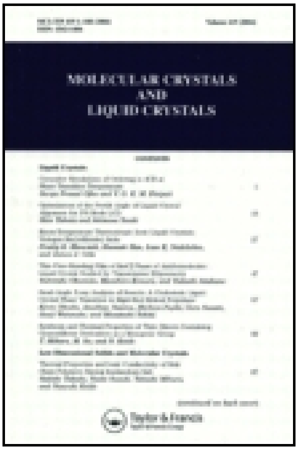

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Electronic Properties of Discotic LC-Materials

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ELECTRONIC PROPERTIES OF DISCOTIC LC-MATERIALS

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Abstract We have made extensive studies of the charge-carrier mobilities in the discotic hexagonal mesophases of triphenylene-based discotic liquid crystals. Using the time-of-flight technique, transient photocurrents were measured yielding charge-carrier mobilities for various electric fields and temperatures. Starting from promising results obtained with the monomeric discotic liquid crystalline model compound hexapentyloxytriphenylene (H5T), we synthesized a *"discotic twin"* with two triphenylene units linked together by a suitable spacer. Additionally, we synthesized a discotic liquid crystalline oligomer consisting of four triphenylene units which are bound to a flexible cyclosiloxane ring. In the dimer and in the oligomer the discotic mesophase can be maintained in a discotic glass. Our data show that in both H5T as well as in the dimer and in the oligomer hole mobilities on the order of magnitude of 10^{-3}cm^2/Vs can be reached. Since the mobilities obtained in the oligomeric compounds are comparable to those found in the monomeric model compound, it becomes clear that the excellent charge-carrier transport properties in the discotic hexagonal mesophase can be preserved in easily processible and anisotropic organic thin films. Therefore, our results are an important step towards the applicability of highly ordered discotic liquid crystalline materials in the field of electronic applications.

INTRODUCTION

In their mesophases, discotic hexagonal liquid crystals self-assemble in stacks, and these stacks are packed in a hexagonal order. As indicated in Fig. 1, the tight packing of the large, electron-rich aromatic molecular units leads to a very favorable π-overlap, and the anisotropic geometry is well-suited for one-dimensional transport processes of excess charge carriers, i.e. conduction and photoconduction. Consequently, in the monomeric discotic liquid crystalline model compound hexapentyloxytriphenylene (H5T) we found hole mobilities on the order of magnitude of 10^{-3}cm^2/Vs[1]; these mobilities exceed typical values obtained in polymer-dispersed systems which are widely used in laser printers or photo copiers by approximately two ordes of magnitude.

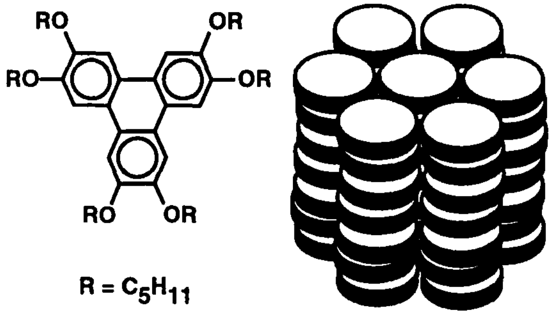

Figure 1: *Hexapentyloxytriphenylene (H5T) and a schematic view of its columnar mesophase*

In order to preserve the high-mobility properties of the model compound H5T in processible and film-forming materials, we synthesized discotic liquid crystalline triphenylene derivatives consisting of more than one triphenylene molecule per unit: In the upper part of Fig. 2 a perfect discotic twin (DIMER) is shown; its mesophase can be supercooled to room temperature, and below room temperature the mesophase can be frozen into a discotic glassy state. In the lower part of Fig. 2 a tetrameric triphenylene derivative is displayed, in which four photoconducting triphenylene units are attached to a flexible cyclosiloxane ring. The TETRAMER does not tend to recrystallize, and again the mesophase can be frozen into a discotic glass. In this paper we report on the charge-carrier transport properties of the abovementioned DIMER and TETRAMER materials.

