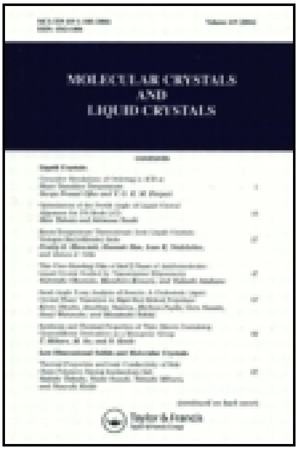

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Charge Transfer Salts of Highly Oriented Fibers of Discotic Liquid Crystal HET-n

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CHARGE TRANSFER SALTS OF HIGHLY ORIENTED FIBERS OF DISCOTIC LIQUID CRYSTAL HET-n

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Abstract The charge transfer salt of highly oriented fibers of discotic liquid crystals of 2,3,6,7,10,11-hexa-alkoxytriphenylene (HET-n) and 2,3,6,7,10,11-hexa-alkanoyloxytriphenylene (HAT-n) can be made by a strand technique followed by a doping process. As a result, the bromine doped HET-5 fiber shows a conductivity of three orders of magnitude higher than that of the bromine doped HET-5 powder.

INTRODUCTION

Recently several planar polycyclic aromatic hydrocarbons were found to be excellent organic donors for the preparation of quasi-one-dimensional conductors. Examples include naphthalene, pyrene, perylene[1], fluoranthene[2], and 1,2,7,8-tetrahydrocyclopentaperylene[3]. These compounds, when oxidized electrochemically in the presence of anions of low nucleophility such as PF_6^-, ClO_4^-, AsF_6^-, SbF_6^-, BF_4^- etc., form needle-like crystals with a common structure. This structure consists of segregated stacks of arene molecules with the molecular rings tilted to the stacking axis[1-4]. This orientation facilitates the intermolecular orbital overlap and gives rise to narrow conduction bands along the molecular stacks.

In addition to the formation of conducting charge-transfer salts, it is possible, through substitution of several long alkyl chains symmetrically around the mesogenic arene core, to convert these molecules into a class of disc-like liquid crystals.[5] Examples are 2,3,6,7,10,11-hexa-alkoxy triphenylene (HET-n, 1) and 2,3,6,7,10,11-hexa-alkanoyloxytriphenylene (HAT-n, 2)[6]. These materials exhibit highly viscous mesophases at temperatures between the crystalline solid and isotropic liquid. In the meso-phase region, due to the incompatibility between aromatic hydrocarbons and aliphatic chains, disc-like molecules tend to pack themselves microscopically in segregated columns (Figure 1) with a vector $\hat{n}$ pointed along the column axis. Structurally this columnar phase is much like the arene core stacking of radical cation salts described above with the alkyl tails remaining liquid like between the stacks. We therefore speculated that, with a proper doping and alignment technique, we might be able to form conductors from the

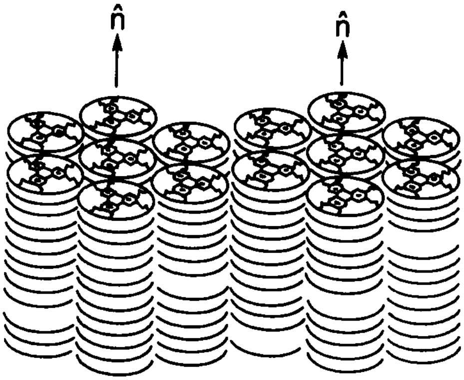


FIGURE 1 Schematic representation of the columnar structure of hexagonal mesophase of HET and HAT.

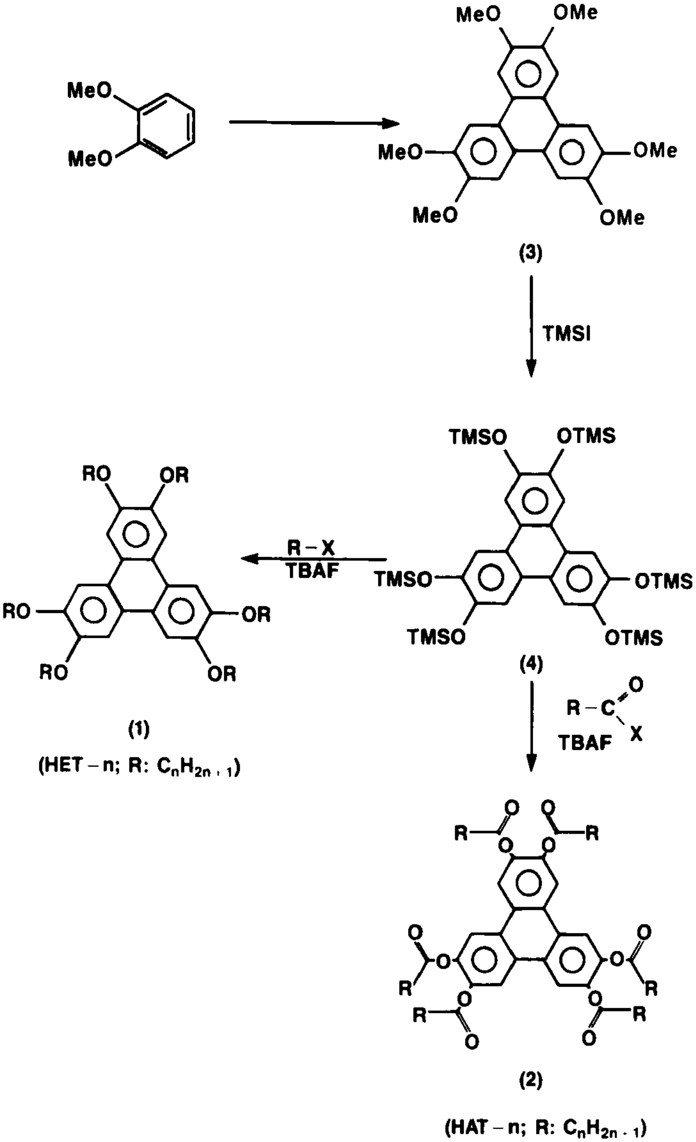
discotic liquid crystal.[7] The study can be approached in two ways. The first involves the alignment of DLC initially and the doping with the appropriate counter anion to form the conducting state. Alternatively we can prepare charge transfer salts of DLC and then align them. Since it is unclear whether the material remains discotic in the doped state, we decided to proceed along the former route.

