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[EI-02] Specific Nature of Monoalkylated Liquid Crystalline Organic Semiconductors for Organic Transistors and Its Generality

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Monoalkylated liquid crystalline organic semiconductors, Ph-BTBT-10, not only provides us with crystalline thin films having uniform and flat surface morphology, thanks to the liquid crystallinity, but also causes the phase transition from monolayered crystals to bilayered crystals when thermally annealed for a short time. Significant improvement in mobility, which reaches almost one order of magnitude, takes place after the annealing when its crystalline thin films are used for an active layer for organic transistors. In the presentation, we will show its generality through observation of phase transition behaviors and evaluation of organic field effect transistors fabricated with a various type of the monoalkylated liquid crystals.

Specific nature of monoalkylated liquid crystalline organic semiconductors for organic transistors and its generality

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Monoalkylated liquid crystalline organic semiconductors, Ph-BTBT-10, not only provides us with crystalline thin films having uniform and flat surface morphology, thanks to the liquid crystallinity, but causes the phase transition from mono-layered crystals to bilayered crystals when thermally annealed for short time. Significant improvement in mobility takes place after the annealing when its crystalline thin films are used for an active layer for organic transistors, which reaches almost one order of magnitude. show that the formation of bilayered crystal and the significant increase of FET mobility in the resulting crystals is not a particular case of Ph-BTBT-10, but is probably general through observation of phase transition behaviors and fabrication and evaluation of organic field effect transistors with a various type the monoalkylated liquid crystals for organic semiconductors.

1. Introduction

For realization of printed electronics, there are several requirements for organic semiconductor materials not only high mobility but also processability of the materials compatible with solution processes.[1] We have proposed a liquid crystal of Ph-BTBT-10 exhibiting highly ordered smectic liquid crystal phase of SmE, which satisfies these requirements.[2] This material is very unique because FET mobility of the crystalline films fabricated from SmE films is very much increased, e.g., about one order of magnitude up to over 10cm^2/Vs, accompanying crystal-to-crystal transition from monolayered crystal to bilayered crystal as shown in Fig. 1, when thermally annealed for a short time.

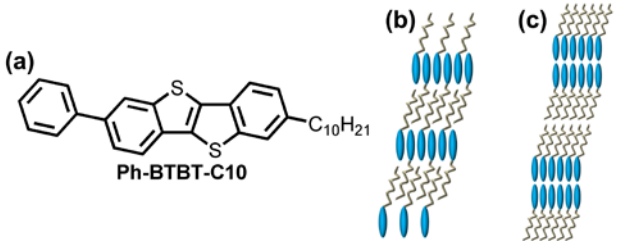

Fig. 1 Chemical structures of Ph-BTBT-10 (a), and schematic diagrams of monolayered crystals (b) and bilayered crystal (c).

The molecular design for mono-alkylated highly ordered smectic liquid crystals would provide a new strategy of the molecular design for high mobility organic transistor materials, if this coincidence of the crystal-to-crystal transition induced thermally and significant increase of FET mobility is not the particular case of Ph-BTBT-10 and general in highly ordered smectic liquid crystals. Thus, we investigated this crystal-to-crystal transition and FET performance before and after thermal annealing in FETs fabricated with as-fabricated polycrystalline thin films of representative types of highly ordered smectic liquid crystals.

There are two types of highly ordered smectic liquid crystals: one is an oligomer type of liquid crystals consisting of several small aromatic core moieties such as a terphenyl $(Ph)_3$ and a terthiophene $(Tp)_3$; the other is smectic liquid crystals having a large π-conjugated aromatic core and an additional small core moiety such as Ph-BTBT derivatives. Thus, we selected Ph-$(Tp)_3$-C_n and Ph-BDT-C_n as a model compound as shown in Fig. 2.

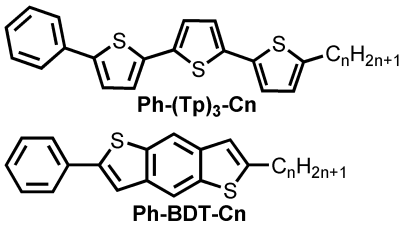

Fig. 2 Chemical structures of Ph-$(Tp)_3$-Cn and Ph-BDT-Cn for model compounds.

