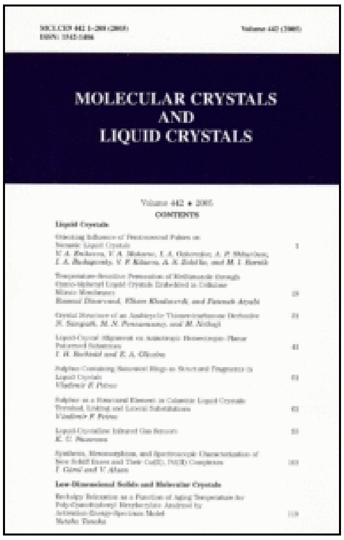

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Drastic Change of Mesomorphism Induced by the Fluorination of Peripherally Attached Phenyl Groups in Triphenylene Mesogens

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Triphenylene mesogens possessing fluorinated phenyl groups connected to the central triphenylene core with ester and ether linkages were compared on the mesomorphism. The results indicate that the fluorination of the peripheral phenyl groups arises strong intermolecular interactions among the peripheral parts to make the molecules stack easily to form a columnar structure. The thermal stability of the columnar mesophases is modified by the replacement of linkage group and the clearing temperature of Col_h *mesophase for the ester derivative is higher than that of the ether one. The carrier mobility evaluated by Time-Of-Flight (TOF) technique is shown to be in the order of* 10^{-3} cm^2 V^{-1} s^{-1} *and* 10^{-2} cm^2 V^{-1} s^{-1} *for the ester and ether derivatives, respectively.*

Keywords Carrier mobility; discotic liquid crystal; fluorination; liquid crystalline semiconductor; organic electronics

Introduction

Intermolecular specific interaction is an interesting tool for controlling molecular orders in both time-averaged (static) and dynamic points of view. Discotic columnar mesophase has been extensively studied as a new type of organic semiconductors and this category of molecular materials is featured by the self-assembling nature of molecules by way of its dynamical situations of molecular aggregations [1]. However, the improvement of carrier mobility is strongly required for liquid crystalline semiconductors toward the application of thin film devices such as organic transistors

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and thus, the higher ordered mesophase is desired to attain such an improvement involving 3-dimentional mesophase (not liquid crystals) [2]. In order to control the molecular dynamic and static orders of mesophase, one of the tools available for chemists is to modify the intermolecular interactions by way of the introduction of functional groups and/or atoms. Fluorine atom is, in this point of view, very attractive because of its unique properties such as low polarizability and strong electronic negativity [3]. These unique properties have been known to cause the characteristic behaviour as molecular aggregations such as fluorophilic/fluorophobic interactions working among the perfluoroalkane and hydrocarbon alkane chains.

Recently, the fluorination effect of mesogenic molecules on semiconducting as well as mesomorphic properties for triphenylene mesogens has been studied to find that the perfluoroalkylation of the peripheral chains in hexaalkoxytriphenylenes leads to stabilisation of hexagonal columnar ($\mathrm{Col_h}$) mesophase [4] and a strong tendency toward the homeotropic alignment comes up for a variety of substrates [5]. Also the carrier mobility behaviour was reported to show that the fluorination does not lead to the suppression of charge hopping phenomenon along the columnar axis [6].

On the other hand, the fluorination of the peripheral phenyl groups of a triphenylene mesogen to which are connected by ester linkages was studied and it was found that the columnar mesomorphism is remarkably enhanced to show a columnar mesophase with a high thermal stability (*ca.* 300°C) [7]. Furthermore, it was revealed that the position and site-number of fluorination on a peripheral phenyl group give rise to a drastic change of mesomorphism with extremely different thermal stability of mesophases [8].

In this work, triphenylene mesogens possessing peripheral fluorinated phenyl groups connected by an ester (**1**) and ether (**2**) linkages were compared on the mesomorphism and in addition the carrier mobility was evaluated by Time-Of-Flight (TOF) technique.

Experimental

The syntheses of compounds **1** and **2** were carried out according to the literatures described elsewhere [5,9].

