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Mesophase Semiconductors: The Alignment Control and Self-Assembling Nature for Transistor Applications

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A new mesophase semiconductor, 2,2′-dioctyl-5,5′-dithienylnaphthalene (8TNAT8) was studied on the mesophase structure by the combination of dilatometry and XRD measurements. It was found that the mesophase has 3-D lattice of triclinic with a layered structure and the molecules align in a way of a herringbone arrangement. This layered structure has a similarity to that of the crystal phase, of which XRD patterns was obtained for a thin film transistor with a top-contact/botto-gate geometry showing a fast transistor mobility ($0.14\,cm^2\,V^{-1}\,s^{-1}$) at room temperature (a crystalline phase). Though the polydomain structures is formed in thin films of the transistor, the molecules are likely to totally align in a way that the molecular long axis is orthogonal to the substrate surface with a small tilt angle and this alignment of molecules is just fitting as a connector between the source and drain electrodes. This implies that mesomorphic properties could be a good character for the uniform alignment of molecules even for the crystalline phase as well as the relatively larger domain formation.

Keywords: alignment control; field effect transistor; liquid crystalline semiconductor; organic electronics; thin film device

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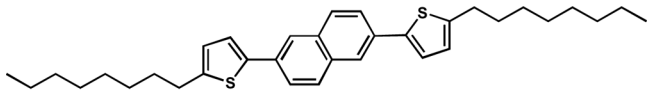
INTRODUCTION

In recent studies on organic semiconductors for transistor applications, the compounds have shown the similarity to mesogens in chemical structure such as the alkylation of π-electronic conjugation systems to obtain the better



2,2'-dioctyl-5,5'-dithienylnapthalene (**8TNAT8**)

solubility into common organic solvents based on a requirement for the wet processing of thin film in device fabrications. Also for these compounds, the mesomorphism could be coming up as a nature of self-assembling of molecules when the molecules form a film with an evaporation of solvent. The increasing importance and interests of liquid crystals in terms of organic semiconductors have been reviewed in some publications [1–4]. Novel organic semiconductors would be furnished with some properties derived from not only the chemical structure of liquid crystals, but also a state of matters where the molecules could be mobile. In particular, field effect transistors are a good candidature for the application of liquid crystalline semiconductors [5]. A certain strategy is strongly required to develop a new organic semiconductors with unique self-assembling nature to spontaneously form a uniformly aligned film of the molecules performing a fast mobility of carriers.

Recently, we reported that a ditheinylbenzene derivative with two terminal alkyl tails forming 3D mesophases shows a fast mobility of charged carriers ($\sim 10^{-1}\,cm^2\,V^{-1}\,s^{-1}$) [6]. However, this compound shows a complicated mesophase transitions and the simpler ones are desired in a practical point of view. More recently, this simple chemical structure of molecule lead us to synthesise an analogue, ditheinylnapthalene derivative **8TNAT8** which has a 3D mesophase with $\sim 10^{-1}\,cm^2\,V^{-1}\,s^{-1}$ of the hole mobility and this compound was applied to a fabrication of a top-contact/bottom-gate type field effect transistor (FET) as shown in Figure 1 to successfully obtain a fast effective mobility as devices with the same order as the bulk material [7]. Even though a non-mono-domain state of the thin film in the device, it performs such fast mobility, probably due to a characteristic property of mesophase as electronic conductors such as "defect-free" nature of domain boundaries [8].

In this work, the correlation between mobility behaviour and 3D order of molecules in the mesophase is simply discussed for **8TNAT8**,

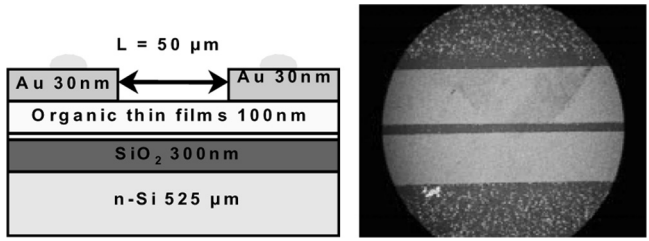


FIGURE 1 A structure of the transistor device fabricated in this work. It is of a bottom-gate/top-contact type with the channel width, $W = 5.5$ mm and the length, $L = 50\,\mu$m. HMDS was used for the surface treatment between the insulator and active layers. The picture shows one transistor fabricated on a silicon wafer with an insulating layer.

where one can see a typical molecular arrangement is realised in the mesophase to get a high efficiency of charge hopping among the molecules.