2. Experiments

We synthesized a series of monoalkylated Ph-$(Tp)_3$-Cn and Ph-BDT-Cn derivatives, and characterized their phase transition behaviors by differential scanning calorimetry (DSC), X-ray diffraction (XRD) study , and observation of polarized optical microscope (POM). Crystalline thin films for fabrication of field effect transistors (FETs) were fabricated by spin-coating of their p-xylene solution at their SmE temperatures on SiO_2 (300nm)/Si substrates.[3] The resulting films were cooled down to a room temperature to obtain polycrystalline thin films, whose

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grain size was around 20 μm. Au was vacuum-evaporated onto the crystalline films through a metal mask for source and drain electrodes to make bottom-gate and top contact transistors, whose structures were illustrated in Fig. 3.

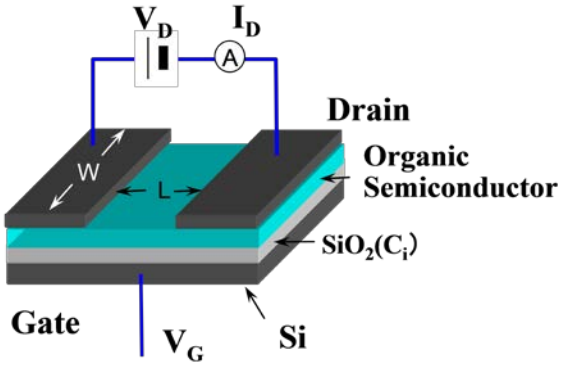

Fig. 3 Schematic diagram of structure of bottom-gate and top-contact type of FETs fabricated for this study.

The FET performance was evaluated by V-I characteristics of the FETs at ambient atmosphere. The FET mobility was estimated from I_D-V_G characteristic in the saturation regime, based on the following equation described below:

$$I_D = \frac{WC_i\mu}{2L}(V_G\text{-}V_T)^2$$

in which μ is the FET mobility, I_D is source-drain current, C_i is the gate capacitance, V_G is the gate voltage , and V_T is the threshold voltage, and W/L is the channel width/length.

3. Results and Discussion

3.1 Characterization of phase transition behaviors

Ph-$(Tp)_3$-Cn synthesized exhibited single liquid crystalline phase, whose POM texture is shown in the inset of Fig. 4, which shows a typical texture of highly ordered smectic phases without accompanying low-ordered liquid crystalline phase. We identified this liquid crystalline phase to be SmE phase by 3 characteristic XRD peaks of (110), (200) and (210) in wide diffraction angles of 2θ = 20-30°, in addition to a sharp peak at a small diffraction angle for (001) corresponding to a layer thickness of the smectic liquid crystal, as indicated in Fig. 4.

Fig. 5 is a summary of the phase transition behaviors of Ph-$(Tp)_3$-Cn.

In the same manner, we identified a single mesophase of Ph-BDT-Cn derivatives to be SmE phase.

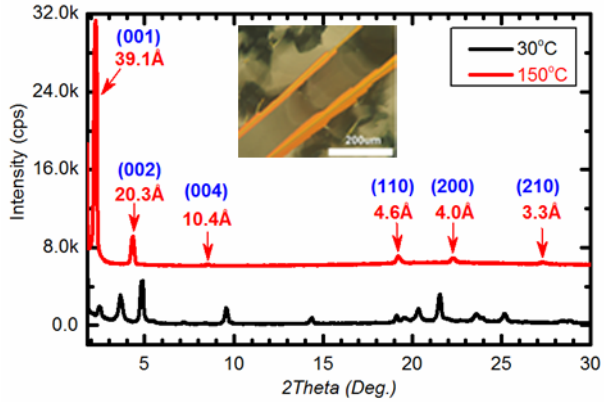

Fig. 4 Bulk film XRD pattern of Ph-$(Tp)_3$-C18 at different temperature on heating. The inset shows a typical POM texture of SmE phase obtained from isotropic phase directly.

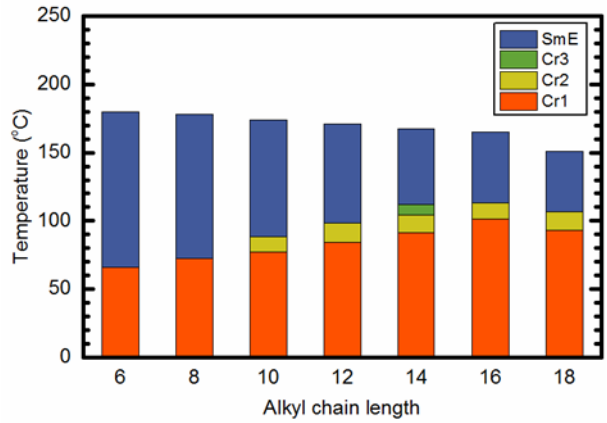

Fig. 5 A summary of phase transition behaviors of Ph-$(Tp)_3$-Cn.

