Effect of ω-hydroxyl Group of Side Chains on Phase Transition Behavior and Charge Transport Properties in Terthiophene Liquid Crystals

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Abstract

We have synthesized liquid crystalline terthiophene (TTP) derivatives having hydroxyl groups in ω-position of side chains, i.e., 5-hexyl-5''-(6-hydroxyhexyl) terthiophene (6-TTP-6ol) and 5, 5''-bis (6-hydroxyhexyl) terthiophene (6-TTP-6diol), and characterized their liquid crystallinity by differential scanning calorimeter (DSC), polarized optical microscopic observation (POM) and X-ray diffraction (XRD) measurement. And charge carrier transport properties by time-of-flight (TOF) measurement. These hole mobilities determined by TOF had not been changed much despite relatively the large dipole of hydroxyl group of 1.8-2.2D, compared with a non-hydroxyl derivative and their values are 10^{-3}-$10^{-2}cm^2V^{-1}s^{-1}$. This fact indicates that the charge carrier mobility is not affected by polar groups, if it is substituted at the far –end position from the TTP core responsible for carrier transport, indicating a possible molecular design of a functionalized liquid crystalline organic semiconductor with polar groups without decreasing the mobility.

Introduction

In 1990s, the electric conduction was discovered in both disc-like[1],[2] and rod-like[3] liquid crystals (LCs), in which the charge carrier was believed to be ionic conduction for a long time because LCs exhibit the fluidity favorable for the ionic conduction.

Since the discovery of the electric conduction, LCs have been recognized to be a new class of organic semiconductors characterized by self-organization and high mobility. In fact, the carrier mobility is next to the organic single crystal, and comparable to those in organic polycrystalline thin films, in which the mobility is in the range of 10^{-3}-$10^{-1}cm^2V^{-1}s^{-1}$. Despite lower mobility than single crystal the LCs are more attractive than single crystals because of advantages described as follows.

(a) LCs have feasibility of wet-processing such as spin-coating, ink-jet and cast techniques without vacuum process, as a result LCs are have high potential for large-area applications.

(b) Generally speaking the structural defects such as disclinations[4] and domain boundaries in LCs are electrically inactive and does not cause deep states[5]. These are quite different from those of crystalline materials.

(c) The mobility depends on neither electric field nor temperature, which differs from that of amorphous material commonly used in xerographic photoreceptors and organic light emitting diodes.

(d) Trace amounts of chemical impurities in LC's can be easily detected by time-of-flight experiments, so that their purities can be guaranteed. [6], [7].

Organic materials have a big advantage of easy functionalization by chemical modification of the molecule over organic materials. We have challenged to functionalize liquid crystals for future applications, while keeping charge carrier transport properties unchanged. As its approach, we had used ω,ω'-dioctylterthiophene (8-TTP-8) as a model compound, which has relatively high mobility up to $10^{-2}cm^2V^{-1}s^{-1}$ in SmG despite a small core of the terthiophene. We have modified side chains with hydroxyl group at the far-end position from the core. By introducing hydroxyl group, we expected improved solubility in protic solvents and additional effects of hydroxyl groups due to the hydrogen bonding in liquid crystalline phases. In this study, we synthesized two terthiophene derivatives, i.e., 5-hexyl-5''-(6-hydroxyhexyl) terthiophene (6-TTP-6ol) and 5, 5''-bis (6-hydroxyhexyl) terthiophene (6-TTP-6diol) systematically substituted with the hydroxyl group in the side chains and characterized their phase transition behaviors and carrier transport properties.

Experiment

Material

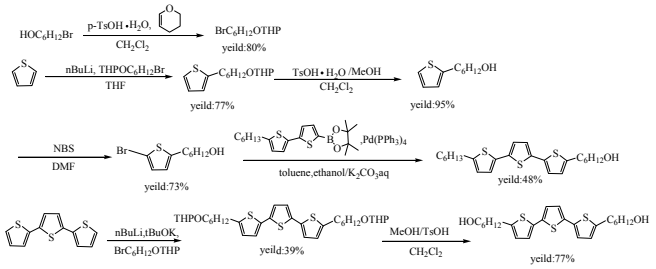
5''-bis (6-hydroxyhexyl) terthiophene (6-TTP-6diol) was synthesized by two steps from terhiophene by alkylation reaction with n-BuLi and alkylharides[10]. On the other hand, 5-hexyl-5''-(6-hydroxyhexyl) terthiophene (6-TTP-6ol) was synthesized by Suzuki coupling reaction between 2-bromo-5-(6-hydroxyl) hexyl thiophene and 2-hexyl-5'-bithiophene pinacol ester in existence of Pd-catalyst [10], as shown in Scheme.1. After isolation and purification of 6-TTP-6diol and 6-TTP-6diol by silicagel column chromatography, we identified these chemical structures by ^{1}H-NMR measurements. Next we expensively purified them further by the column chromatography and recrystallization in either isopropyl alcohol or n-hexane in the existence of activated carbon for time-of-flight experiments.

