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PHOTOCONDUCTIVITY IN DISCOTIC LIQUID CRYSTALS: A NEW CLASS OF HIGH-MOBILITY MATERIALS

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Abstract Using a time-of-flight technique, different transport mechanisms, deep trapping, multiple shallow trapping and Gaussian transport, can be observed in the different temperature and phase regions of the liquid-crystalline (LC) photoconductor hexapentyloxytriphenylene (HPT). Transient photocurrents and carrier mobilities for various temperatures, electric fields, and sample histories were examined. The ideal intrinsic Gaussian transport, observed for holes in the mesophase, puts HPT into a new class of high-mobility materials with both hole mobilities on the order of $1 \cdot 10^{-3}\mathrm{cm}^2/\mathrm{Vs}$ and a steplike current decay. These features result from the fact that there is obviously neither a positional disorder nor an energetic disorder, which would impair efficient charge transport. This is probably achieved by special molecular packing mechanisms in combination with the dynamical processes of the LC phase and due to favourable properties of the HPT molecule, which has a rigid and conjugated core, a symmetric structure, and no permanent dipole moment.

Keywords: discotic, liquid crystal, photoconductivity, mobility, disorder, mesophase

INTRODUCTION

In liquid-crystalline (LC) systems two basic principles of nature are combined, namely order and dynamics. These two principles do not only result in the self-organization leading to structures such as mesogenic LC phases, but they also can promote dynamical transport processes.

Transient photoconductivity data will be presented for the discotic LC hexapentyloxytriphenylene (HPT), the data will be discussed at the level of our present, preliminary model.

As shown in Figure 1, the disc-like HPT molecules build up stacked arrays, which are arranged in a hexagonal lattice forming the columnar discotic hexagonally ordered (D_{ho}) mesophase.

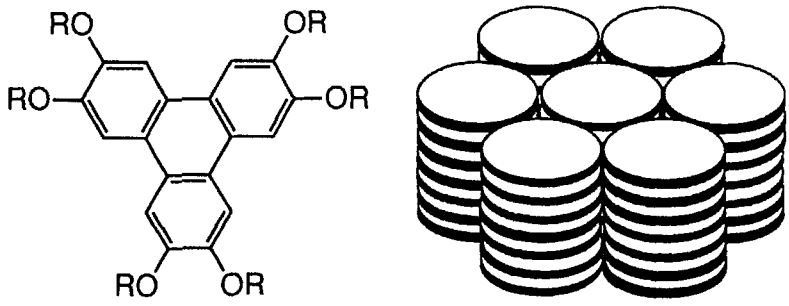

FIGURE 1 Hexapentyloxytriphenylene and a schematic view of its columnar mesophase ($R = C_5H_{11}$).

Due to the finite viscosity of the molecules in the mesophase, this order is not a static one, and there are dynamical processes such as bending of the columns, rotation of the discotic mesogens, or density fluctuations within the columns.[1-3]

The conjugated core of the triphenylene molecule also provides the HPT system with a functionality which is well suited for electronic transport processes. The columns are forming an efficient quasi one-dimensional transport path which is given by the mutual arrangement of the molecular stacks, the overlap and delocalization of the π-electron system. This has also been verified by exciton energy migration measurements,[4,5] by conductivity measurements in doped hexaalkoxytriphenylene,[6] and by photoconductivity measurements.[7-9]

The latter gave carrier mobilities of about $10^{-3}cm^2/Vs$ for holes in the mesophase.[7] This value lies in an intermediate range between amorphous polymeric systems with typical mobilities of 10^{-8} to $10^{-6}cm^2/Vs$ on the one hand and organic single crystals with mobilities of $1cm^2/Vs$ on the other hand. In this mobility scale which covers more than eight orders of magnitude there have also been some reports on exceptionally highly doped polymer systems with mobilities up to $10^{-3}cm^2/Vs$[10-12] and there are the conjugated and quasi-conjugated polymers which yield mobility values in the same range.[13-15]

We think, however, that the LC-concept of achieving high mobilities offers a new avenue for establishing organic high-mobility systems.

EXPERIMENT

The HPT molecules under investigation are characterized by a columnar discotic hexagonal ordered mesophase. The respective transition temperatures are K 69 D_{ho} 122 I.[16] HPT can be easily oriented homeotropically by slow cooling from the isotropic into the mesophase, yielding relatively large uniform domains.

