other hand, the presence of SWNTs improves the local orientational ordering of molecules in the nematic phase. Consequently, the threshold voltage required to switch the molecules from planar (bright state) to homeotropic (dark state) configuration is substantially reduced in the presence of the SWNTs (*111*).

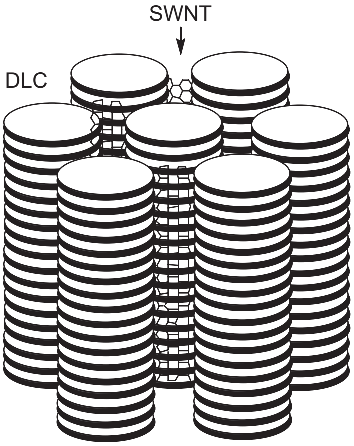


Figure 6. Dispersion of SWNTs in a columnar matrix.

7. Summary and outlook

Over 20 million chemical compounds are known in the chemistry world. The number of LCs (about 95,000) and particularly DLCs (only about 3000) is certainly 'a drop in the ocean'. However, the LC industry is a multi-billion dollar industry. Only a few liquid crystalline compounds are used in practical displays and other devices. New materials are required not only to understand the structure–property relationship, but also to find applications in devices. LCs are important not only in the display and semiconducting industries, but also in pharmaceutical industries and, therefore, their future is bright.

In this review article, we have given a glimpse of the author's and collaborators' research work mainly on DLCs. A vast amount of literature is available on these topics that could not be covered due to paucity of space. Nevertheless, relevant references have been given in original papers. Interested readers may look them or contact the author.

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