EXPERIMENTAL

The DIMER was synthesized according to Ref. [2,3,4,5], and the TETRAMER was synthesized according to Ref. [6], respectively. Subsequently, both compounds were highly purified by flashchromatography and by several recrystallizations. Further details of the sample preparation have been given previously [1,5,7].

Irradiation of the samples (thickness typically 10μm) with a strongly absorbed nitrogen laser pulse leads, under a high external field, to the creation of electron-hole pairs in close proximity to the front surface. Depending on the polarity of the external electric field, the motion of the charge carriers which preferably are holes in our case causes a displacement current which can be recorded in the outer electronic circuit over several orders of magnitude in the time and current. Again, details of the experimental setup are given in Refs. [1,5,7].

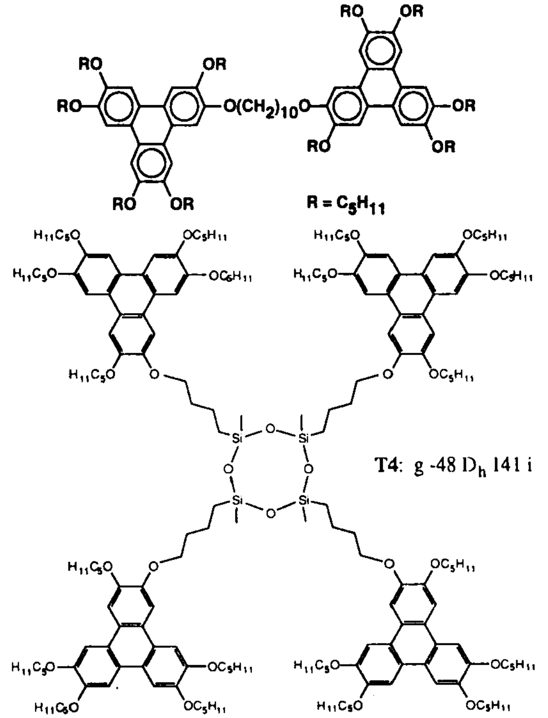

Figure 2: *Chemical structures of the DIMER (upper part) and the TETRAMER (lower part). The phase behavior is cr 337K (G 214K) D_h 408K I for the DIMER[2,3,5], and G 225K D_h 414K i for the TETRAMER[6]*

RESULTS

The field- and temperature independent hole mobilities of approximately $10^{-3}cm^2/Vs$ measured for H5T[1] can now be understood within the framework of disorder and thermal activation: Temperature-dependent disorder effects in the mesophase are compensated by an activated transport behavior enhancing a trap-dominated or polaronic mobility.

Most interesting for the DIMER is the unusual temperature dependence of the hole mobilities. The data which cannot be interpreted by standard theories [8,9,10], are shown in Fig. 3. The mobility values have been determined over a wide temperature exceeding a range of 200K. At low temperatures below the glass transition temperature T_g (214K) which has been determined by low-temperature differential scanning calorimetry (DSC)[5] the mobility data can be well described by a thermally activated behavior with an activation energy of (0.20±0.1)eV. At temperatures above T_g there are mainly two processes which strongly influence the transport of charge carriers: the thermal enhancement of the mobility is still present in the supercooled discotic hexagonal mesophase as well as in the mesophase itself. Additionally, with increasing temperature, the frozen-in molecular dynamics are enhanced, thus leading to a mobility increase of approximately one order of magnitude. Rising the temperature further to above room temperature, the mobility enhancement due to the dynamic healing of defects caused by moderate molecular dynamics is overcompensated by increasing effects of disorder[2,4,5]. In conclusion, the mobility data for the DIMER can be understood, if one combines features of common charge-carrier transport theories with features of the specific and temperature-dependent (dis)order and molecular dynamics of the discotic hexagonal mesophase.