EXPERIMENTAL

The compound was synthesised by the three-step reaction and the purification was carried out by column chromatography (silica-gel, CH_2Cl_2) followed by recrystallisation from toluene. The final procedure of purification was sublimation *in vacuo* [7].

Phase transition behaviour was studied in the combination of polarised optical microscopic (POM: Olympus BH2 equipped with a temperature-controllable hotstage, Mettler FP52) observation of textures, DSC (TA Instruments, Modulated DSC3000 and XRD (Rigaku, Rint2000 with a hand-made oven) measurements.

Dilatometry experiments were done using a hand-made apparatus equipped with a temperature controller.

RESULTS AND DISCUSSION

Figure 2 shows a DSC thermogram of 8TNAT8. This compound has only one mesophase (Crystal-mesophase transition at 93°C and mesophase to isotropic at 182°C) with highly ordered structure indicated by the large value of phase transition enthalpy for the isotropisation (29 kJ/mol). POM observations confirm the mesophase shows highly viscous state, leading to the rather difficulty to get a uniform mono-domain film. The TOF technique was applied to the carrier mobility measurements to find out that it reaches to $0.14\,cm^2\,V^{-1}\,s^{-1}$ for hole with a slight temperature dependence (Fig. 3).

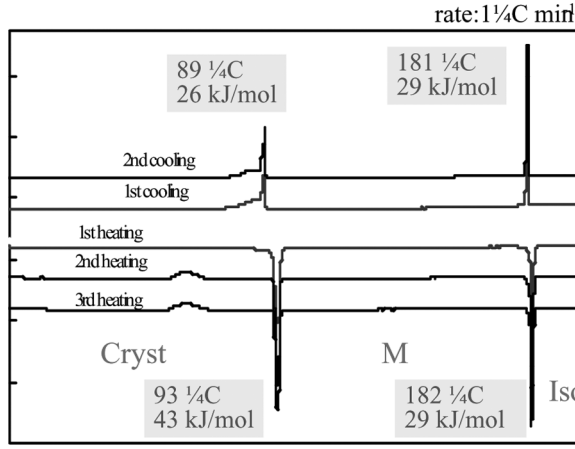


FIGURE 2 DSC thermograms of 8TNAT8 (heating and cooling rates: 1°C min^{-1}).

The XRD pattern for the mesophase of powder sample shows very clear reflections. But any series of reflections corresponding to a layered order of molecules like smectic liquid crystals could not be detected for poly-domain samples (Fig. 4). One can see several clear reflection peaks in the wider angle region and this indicates that the mesophase has a highly order and the analyses under the postulation of highly ordered smectics were in vain. However, a small and broad

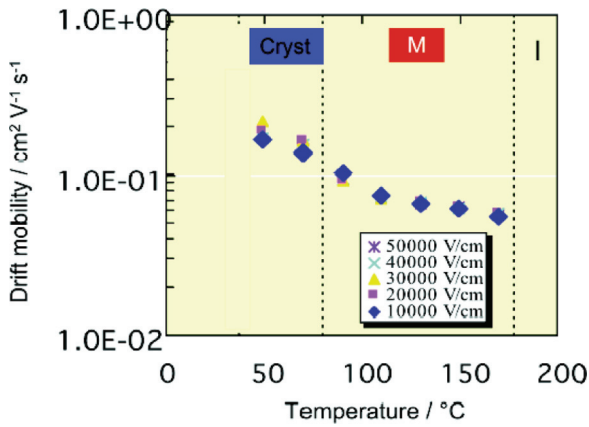


FIGURE 3 Temperature dependence of hole mobility obtained by TOF technique.

