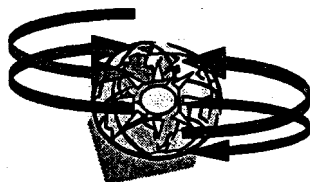


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Supramolecular Assemblies of Disk-Shaped Molecules

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Abstract. Columnar phases of **discotic** liquid crystals display large charge carrier mobilities and, therefore, can be exploited for various applications such as, one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, field-effect transistors and gas sensors. Some chemical aspects of our recent work on the synthesis, characterization and mesomorphic behavior of some electron-rich and **electron-deficient discotic** liquid crystals are presented.

Keywords: Self-assembly, supramolecular order, **discotic** liquid crystals, columnar phase, nematic phase

1. INTRODUCTION

The hierarchical self-assembly of disc-shaped molecules leads to the formation of **discotic** liquid crystals (DLCs).¹ Mesophases formed by disc-shaped molecules are primarily two types: (1) nematic and (2) columnar. In the nematic **discotic** phase, the molecules stay in more or less parallel position having orientational order but no long-range positional order. On the other hand, in columnar mesophases, molecules assemble themselves one on top of the other in columns packed parallel on a two-dimensional lattice (Fig. 1). The molecules may be arranged in a regular ordered manner or aperiodically.

The core-core separation in a columnar mesophase is usually of the order of 3.5 \AA so that there is considerable overlap of π -orbitals. As flexible long aliphatic chains surround the core, the intercolumnar distance is usually $20\text{-}40 \text{ \AA}$, depending on the lateral chain length. Therefore, interactions between neighboring molecules within the same column would be much stronger than interactions between neighboring columns. Consequently, charge migration in these materials is expected to be quasi-one-dimensional. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than in the perpendicular direction. Thus the columns may be described as molecular wire (Fig. 1). Charge carrier mobilities in the range of 10^{-3} to $0.71 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ along the columns have been observed in various columnar mesophases.⁴ Electroluminescence and photovoltaic devices based on **discotic** liquid crystals have been prepared recently. Mechanism of charge transport and one-dimensional energy migration has also been studied extensively in these materials.

Like organic materials, **discotic** liquid crystalline semiconductors are also two types; p-type, in which the majority of charge carriers are holes and n-type, where the majority of charge carriers are electrons. Prominent examples of p-type DLCs are the derivatives of triphenylene, dibenzopyrene and hexabenzocoronene cores while tricycloquinazoline, anthraquinone and

perylene derivatives are common n-type DLCs. The chemistry of some of these materials, prepared in our lab, is described below.

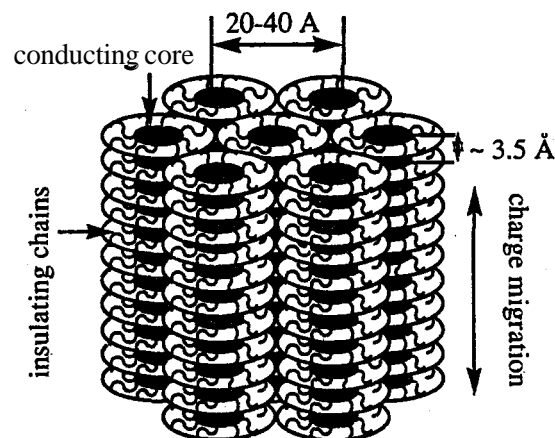


FIGURE 1. Schematic view of charge migration in columnar phase.

