

Molecular engineering of discotic nematic liquid crystals

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Abstract. Connecting two columnar phase forming discotic mesogens via a short rigid spacer leads to the formation of a π -conjugated discotic dimer showing discotic nematic (N_D) phase. Attaching branched-alkyl chains directly to the core in hexaalkynylbenzene resulted in the stabilisation of N_D phase at ambient temperature. Pentalkynylbenzene derivatives possessing a combination of normal- and branched-alkoxy chains display a very broad N_D phase which is stable well below and above the room temperature.

Keywords. Discotic nematic liquid crystals; discotic dimers; multiynes; alkynylbenzene; liquid crystal display.

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1. Introduction

Twenty-five years have passed since the first discotic liquid crystals (LCs) have been synthesised at the Raman Research Institute in Bangalore [1]. During these two and half decades, more than 3000 discotic LCs have been prepared and characterised [2,3]. Discotic LCs constitute a vital family of functional materials with immense applications such as photoconductors, one-dimensional conductors, light emitting diodes, photovoltaic solar cells, gas sensors, etc. [4].

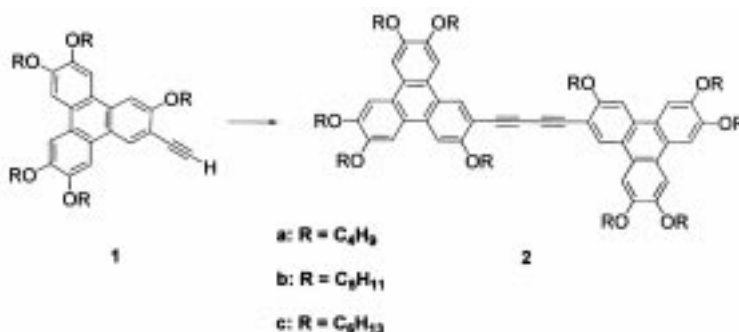
Discotic LCs are mostly composed of a π -conjugated central core substituted with usually 3 to 8 flexible aliphatic chains at its periphery. Probably because of intense π - π interactions, a majority of these materials (about 95%) form columnar mesophases and only a small number show a nematic phase. In the columnar phases molecules are stacked one on top of the other into columns and the columns possess two-dimensional long-range positional order. In the discotic nematic phase, there is only an orientational order of the discs with no long-range translational order. The negative birefringence film formed by polymerised nematic discotic LCs has been commercialised as compensation foils to enlarge the viewing angle of twisted nematic liquid crystal displays (LCDs) [5]. We have recently proposed a wide viewing liquid crystal display device based on discotic nematic LC [6].

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

2. Design and synthesis of discotic nematic liquid crystals

Molecular assembly of columnar phase forming discotic LCs with basic structural features, flat or nearly flat aromatic cores surrounded by flexible alkyl chains is often simple and a number of monomeric discotic LCs displaying columnar phases have been prepared using this technique. Discotic dimers in which two molecules are connected to each other via a long flexible alkyl chain spacer also form columnar phases as the molecules have sufficient flexibility to stack in adjacent columns [7]. Similarly, discotic oligomers and polymers are also reported to form columnar mesophases [8].

It was anticipated that linking two discotic molecules via a short rigid spacer might experience some steric hindrance due to overlapping or interdigitating aliphatic side chains and a weak distortion of the planarity of the core. This may reduce the strong π - π interactions. The rigid molecules may stay in more or less parallel position having orientational order but may lose their long range translational order and, therefore, likely to form discotic nematic phase. Compounds **2a-c** were designed to verify this idea [9]. These twins were prepared by the dimerisation of free monoacetylenes **1a-c** which in turn can be prepared from monobromopentaalkoxytriphenylenes [9].



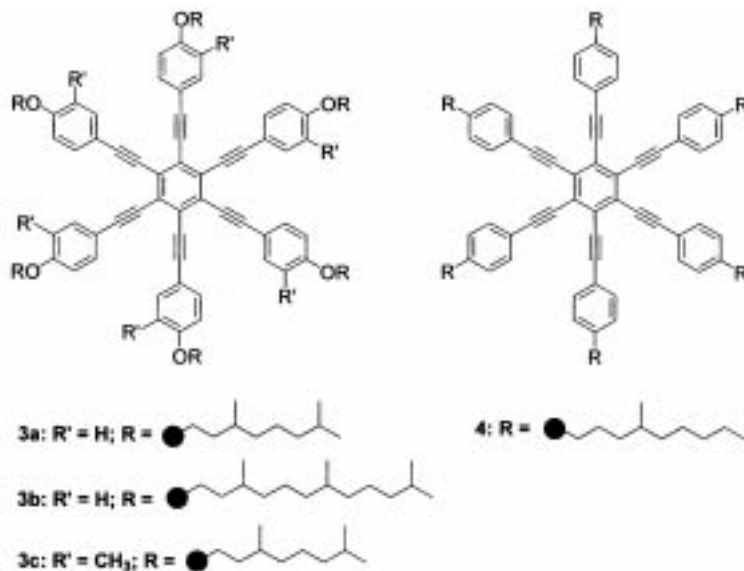
As predicted, all the dimers form discotic nematic phase over a wide temperature range. The crystalline compounds **2a**, **2b** and **2c** melt at 188.6, 161 and 135.3 °C respectively to nematic phase. The liquid crystalline phase changes to isotropic phase at 243.5, 215.9 and 172.8° respectively. Upon cooling the isotropic liquid, classical Schlieren texture was observed in all the cases. The crystallisation occurs at 172.8, 152.8 and 126.5 °C respectively in all the three materials on further cooling.