Characterization of liquid crystallity and charge carrier transport properties.

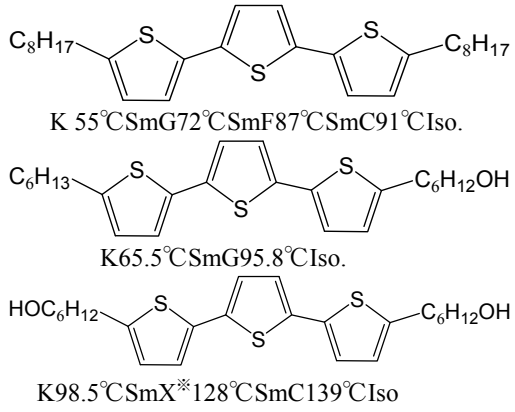
We investigated liquid crystality and their phase transition behavior of these terthiophene derivatives by differential scanning calorimeter (DSC), polarized optical microscopic observation (POM) and X-ray diffraction (XRD) measurements.

For TOF measurements, we prepared liquid crystal cells with two semitransparent aluminum electrodes. The cell thickness was controlled to be ca.15μm by glass spacer. We used a N_2 pulse laser

as a light source for generating photocarriers, whose wave length and a pulse width were 337nm and 600ps, respectively. The transient photocurrents were recorded by a digital oscilloscope (Nicolet Pro
92). The bias voltage was applied to the sample, which was set on the sample stage, in which the temperature was controlled at a given temperature, by a power supply unit (Keithley 237).



Scheme 1. Schematic structure and synthetic route of 6-TTP-6diol and 6-TTP-6ol.



※SmX indicates an unidentified smectic mesophase.

Figure.1. The chemical structure of liquid crystalline terthiophene derivatives and their phase transition behavior.

Figure 1. shows chemical structures of 6-TTP-6diol and 6-TTP-6ol, and phase transition behaviors determined. It is clear that by introducing hydroxyl groups in the side chains, the phase transition temperature was shifted to a higher temperature range compared with the 8-TTP-8, probably due to hydrogen bonding in the molecules.

Figure 2. shows typical transient photocurrents for positive carriers of the SmX phase of 6-TTP-6diol at 100℃ in both linear and double-logarithmic (inset) plots. These transient photocurrents are so-called "non-dispersive", where we can see a clear shoulder indicating transit time of the carriers. The hole mobility of 6-TTP-6diol was determined to be $8.3 \times 10^{-4} cm^2V^{-1}s^{-1}$ for the SmC at 130°C and $1.2 \times 10^{-2} cm^2V^{-1}s^{-1}$ for the SmX at 98.9°C, respectively. These mobilities are not changed much compared with those for the SmC and SmG phase reported in the dialkyl terthiophenes, e.g., 8-TTP-8[11], [12] different form the previous results reported that the charge carrier transport is affected by polar groups such as nitro and amide groups introduced in LC molecules due to the energetic disorder caused by the carrier-dipole interaction. [13], [14] This difference is due to the position of hydroxyl groups in a side chain probably, that is, the end position of side chain far from the terthiophene moiety responsible for hole conduction. In fact, the energetic disorder σ is reduced as a function of the distance d between the terthiophene core and the dipoles defined as $\sigma \propto d^{-1}$[15], in which d is carrier more than 10A in this case. These facts give us an important indication that additional ill-effect of polar groups on the charge carrier transport in the Sm LCs, which often accompanies the chem−ical modification of molecules with functional groups; can be min-imized by selecting an appropriate position for chemical modifyca-tion.

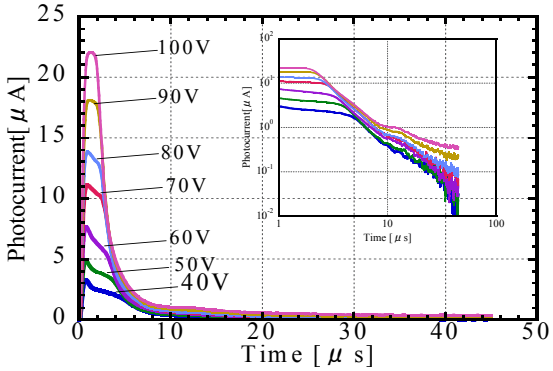


Figure 2. Typical transient photocurrents for positive carriers in the SmX phase of 6-TTP-6diol at 100℃ in linear and double-logarithmic (inset) plots. The cell thickness was 15 μm.