In this paper we present an efficient synthesis of HET-n (1) and HAT-n (2) and the use of a strand technique[8] to align these discotic liquid crystals into highly oriented fibers. Synchrotron x-ray scattering studies[8] have shown the single crystal quality of these fibers. We also report the study of the doping and the conductivity of these aligned fibers.

SYNTHESIS OF DISCOTIC LIQUID CRYSTALS

Both of HET-n and HAT-n are synthesized by a new route from a common intermediate of hexamethoxytriphenylene[9] (3) as shown in Scheme 1. The demethylation reaction of hexamethoxytriphenylene with trimethylsilyliodide was carried out in a chloroform solution at its refluxing temperature. Without the isolation of intermediate (4), the reaction mixture was treated very slowly with tetrabutylammonium fluoride (TBAF) in the tetrahydrofuran solution in the presence of alkylhalide or alkanoyl chloride at 80°C to afford hexa-alkoxytriphenylene (1) in a 54% yield or hexa-alkanoyloxytriphenylene (2) in a 72% yield.

The phase sequences of three examples of (1) and (2), which are used in this study, are described in Figure 2 and Figure 3. Among them HAT-11 exhibits multiple first order


MeO
MeO
MeO
OMe
MeO
OMe
MeO
OMe
(3)
TMSI
TMSO
OTMS
TMSO
OTMS
TMSO
OTMS
(4)
R – X
TBAF
RO
OR
RO
OR
RO
OR
(1)
(HET – n; R: CnH2n+1)
R – C O X
TBAF
R
O
(2)
(HAT – n; R: CnH2n+1)

SCHEME 1

columnar phase transitions between 117°C and 57°C by decreasing the temperature. To date x-ray scattering studies[8,10] are able to resolve the structure of both two-dimensional hexagonal D2 columnar phase and centered rectangular D1 columnar phase. We thus use these two phases to study the alignment process. In the case of HET molecules, both HET-5 and HET-7 exhibits only a single hexagonal columnar phase[11].