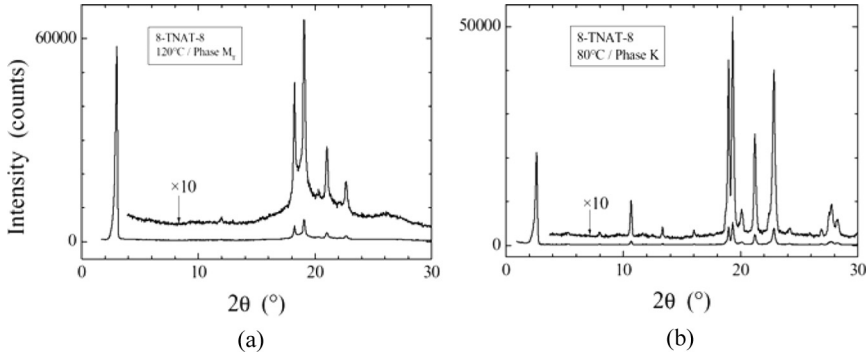


FIGURE 4 XRD patterns of the powder sample of 8TNAT8. (a) mesophase at 120°C and (b) crystalline phase at 90°C.

halo is seen in the wider angle region, meaning the disordered states of alkyl chains.

Dilatometry is a strong tool to clarify the molecular packing manner with XRD techniques and the results are shown in Figure 5. The molecular free volume changes on temperature and especially stepwise changes are observed at the phase transitions from the crystal-mesophase and the mesophase to isotropic phases. One can estimate the cross section area of rod-like molecules by this data, which relates to molecular packing. The combination of dilatometry and XRD measurements give some results for the mesophase structure. The

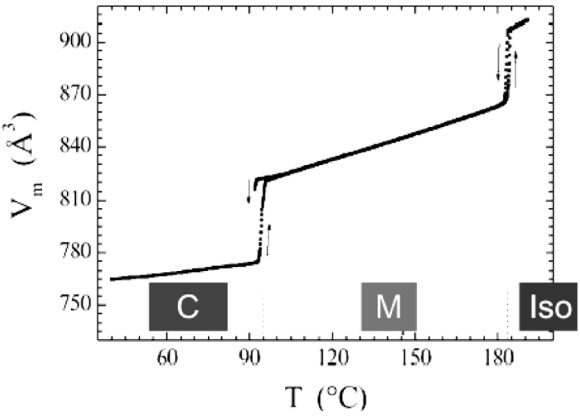


FIGURE 5 Molecular free volume change of 8TNAT8 by dilatometry technique.

mesophase is of 3D plastic phase with a triclinic lattice ($a = 9.839$ Å, $b = 5.677$ Å, $c = 29.87$ Å, $\alpha = 91.9°$, $\beta = 91.35$ Å, $\gamma = 90°$, $Z = 2$). The rod-shaped molecules align like smectic liquid crystals to form a 2D-layered structure with a herringbone-type packing of molecules. The temperature dependence of the averaged distance of molecules within the layers could explain the increase of mobility on cooling and this is the behaviour based on the disordered model. This structure of mesophase resembles to that of smectic E mesophase. These imply that the molecular design which has being developed empirically for liquid crystalline compounds so far is good for the molecular design for the highly ordered meso-phase with a herringbone packing which is an important order for more efficient charge hopping [9].

The XRD pattern obtained for a thin film deposited as the active layer of field effect transistor, which shows a fast FET mobility shows a very clear reflections corresponding to the layered structure even for the polydomain system. This layered structure (crystalline phase) is seen to be very similar to the mesophase structure even in the thin film device and this is the implication from the comparison of XRD patterns of the mesophase and crystalline one for the powder samples.

Considering the characteristic properties of mesogens such as good solubility into common organic solvents and self-assembling nature for spontaneous molecular alignment, the better performance of organic semiconductors could be attained by the application of molecular designs of mesogens.

CONCLUSION

A long-chain dithienyl naphthalene derivatives, 8TNAT8 was studied as to the mesophase structure by the combination of dilatometry and XRD measurements. It was found that the mesophase has a 3-dimentional lattice like plastic crystals with a layered structure like smectic liquid crystals. This means the mesophase could act as 2-dimentional charge transport media and additionally a herringbone packing as the time-averaged order is realized within a layer which could lead to a fast mobility of charged carriers. The molecules within domains of thin films deposited as the active layer of transistors spontaneously align where the 2D layers are parallel to the substrate and this is also similar situation to the mesophase order. These indicate that alignment control and self-assembling nature of organic semiconducting molecules could be attained by the molecular design of liquid crystalline semiconductors.

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