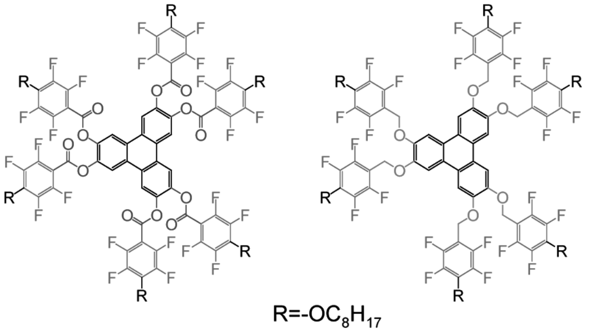
The phase transition behaviour was studied in the combination of texture observation by a polarised optical microscope (POM: Olympus BH2) equipped with a temperature-controllable hot-stage (Mettler FP82HT + FP90), DSC (TA Instruments, DSC2920) and X-Ray Diffractometer (Rigaku, Rint2000 with a hand-made oven) measurements.

The carrier mobility, μ was evaluated according to the equation (1) with the transit time τ, applied voltage, V and sample thickness, d in the cell obtained by Time-Of-Flight (TOF) technique. The details of the set-up was described in ref. 10.

$$\mu = d^2/V\tau \tag{1}$$

Results and Discussion

Figure 1 shows DSC curves of **1** and **2**. Both compounds exhibit an enantiotropic mesophase with a different phase transition enthalpies (ΔH) for the isotropisation. The mesophases were assigned to be a hexagonal columnar ($\mathrm{Col_h}$) one as seen in

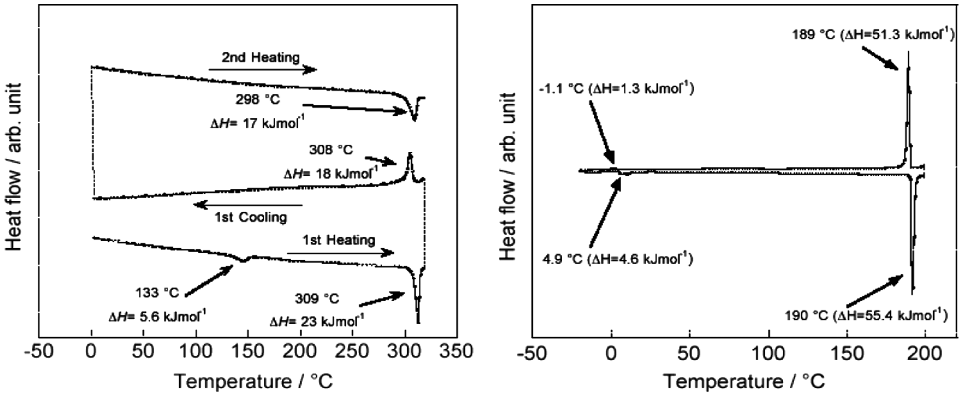


1 **2**

Figure 1. Chemical structures of compounds, **1** and **2**.

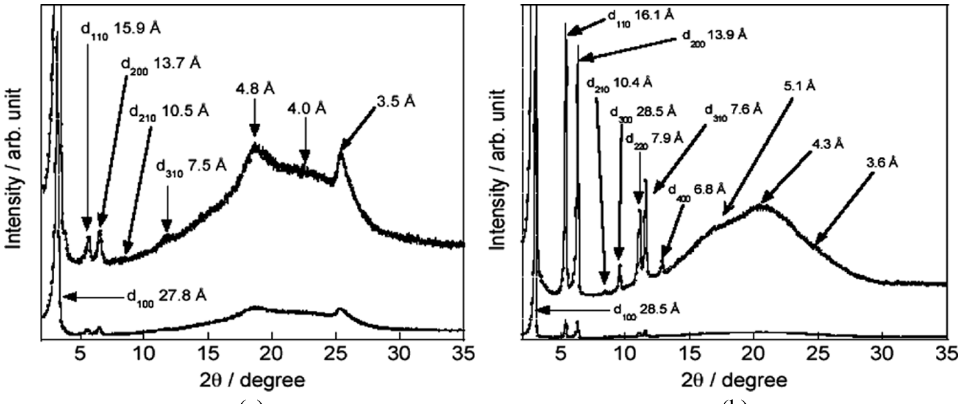
the XRD patterns for the non-aligned samples, where one can see a series of reflections with a spacing ratio of $1{:}1/\sqrt{3}{:}1/2$ in the small angle regions.