3.2 As-fabricated and thermal annealed polycrystalline thin films

We fabricated polycrystalline thin films by spin-coating a p-xylene solution of the liquid crystalline materials at their SmE temperature. The resulting polycrystalline thin films had uniform and flat surface morphology thanks to soft nature of SmE phase as-spun and crystallization at lower temperature, whose grain size was around 20μm. Judging from a peak at 2θ = ~2.5°, which corresponds to a layer thickness and a molecular length of each molecule, the resulting films were monolayered crystals irrespective of Ph-$(Tp)_3$-Cn and Ph-BDT-Cn derivatives, in which the molecules sit perpendicular to the substrate surface.

We investigated the effect of thermal annealing of the as-fabricated films on crystal structure of the films.

We annealed each film at a different temperature lower than its crystal-to SmE phase transition temperature for 5 min, and examined the crystal structure of each film. Fig. 6 shows XRD patterns as a function of annealing temperature, in which the as-fabricated films were annealed for 5 min at each temperature.

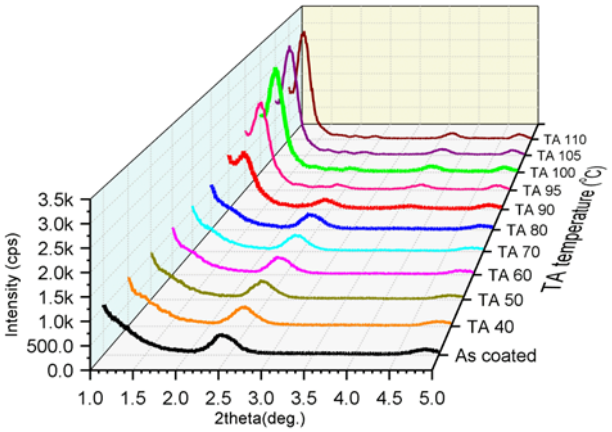

Fig. 6 Thin film XRD pattern of Ph-TTP-C18 as a function of thermal annealing temperature in the crystal state for 5min, then cooling to room temperature)

Judging from a fact that the diffraction peak for monolayered crystal decreased as an increase of new diffraction peak at a smaller angle of 2θ = 1-1.5°, the crystal film structure was changed from monolayered crystal to bilayered crystal, in which two molecules sit in head-and-head manner in the molecular layers.

In fact, we obtained similar results when Ph-BTBT-Cn was thermally annealed in the same manner.

These facts that monolayered crystals of Ph-(Tp)$_3$-Cn and Ph-BDT-Cn derivatives as-fabricated were be transformed into the bilayered crystals by thermal annealing to bilayered crystals proves this crystal-to-crystal transition is not a particular case of Ph-BTBT-10 films as fabricated from SmE films.

3.3 FET performance before and after thermal annealing

We fabricated bottom-gate and top contract FETs with Ph-(Tp)$_3$-Cn and Ph-BDT-Cn polycrystalline thin films as-fabricated *via* SmE phase and investigated FET performance in FETs before and after thermal annealing.

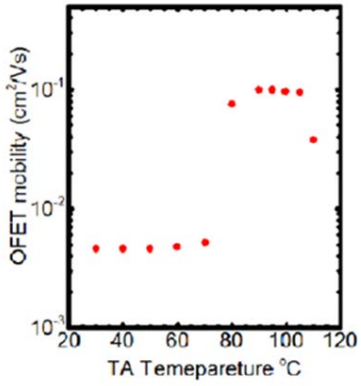

Fig. 7 FET mobility of Ph-TTP-C18 as a function of thermal annealing temperature in the crystal state for 5min, then cooling to room temperature).

Fig. 7 shows FET mobility at a room temperature after annealing at different temperatures for 5 min. It is very clear that the FET mobility was very much increased by more than one order of magnitude after thermal annealing at temperature range close to the phase transition temperatures.

Fig. 8 shows Transfer and output characteristics in the FET fabricated with Ph-(Tp)$_3$-C18 before and after thermal annealing.

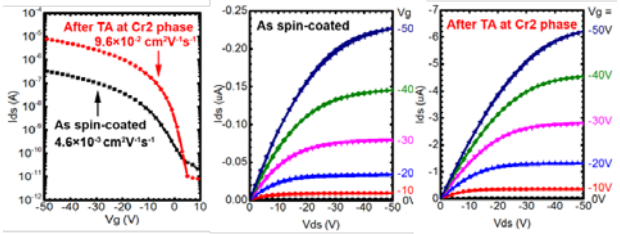

Fig. 8 Transfer and output characteristics of FET fabricated with polycrystalline thin films of Ph-(Tp)$_3$-C18 before and after thermal annealing at 100°C for 5min.