HPT was synthesized according to the literature[16] and subsequently highly purified by flashchromatography and several recrystallizations. It was filled into quartz glass cells of typically 10 μm thickness, which were coated with semitransparent aluminum electrodes before filling.

During the experiments the samples were temperature controlled electronically.

The transient photocurrents generated by strongly absorbed short laser pulses (nitrogen laser, wavelength 337 nm, maximum pulse energy 5 mJ, pulse width 10 ns, penetration depth below 1 μm), which were due to electrons or holes (depending upon the cell polarity) were recorded using a typical time-of-flight (TOF) setup as shown in Figure 2.

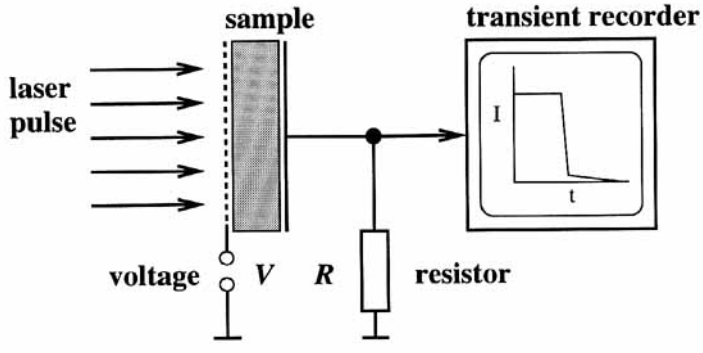

FIGURE 2 Schematic view of a typical time-of-flight setup.

The dynamic range of the TOF setup ranges over nine orders of magnitude in time from 10 ns to 10 s and has a dynamic range in amplitude of seven orders of magnitude with a maximum sensitivity of 10^{-10}A. More details of the experimental setup have been reported elsewhere.[7,17]

RESULTS

By analysing the measured transient photocurrents three main aspects of photoconductive materials can be investigated:

(i) Conclusions can be drawn about the involved charge carrier transport mechanisms.

(ii) The effective carrier mobilities μ can be calculated in a rather straightforward way using the well-known relation

$$\mu = \frac{l^2}{t_T U} \tag{1}$$

where t_T is the carrier transit time as derived from the transient current, l is the sample thickness and U the applied voltage across the sample.

(iii) The quantum yield of the carrier generation can be obtained by dividing the number of charge carriers by the number of absorbed photons. (The latter is beyond the scope of this paper.)

Transient Photocurrents

In Figure 3 the transient photocurrents for various experimental conditions are shown in a linear plot. HPT is displaying—as one of the few, if not the only known photoconducting system—the whole spectrum of photoconductive transient features.

The hole current in the mesophase (curve (c)) is characteristic of a trap-free and bandlike transport mechanism which is also referred to as Gaussian or non-dispersive transport in the literature. The current is constant, even at shortest times, until it drops to zero rather abruptly at the transit time. This behaviour is normally typical for many inorganic semiconductors but very exceptional for organic systems and resembles with minor variations data published e.g. for thin films of amorphous selenium.[18]

In contrast, the photocurrent in the crystalline phase shows (curve (a)) both, for holes and electrons, a totally featureless decay. This and a slope of –1 in the double-logarithmic plot[7] (not shown in this figure) suggest a transport mechanism dominated by deep trapping, the latter is also called totally dispersive transport in the literature.

The electron current in the mesophase (curve (b)) exhibits a transition from dispersive to non-dispersive transport, meaning a fast decay of the photocurrent at short times, a transition to a plateau region followed by a long time tail for times

longer than the transit time. These features are typical for multiple shallow trapping, where a narrow conduction band interacts with a set of shallow traps.[17]

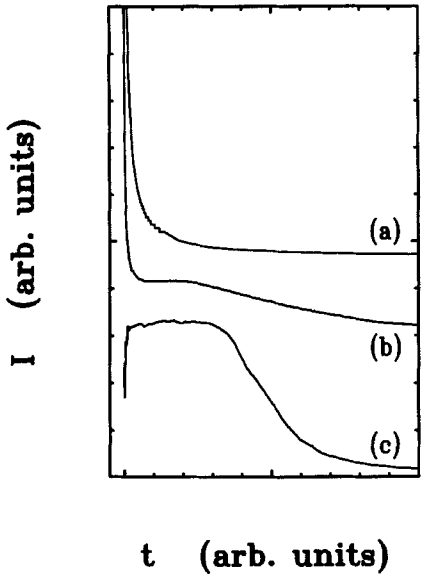

FIGURE 3 Linear plot of typical transient currents I as a function of time t at an electric field of $0.4 \cdot 10^5$V/cm and at various temperatures T and polarities: curve (a), $T = 26$°C, crystalline phase; curve (b), $T = 77$°C, mesophase, electrons; curve (c), $T = 77$°C, mesophase, holes.