It was seen that the ester derivative **1** exhibits a Col$_h$ mesophase with the higher thermal stability than **2**. However, the phase transition enthalpy for the isotropisation of **1** is smaller than that of **2**. This indicates that the Col$_h$ mesophase of **1** has relatively lower order of molecules as Col$_h$ mesophase than **2**. The XRD patterns of both compounds show a difference in the wider angle region and **1** clearly exhibits a reflection at *ca.* 3.5 Å which corresponds to a time-averaged stacking distance of the stacked molecules within a column, whilst it is not almost detectable for **2** in the same region. This reflection is though to come from the central aromatic part of molecule, triphenylene, as the correlation of the fluorinated phenyl groups appears in the smaller angle region (*ca.* 5.8 Å) corresponding to the averaged width of the rotating fluorinated phenyl groups. Therefore, the apparent difference seen at *ca.* 3.5 Å indicates the difference of molecular stacking for the central part of molecules, implying a frustration of molecular packing is present as to the central core part within a columnar structure. This is probably caused by the strong attractive interactions working among the fluorinated phenyl groups in the columnar stacks of molecules.



(a) (b)

Figure 2. DSC curves of (a) **1** and (b) **2** (heating and cooling rate: 5°C min^{-1}).



(a) (b)

Figure 3. X-Ray diffraction patterns of (a) **1** and (b) **2** at 160°C and 180°C, respectively.

On the other hand, TOF measurements were carried out to obtain the drift mobility in the $\mathrm{Col_h}$ mesophases of **1** and **2**. Figure 3 shows transient photocurrent decay curves for the positive charge for **2** at 180°C in the double logarithmic plots. The applied field dependence of mobility was not observed and this is of a typical character for liquid crystalline semiconductors [11]. The obtained mobility value is in the order of $10^{-2}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and this means the mobility was improved by one order of magnitude in comparison to that of **1** [8]. Considering the difference observed in the XRD patterns for the stacking periodicity of molecules within a column, this improved mobility of **2** does not come from the molecular correlation along the columnar axis and thus, it would be ascribed to the better conformation of triphenylenes possessing the C_3 symmetry of rotation around the axis perpendicular to the molecular plane. It may be supported by the fact that a number of

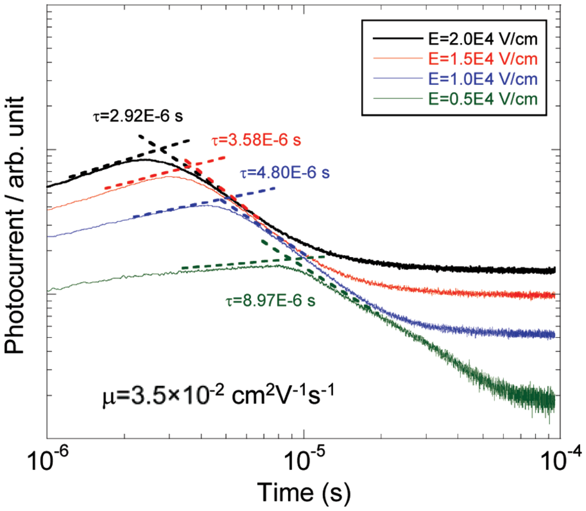


Figure 4. Double logarithmic plots of the transient photocurrent decay curves of **2** at 180°C for the positive charge.

reflections come up in the XRD pattern of **2** and are indexed to be of the higher Miller indices. This also implies that the pinning of the peripheral part of molecules by a strong attractive force for the stacking molecules within a columnar structure could an interesting tool for modifying the rotational conformation of molecules within a column to have the better situation for charge hopping along the columnar axis. Theoretical studies of charge hopping phenomena in columnar mesophases have revealed that the molecular conformation for columnar stacks seriously affect the transfer integral, a most important factor for the determination of charge hopping rate [12].

Conclusion

Fluorination of the peripheral phenyl groups connected to the central triphenylene core leads to a drastic enhancement of thermal stability for Col_h mesophases. The dynamics of columns was modified by replacing the ester linkage with the ether one, though the mesophases are identical to each as a Col_h one. The drift mobility in the Col_h mesophases is improved by the replacement of the linkage group and this implies a possibility that the ether linkage makes molecules into the better conformation in the stacked columnar structure for charge hopping. Fluorination of the peripheral phenyl groups is a good tool for arising strong attractive interactions in the mesophase formation leading to the enhancement of columnar formation for discotics and this could provide a design strategy of new mesophase semiconductors.

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