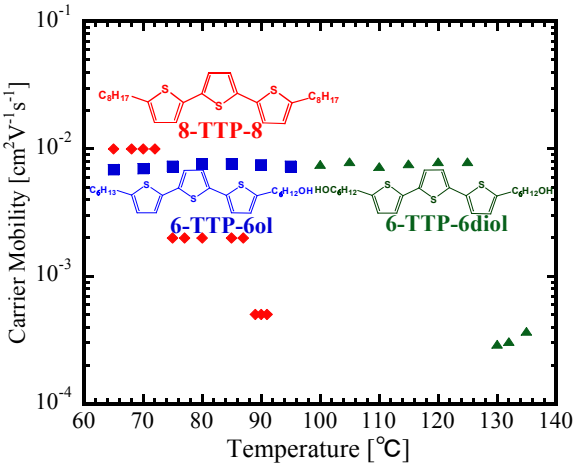


Figure 3. The temperature dependence of hole mobility in Sm mesophases of 6-TTP-6diol (▲), 6-TTP-6ol (■), and 8-TTP-8 (◆) for a reference.

In summary, we have investigated chemical modification of LC terthiophene derivatives with hydroxyl groups at the side chains. It resulted in thermal stabilization of LC phases and less effect of the dipole of hydroxyl groups on the charge carrier transport properties in the Sm phases. The present results give important information about how we can reduce the additional ill-effect of chemical modification with polar groups in LC materials.

Conclusion

We have synthesized OH-substituted terthiophene derivatives systematically, and characterized their phase transition behaviors and carrier transport properties in their mesophases. The OH-sub-

stituted terthiophene derivatives exhibited highly ordered Sm phases of SmG and SmX phases, whose phase transition was shifted to a temperature range higher than that of non-hydroxyl 8-TTP-8, probably due to hydrogen bonding among the molecules.

The positive carrier mobilties in these mesophases were 10^{-3}-10^{-2} $cm^2V^{-1}s^{-1}$, whose value was similar to that of the SmG phase of non-hydroxyl derivative, 8-TTP-8, and depended on neither temperature nor electric field in each LC. Therefore, we conclude that the end position of alkyl side chain is the best position to minimize additional effect of dipolar groups on the charge carrier transport in f-unctionalized liquid crystalline organic semiconductors.

References

[1] D. Adam, F. Closs, T.Frey, D. Funhoff, D.Haarer, H. Ringsdorf, P.Schuhmacher, and K. Siemensmeyer Phys. Rev. Lett. Vol.70 No.4 457-460 (1993)

[2]H. Iino and J. Hanna Appl. Phys. Lett. Vol.87, No.87 192105 (2005)

[3] M. Funahashi and J. Hanna Phys. Rev. Lett. Vol.78 No.11 2184-2187 (1997)

[4] M. Funahashi and J. Hanna Appl. Phy. Lett. Vol. 73 No. 25 Vol. 3734-3735 (1998)

[5] H. Maeda, M. Funahashi, and J. Hanna Mol. Cryst. Liq. Cryst., Vol.366 369-376 (2001)

[6] M. Funahashi, J. Hanna Chem. Phys. Lett. 397 319-323 (2004).

[7] H. Ahn, A. Ohno, and J. Hanna Jour. Appl. Phys. 102 093718 (2007)

[8] H. Iino and J. Hanna Mol.Cryst. Liq. Cryst Vol. 510, pp.259-267(2009)

[9] H. Iino, and J. Hanna, Adv. Matter., Vol. 23: pp.1748–1751, (2011)

[10] J. Leroy, N.Boucher, S. Sergeyev, M. Sferrazza, and Y. H. Geers Eur. J. Org. Chem., 1256-1261 (2007)

[11]M. Funahashi, J. Hanna Appl. Phys. Lett. Vol. 76, No.18 pp. 2574-2575 (2001)

[12] M. Funahashi and J. Hanna Mol.Cryst. and Liq. Cryst. vol. 368 pp. 303-310 (2001)

[13] H. Iino, and J. Hanna Jour. Appl. Phys.100 043716 (2006)

[14] Y. Miyake, P. Hu, K. Zhao, H. Monobe, A. Fujii, M. Ozaki, and Y. Shinizu Mol. Cryst. Liq. Cryst.Vol.525 97-103 (2010)

[15] A. Ohno, T. Nakamura, and J. Hanna Mol. Cryst. Liq. Cryst. Vol.510 293-299 (2009)

Biography

Toyohiro Fukuda was graduated from Yamagata University in 2009 and obtained the master degree in organic device engineering science from the same university. He is a third grade graduate student in educator course in Department of Electronics and App-lied Physics, Interdisciplinary Graduate School of Science and Technology, Tokyo Institute of Technology. He has challenged to functionalize liquid crystalline semiconducting materials for application of organic electronics devices.