Carrier Mobilities

Carrier mobilities are calculated according to Eq. 1; the transit times are defined as given by the intercept of the pre- and post-transit slopes in the logarithmic current versus time plot. This procedure, even though it is empirical, is commonly used in literature.[19] The temperature and field dependence of the carrier mobilities have been discussed in detail in an earlier publication.[7]

The most remarkable results are the following:

(i) The high carrier mobilities for holes in the mesophase of 10^{-3}cm^2/Vs are comparable to those obtained for conjugated and quasiconjugated polymers[13-15] and exceed those obtained for conventional amorphous systems by several orders of magnitude. Electron mobilities in the mesophase are on the order of 10^{-5}cm^2/Vs. This means that HPT is one of the few organic systems which show both intrinsic transport for holes and, in addition, electron transport.

(ii) In the mesophase the temperature-independent carrier mobilities for holes and the thermally activated electron mobilities, which obey an Arrhenius law with an activation energy of 0.6eV, can be interpreted within the frame of a Gaussian and a multiple shallow trapping transport mechanism, respectively (see also Figure 5).
(iii) The carrier mobilities for holes in the mesophase are independent of the external electric field. This fact is shown even more clearly in Figure 4. The inverse transit time t_T^{-1} versus the applied voltage U yields a linear dependence which means that the carrier mobility μ is constant and can be determined from the slope as $9.5 \cdot 10^{-4}\text{cm}^2/\text{Vs}$ according to Eq. 1.

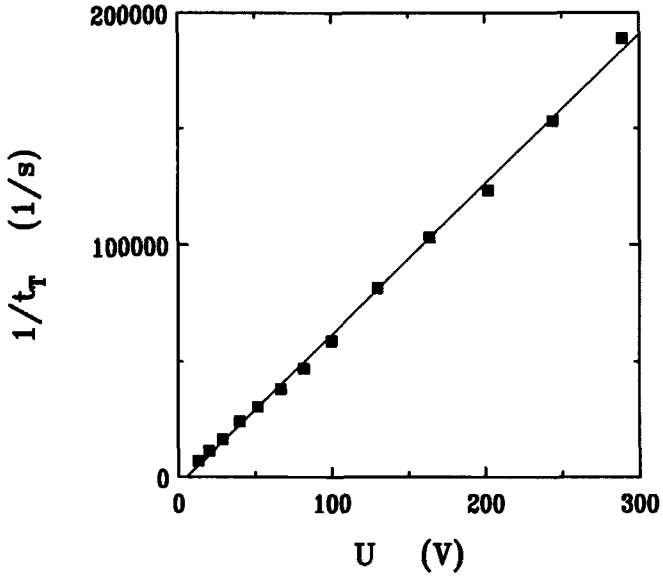

FIGURE 4 Inverse transit time t_T^{-1} as a function of the applied voltage U for holes in the mesophase at a temperature of 75°C

For the multiple shallow trapping mechanism as observed for electrons in the mesophase one would expect a field dependence of the carrier mobilities characterized by the relation $\lg \mu \propto \sqrt{E}$. However, also in this case a field-independent mobility was obtained from the measurement. Such a relatively constant drift mobility of the carriers in the corresponding field range would be plausible within the framework of a hopping model for energetically and spatially disordered sites for certain sets of the disorder parameters.[20]

Sample History

The size and the presence of uniformly and ideally oriented homeotropic areas in our sample cells, which can be observed under the polarizing microscope, depends on the cooling rates from the isotropic phase to the mesophase or on the heating conditions from the cystalline phase into the mesophase, respectively. In contrast to the macroscopic sample appearance, the sample history has a negligible influence on the carrier mobilities, which is illustrated in Figure 5.