We observed significant increase of FET mobility in FETs fabricated with Ph-BDT-Cn after thermal annealing as well. Fig. 9 shows transfer and output characteristics of FETs fabricated with Ph-BDT-Cn before after thermal annealing at 130°C.

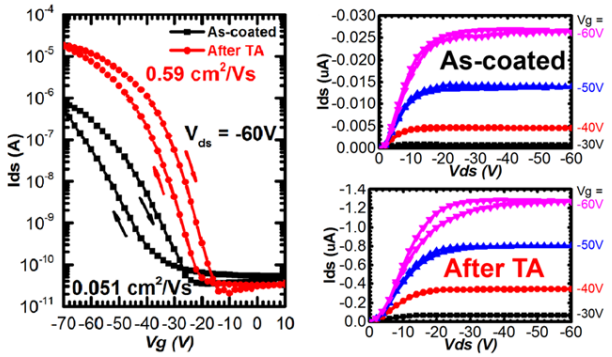

Fig. 9 Transfer and output characteristics of FET fabricated with polycrystalline thin films of Ph-BDT-C14 before and after thermal annealing at 130°C for 5min.

After systematic study of the thermal annealing on FET performance with different Ph-(Tp)$_3$-Cn and Ph-BDT-Cn derivatives, we learned that the enhancement of FET mobility in FETs fabricated with these materials was generally observed irrespective of Cn, even though the enhancement ratio of FET mobility before and after thermal annealing was different from material to materials, as shown in the case of Ph-(Tp)$_3$-Cn in Fig. 10.

It is well know that the thermal annealing of organic FETs at a certain temperature result in improvement of FET performance in some extent, which includes enhancement of FET mobility due to the improvement of

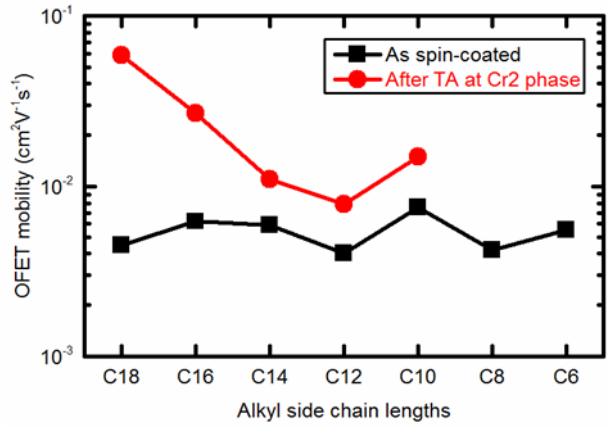

Fig. 10 FET mobility in FETs fabricated with polycrystalline thin films of Ph-(Tp)$_3$-Cn before and after thermal annealing.

crystallinity and electrical properties at the electrode interfaces. However, the enhancement ratio is rather limited within several times in general, compared with the present results up to one order of magnitude or more. In fact, the monolayered crystals derived from SmE phase of mono-alkylated smectic liquid crystals are not perfect or disordered, compared with those of Di-alkylated one; therefore, it is very plausible that the crystal-to-crystal transition to the bilayered crystals results in improvement of the films crystallinity because the disorder is swept away during the rearrangement of molecules to form bilayered crystals, which are thermodynamically stable. However, the exact reason why such a significant increase in the mobility takes place after the transition from monolayered crystals to bilayered ones has not been clarified yet.

4. Conclusion

We investigated the crystal-to-crystal phase transition from monolayered to bilayered crystals thermally induced in polycrystalline thin films fabricated *via* the SmE phase of mono-alkylated liquid crystals and significant mobility enhancement after the transition, which was discovered recently in Ph-BTBT-10 exhibiting SmE phase, with two representative types of highly ordered smectic liquid crystals, i.e., Ph-(Tp)$_3$-Cn of an oligomer type and Ph-BDT-Cn having small and large π-conjugated core moieties. The systematic study with these materials revealed that these unique phenomena are not a particular case of Ph-BTBT-10 but probably general in highly ordered smectic liquid crystals having a single side chain, which is essential to form bilayered crystals.

Therefore, the present results provide a new strategy of molecular design for high mobility in organic field effect transistors, i.e., utilization of mono-alkylated highly ordered smectic liquid crystals. In addition, to answer a question, i.e., why does such a significant enhancement of mobility after the crystal-to-crystal transition take place?, gives an insight into molecular structure and property relation in organic crystalline semiconductors.

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