2. SYNTHESIS

2.1 Triphenylene-based DLCs: The best studied core system in the field of DLCs is triphenylene (TP). It was demonstrated by Billard *et al.* in 1978 that triphenylene hexaesters display columnar phases.⁵ Triphenylene derivatives are thermally and chemically stable and show a variety of mesophases having interesting electronic properties. At present more than 500 discotics based on a TP core are known in the literature.⁶

The discovery of very high one-dimensional charge carrier mobility in hexahexylthio-TP vitalized research activities in the field of **discotic** liquid crystals. This compound forms a self-organized helical columnar phase at low temperatures with nearly crystalline order in addition to the normal columnar phase. The photoinduced charge carrier mobilities up to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were achieved in the helical phase. With the exception of organic single crystals, these were the

highest electronic mobility values reported till that time.⁴ However, due to problems of low yield and purity, potential utility of this compound and other related materials has not yet been fully explored. Here, we report the synthesis of highly pure hexaalkylthio-TP derivatives in very high yields.

The synthesis of **hexaalkylthio-TPs**, involving the thiolate anion substitution of **2,3,6,7,10,11-hexabromo-TP (1)** with excess of sodium alkylthiolate in a polar aprotic solvent, has been reported in the literature.⁷ The **hexaalkylthio-TPs (2)** prepared by using these methods are often contaminated with a very small amount of inseparable impurity, that can be detected by differential scanning calorimetry (DSC). To achieve a highly pure product for various physical studies, several recrystallizations are required which resulted in the loss of a lot of material. Presuming that the impurity is due to partial dealkylation of the hexathioether that could be formed by the nucleophilic attack of the excess of thiolate ion, we realkylated the crude product *in situ* with an appropriate alkyl halide. This has a dramatic effect on the purity and yield of the product.

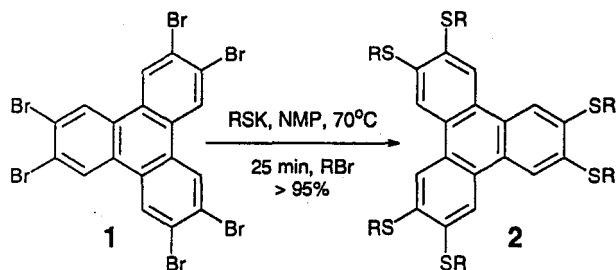


FIGURE 1. Synthesis of hexaalkylthiotriphenylenes (Scheme 1)

In our modified method, we generated thiolates with potassium-*t*-butoxide in NMP and subsequently heated with **hexabromo-TP** at 70 °C for 25 minutes in the same solvent. In order to realkylate the exposed thiophenolate group(s), we worked-up the reaction mixture with an appropriate **alkyl bromide**. (Scheme 1). This modification not only enhanced the yield of the desired material (> 95%) but also greatly facilitated purification as besides the **dialkylsulfide**, no other side product was detected.

We have developed a number of methodologies to prepare a variety of other p-type DLCs.⁸

2.2 Tricycloquinazoline-based DLCs: Both, p-type and n-type organic semiconductors are required for various device applications such as photovoltaic solar cells, light emitting diodes, etc. Most of the **discotic** liquid crystals are electron rich (p-type) systems and only a few electron deficient (n-type) discotics are known. Tricycloquinazoline (TCQ) is an attractive e-deficient **discotic** core as it possesses C_3 symmetry, its derivatives are colored and it shows extraordinary

thermal and chemical stability. The molecule exhibits intriguing physical characteristics, such as a low ionization potential and interesting spectroscopic and electronic properties.⁹