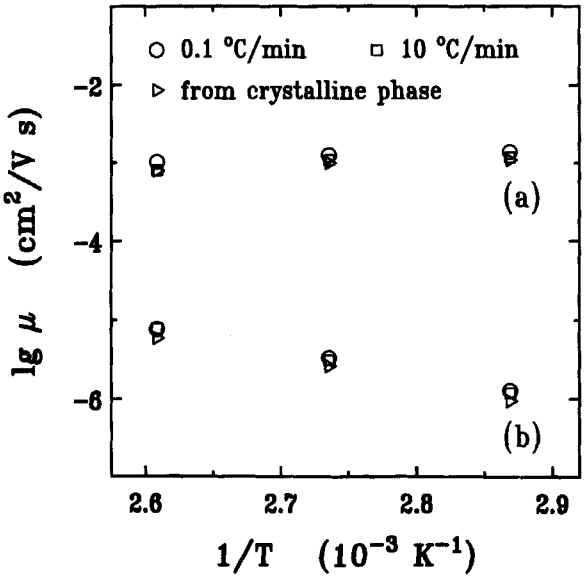

FIGURE 5 Dependence of charge carrier mobilities on previous heat treatments of the sample; plotted is the carrier mobility μ vs T in an Arrhenius form at an electric field of $0.4 \cdot 10^5$V/cm: (a) hole mobilities; (b) electron mobilities.

Reaching the mesophase by heating the sample from the crystalline phase or by cooling from the isotropic phase with different rates does not change the obtained values of the carrier mobilities within the experimental error.

DISCUSSION

A Gaussian or non-dispersive transport mechanism for hole transport in the mesophase can be inferred from the transient current shape and from the temperature- and field-independent mobilities. This is probably due to the following major microscopic reasons.

The main reason is probably the uniform orientation of the mesogens on a macroscopic or at least a mesoscopic scale because of the LC order principle, which is caused by the highly two-dimensional and rigid triphenylene core. The conjugated triphenylene cores provide an efficient transport path along the columns due to the quasi one-dimensional order, the overlap, and the delocalization of the π-electrons within the columns. Obviously no positional or off-diagonal disorder exists, which is omnipresent in all conventional organic systems and which could impede an efficient charge transport.

In addition, the observed transport phenomena are supported by the dynamical aspects of the LC phase. In general, there do not exist any grain boundaries in the D_{ho} phase of HPT,[21] and some defects probabley "heal" because of the possible dynamical fluctuations, i.e. molecular rotations, bending or density fluctuations.[1-3] This is also proven experimentally, since the carrier mobilities in the mesophase are independent of the sample history as shown and discussed in conjunction with Figure 5.

Another main microscopic basis for the observed Gaussian transport is the absence of or at least a neglectible influence of energetic or so-called diagonal disorder for hole transport in the mesophase. The absence of diagonal disorder may be due to the fact that the HPT molecules have no permanent dipole moment, are symmetrical, and have a rigid core which does suppress intramolecular motion within the triphenylene core. It is known from amorphous systems that, for instance, permanent dipole moments, variations of the mutual orientations or distances between sites can induce a variation and distribution of site energies.[22,23] Also intramolecular motions can cause energetic disorder.

Finally, the HPT molecules should be good donor molecules forming rather well stabilized radical cations to give rise to an efficient and trap-free hole transport.

The presence of each of the above discussed requirements for high mobility materials is, in our opinion, the reason for the exceptional transport properties of the HPT material.

In the polycrystalline phase the dynamical fluctuations of the molecues in the

mesophase are "frozen in" which results in e.g. grain boundaries. The latter can cause deep traps for the charge transport process; the result is a totally dispersive and trap dominated transport.

Despite the desirable properties of the D_{ho} phase with respect to the transport of holes, the electron transport in the mesophase is—in contrast to the hole transport—dominated by multiple shallow trapping, since the HPT molecules are probably poor acceptors and form comparatively instable radical anions. The latter argument, however, is still rather speculative.

For potential technical applications, e.g. in Xerography, both the comparatively high hole mobilities in the mesophase of $1 \cdot 10^{-3} cm^2/Vs$ and the Gaussian transport with its step-like current decay are most desirable, yet, the LC phase may cause problems for straight forward applications.

ACKNOWLEDGMENTS

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