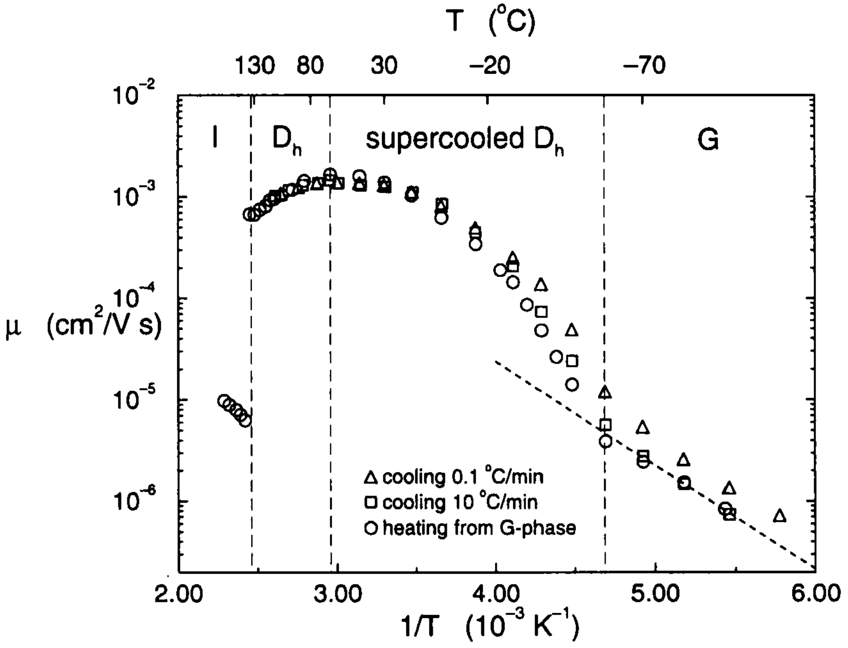

Figure 3: *Arrhenius plot of the DIMER hole mobility versus inverse temperature for various annealing conditions.*

The recrystallization tendency which is still present in the DIMER, is completely absent in the TETRAMER moiety. In other words, in this oligomeric triphenylene derivative, the mesophase and the discotic glassy state are not 'separated' by a metastable supercooled mesophase; here order and anisotropy can be directly frozen into the glassy state. With respect to applications, it is remarkable that the charge carrier transport properties of the monomer can be transferred almost completely into a discotic oligomer with good film-forming properties. In Fig. 4 the photocurrent transient of the TETRAMER is shown in a double-logarithmic plot. At the temperature of 358K, the transit time t_T corresponds to a mobility of approximately $8 \cdot 10^{-4} cm^2/Vs$. This is comparable to the values reported for the monomer H5T and for the DIMER. The detailed analysis of the field- and temperature dependent charge-carrier transport properties of the TETRAMER is currently under investigation and will be subject of further investigations.

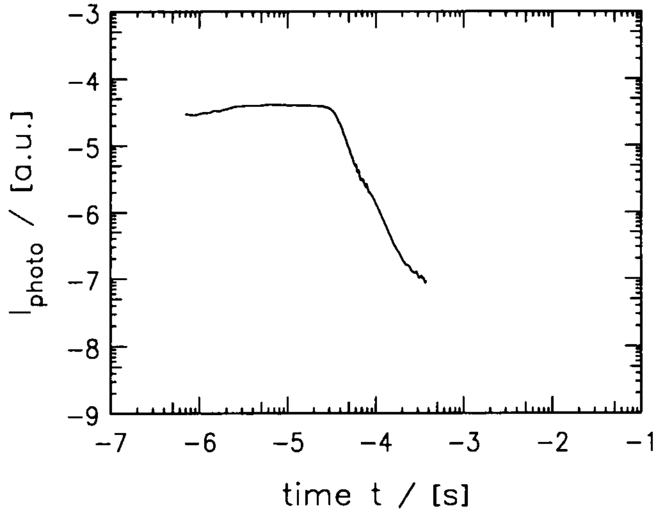

Figure 4: *Double logarithmic plot of a typical transient photocurrent I as a function of time t at a temperature of 358K.*

DISCUSSION

With respect to high mobility organic systems, besides the concepts of conjugated and quasiconjugated [11,12,13] polymers or amorphous triphenylamine derivatives [see, e.g.14], it becomes evident that in our approach using discotic liquid crystals really high mobilities which are comparable to those obtained in organic single crystals can be reached [7] . Microwave conductivity studies [15,16] show also that the charge-carrier transport process can be extremely effective in closely stacked and highly ordered molecular arrangements.

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