3. Design and synthesis of room-temperature discotic nematic liquid crystals

Benzene-centred multiynes are the mesogens of choice to prepare room-temperature discotic nematic liquid crystals as a number of compounds of this class are already known to show stable discotic nematic phase [2,10]. Therefore, some minor structural modifications may lead to materials having room-temperature discotic nematic phase.

The use of branched chains in liquid crystals often reduces melting and isotropic temperatures. 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 discotic liquid crystals forming

columnar mesophases [11]. Compounds **3a** and **3b** were designed and prepared to check if this technique is also effective in the case of alkoxyalkynes-based discotic nematic liquid crystals. Disappointingly, compound **3b** having 3,7,11-trimethyldodecane periphery was found to be non-liquid crystalline and compound **3a** with 3,7-dimethyloctane periphery showed only a high-temperature mesophase. It melts at 80°C to a nematic phase which clears at 124°C. On cooling the nematic phase appears at 123°C and crystallises at 64°C.

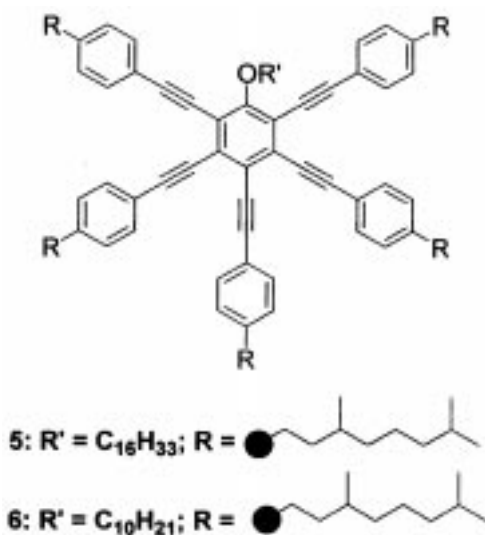


It has been observed that in the case of several triphenylene-based discotic nematic liquid crystals, a lateral methyl group substitution reduces the transition temperatures significantly [12]. Surprisingly, compound **3c** with a lateral methyl group and branched-alkoxy chain substitution does not show any such effect. In fact, the isotropic temperature increases on lateral methyl group substitution in hexaalkynylbenzene. Compound **3c** on heating exhibits a N_D phase at 71°C. Its colour changes from light yellow to brownish on heating to isotropic temperature (broad 147–160°C) indicating partial decomposition of the material at higher temperature.

From the reported thermal data of alkyl- and alkoxy-substituted hexaalkynylbenzene derivatives [10], it is clear that when the peripheral alkyl chains are attached to the phenyl ring in the hexaalkynylbenzene via oxygen atom, the melting and clearing temperatures are higher compared to when the alkyl chains are directly attached to the ring. For instance, the thermal behaviour of the heptyl-substituted hexaalkynylbenzene is Cr 99°C N_D 132°C while the thermal behaviour of the heptyloxy-substituted hexaalkynylbenzene is Cr 109°C N_D 193°C I [10]. Again, as mentioned above, it is also known that when the peripheral aliphatic side chains of various cores are branched, the mesophase is widened but the type of the mesophase formed is not affected by the introduction of branching in many cases [11]. Therefore, it may be logically concluded that by replacing the normal alkyl chains by branched alkyl chains connected directly to the phenyl ring, the melting points of alkynylbenzene derivatives may reduce and thus, stabilise the mesophase. Compound **4** designed on this basis was indeed found to exhibit a nematic phase at ambient temperature. It rep-

resents the first example of a room-temperature discotic nematic liquid crystal [13]. The compound exhibits the N_D phase between -12°C and 68°C .

A number of pentaalkynylbenzene derivatives are known to show N_D phase [10]. In these multiynes, five positions of a benzene ring are usually substituted with phenylalkynyl moieties and the remaining one position by a normal alkoxy chain. From the thermal data of known derivatives, as expected, it can be seen that increasing the length of normal alkoxy chain, decreases the melting and isotropic temperatures. An interesting example in this series is compound **5** which shows a phase transition $T_g - 36^\circ\text{C}$ N_D 23°C I [10]. It is expected that shortening the *n*-hexadecyl chain would increase the isotropic temperature and thus stabilise the N_D phase at room temperature. Accordingly, compound **6** was designed and prepared. The synthesis involves alkylation of pentabromophenol with decylbromide followed by the five-fold condensation of branched-alkoxy chain-substituted phenylacetylene using Sonogashira reaction conditions. The compound was found to be discotic nematic at room temperature. Its differential scanning calorimetry exhibits a glass transition at about -35°C and the isotropic temperature at 40°C .



4. Conclusion

It has been shown that the less common discotic nematic phase can be created by a careful synthetic design. Discotic dimers in which two columnar phase forming molecules were connected to each other via a short rigid spacer exhibit discotic nematic phase. The discotic nematic phase of hexa- and penta-alkynylbenzenes can be stabilised well below and above the room temperature either by attaching branched-alkyl chain directly to the phenyl ring or by a combination of normal and branched-alkoxy chains substitution. These materials may be useful for wide viewing LCD devices.

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