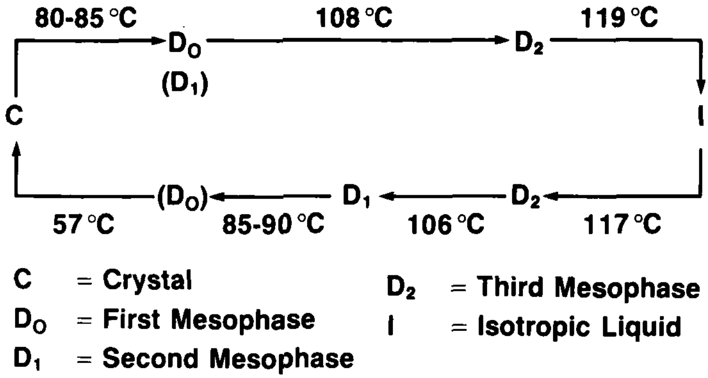


FIGURE 2 Phase sequence of HAT-11

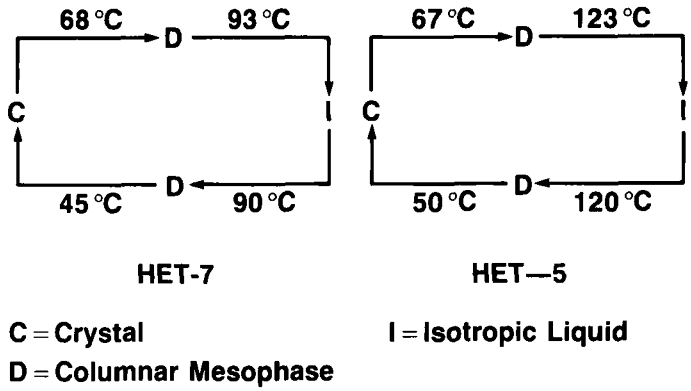


FIGURE 3 Phase sequence of HET-5 and HET-7

STRAND ALIGNMENT TECHNIQUE

It has been known that certain rod-like liquid crystal molecules can be aligned or reoriented into a highly ordered matrix by the application of external electric or magnetic field[12], by the chemical modification on surface (surface alignment)[13], or by a film technique[14]. However, due to the lack of anisotropic dielectric dipole moment and the planar symmetrical molecular structure of discotic liquid crystal, the external electric field cannot be used for alignment. The use of an external magnetic field for the DLC alignment is also not promising. Only a partial alignment of DLC with a short-range translation order can be achieved by a rotating magnetic field[15]. Furthermore, the reported surface alignment[16] might have a good potential of success.

Recently the strand technique[8,17] has been proven to be a reliable technique to date for the alignment of DLC. The origin of this technique relies on the tendency of DLC ordering at its columnar phase temperature. Experimentally freely suspended fibers of DLC are drawn in a two-stage oven consisting of a mechanically operated pin and a reservoir cup. The temperature of both pin and cup is monitored to a stability of 0.01°C. The metal pin is connected to a series of gears which provide a slow, smooth pulling motion of the pin. The process is operated at a narrow temperature range within the columnar phase of discotic liquid crystal (1) and (2). A typical fiber of 1-3 mm long with a diameter between 50 μm and 400 μm is obtained. The resulting colorless and semi-transparent fibers are apparently stable and isolatable. Colorful, highly crystalline textures can easily be observed by viewing the oriented fiber in a polarizing microscope.

The single crystal quality of both fibers of (1) and (2) are substantiated by synchrotron x-ray scattering studies.[8] In those reports the degree of liquid ordering of molecules inside columns of these DLC fibers has also been studied. The x-ray scattering data reveal only a liquid-like short range ordering in HAT-n fibers. However, in HET-n series of compounds, the liquid peak (Figure 4) narrows as n (chain length) decreases indicating longer ranged intermolecular correlations. This correlation length increases significantly from 3-4 nearest neighbor to more than 12 nearest neighbor as n decreases from 11 to 6.

DOPING AND CONDUCTIVITY STUDY OF DLC FIBERS

The degree to which conduction will occur along the discotic stacks depends strongly on the intermolecular correlation (ordering). As pointed out by the x-ray scattering data this correlation grows as the alkyl chain length decreases. For this reason we have used the HET-5 as the initial compound for the conductivity measurements.

Fibers of HET-5 were grown in the fashion described above and then cooled into the solid phase. The fiber was then removed from the oven, mounted with gold leads in a two-probe configuration and placed in bromine vapors. Conductivity of these fibers was found to increase by 4 orders of magnitude over the undoped sample to a semiconducting value of 10^{-4}-10^{-5} $\Omega^{-1}cm^{-1}$. This value is consistent with a Mott-Hubbard insulator resulting from a 1:1 complex with Br^{-}. This value was 2~3 orders of magnitude higher than that measured for powder samples of HET-5

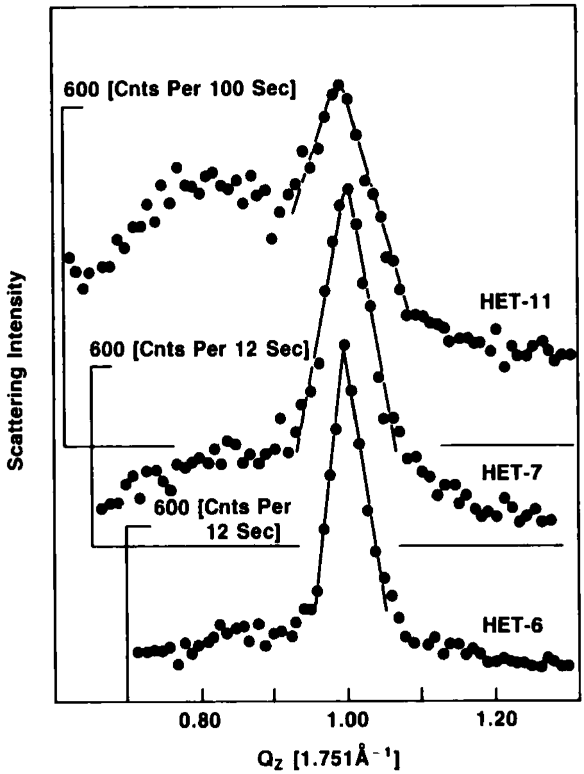


FIGURE 4 X-ray scattering scan along the stacking direction of HET-n compounds. The strong structural evolution in the columns as a function of chain length is observed.

doped with bromine, resulting from the high anisotropy expected for these materials. Similar results were obtained by doing an in situ sample of a HET-7 strand at temperatures above the discotic transition.

CONCLUSION

In conclusion we report on preliminary conductivity measurements on charge transfer salts of discotic liquid crystals. We find that we can increase the conductivity of bromine doped HET-5 by first aligning the molecules with a strand technique. This offers a promising new route to the synthesis of low-dimensional conductors.

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