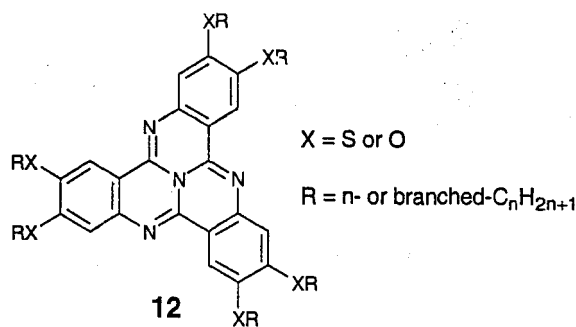


Figure 2 : Scheme 2

We have prepared a broad spectrum of homologous 2,3,7,8,12,13-hexaalkoxy- and hexaalkylthio-TCQ derivatives 12 with alkyl side chain lengths varying from 3 to 18 carbon atoms.⁹ Replacing the normal alkoxy chains by branched chains causes depression in the isotropic temperature and stabilization of the mesophase. Thus the TCQ derivative with six 3,7,11-trimethyldodecyloxy chains displays the columnar phase between -50 °C to 143 °C. X-ray studies indicates that the mesophase formed by these compounds is Col_h type with a very short core-core distance (3.29 Å) which is one of the lowest core-core separation known in **discotic** liquid crystalline systems. The one-dimensional charge mobility in this compound at room temperature was found to be close to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

2.3 Gold nanoparticles in columnar matrix: There has been a growing interest in gold nanoparticles (GNPs) as the physical properties of nano-sized metal particles are very different from those of bulk material. For instance, the conductivity of bulk gold is very high ($4.3 \times 10^7 \Omega^{-1} \text{ m}^{-1}$) while GNPs of 1-2 nm are only semiconducting ($1.4 \times 10^3 \Omega^{-1} \text{ m}^{-1}$). Therefore, potential applications of these nanoparticles in the field of catalysis, nonlinear optics, chemical and biological sensors, **molecular recognition**, nanotechnology, etc., have been envisaged.^{11,12} Recently, **Hasobe et al.** prepared efficient photovoltaic solar cells using composite nanoclusters of porphyrins and fullerenes with gold nanoparticles.¹³

As described above, DLCs have now been well-recognized as one-dimensional semiconductors. The intercalation of gold nanoparticles into a matrix of **discotic** liquid crystals may leads to novel composites with interesting properties useful for many device applications. With this in view, we have incorporated gold nanoparticles in the supramolecular order of

various disc-shaped molecules by doping alkanethiol-protected gold nanoparticles in DLCs.¹⁴

Hexanethiolate-stabilized gold clusters (Fig. 3) were prepared following the reported method. The hexahexylthio-TP (HHTT) was prepared as mentioned above. Binary mixtures of GNPs and HHTT were prepared by mixing the two components in dichloromethane followed by removal of solvent and drying in vacuum. All the composites were analyzed by differential scanning calorimetry and polarizing optical microscopy. The conductivity of these composites was measured by a four-point probe.

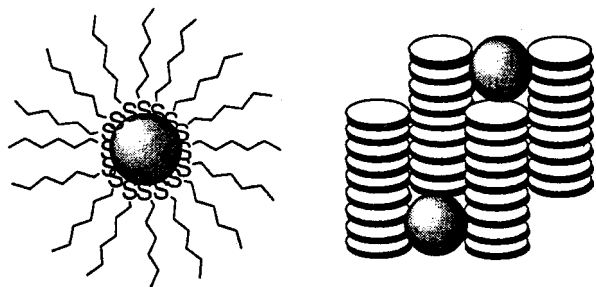


FIGURE 3: Alkanethiolate-covered gold nanoparticle and their possible inclusion into a discotic liquid crystalline matrix.

Polarizing optical microscopy, differential scanning calorimetry and conductivity results indicate inclusion of thiolate-protected gold nanoparticles into a discotic liquid crystalline matrix. Increasing the amount of GNPs, increases the tendency of phase segregation and decreases the isotropic temperature. The conductivity of DLC-GNP composites is significantly higher (~ 250 times) compared with the pure discotic compound. Therefore, these inorganic-organic liquid crystal hybrid systems may be extremely important for many device applications such as photoconductors, light emitting diodes, photovoltaic solar cells, sensors, optical data storage, thin film transistors, etc.

3. CONCLUSION

In this paper, we have described briefly the chemistry of some p-type and n-type discotic liquid crystalline materials. Discotic molecules are of interest for their intriguing supramolecular architectures. Their strong π - π interactions within a column lead to high one-dimensional electronic mobilities, a property that is essential in the development of many eco-friendly devices.

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