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Structure, Physical Properties and Thin-Film Transistor Characteristics of Sexithiophene Isomers

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We have synthesized unsubstituted oligothiophenes with both terminal thiophene rings linked at β-positions. The correlation between molecular structure, character of a single molecule such as conjugation length, and physical properties as solid has been investigated. Moreover, the influence on electric properties of their thin films has been investigated. It was revealed that π-conjugation length of the molecule considerably influences the field-effect transistor characteristic.

Keywords: charge mobility; conjugation length; isomer; oligothiophene; molecular structure; thin film transistor

INTRODUCTION

Organic electronic devices based on organic semiconductor thin films, being light and flexible, have been intensively investigated for applications to sheet displays, electronic papers, information tags, biosensors, and so on. For further improvement of device function,

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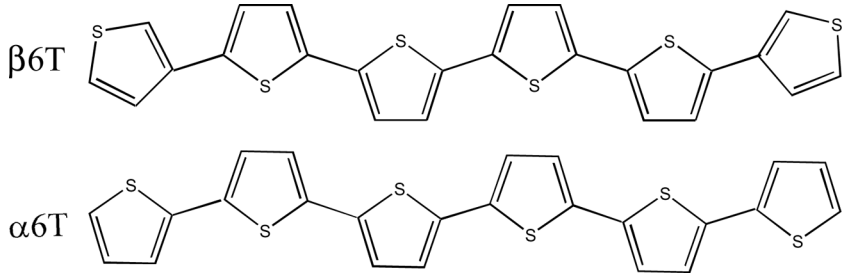

SCHEME 1 Chemical structures of sexithiophene isomers.

detailed understanding of the relation between physical properties and various factors such as molecular structure, conformation and molecular packing in solid is indispensable [1–3].

Recently, π-conjugated oligomers of short chain lengths have received much attention for detailed investigation, because oligomers are well-defined chemical systems and their conjugation chain length can be exactly controlled. Among them, oligothiophenes are regarded as a promising material for future electronic and optoelectronic devices, and have been applied to active layers in field-effect transistors (FET) and light-emitting diodes.

α-Sexithiophene (α6T, see Scheme 1), which is an unsubstituted oligothiophene that has been most actively investigated since Horowitz *et al*. reported the FET based on the compound [4]. So far, FET characteristics [5–10], optical properties of thin films [11], crystal structure including polymorphs [12,13] and so on have been reported. Chain length dependency on the structure and electric properties by comparison with α-quater-, quinque-, septi- and octithiophenes (α4T, 5T, 7T and 8T) has been also an interesting subject [1,2,14,15].

We have recently synthesized an unsubstituted thiophene hexamer with thiophene rings at both ends of the molecule linked at 3-positions (Scheme 1, abbreviated as β6T), a structural isomer of α6T [16]. In this article, the correlation between its molecular structure, character of a single molecule such as conjugation length and physical properties as solid has been investigated in comparison with α6T. Moreover, electric properties of thin films of these two sexithiophenes have been investigated.

EXPERIMENTAL

Materials

2,2′:5′,2″:5″,2‴-Quaterthiophene, 3-thiopheneboronic acid, 2,5′-dibromobithiophene and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$)

were purchased from Aldrich, 1,3-bis(diphenylphosphino)propane nickel(II) chloride ($NiCl_2$(dppp)) from Tokyo Kasei Kogyo Co. Ltd., and magnesium turnings from Nakarai Tesque Inc., and used without further purification. Other chemicals were purchased from Wako Chemicals Co., and used as received. 2-Bromobithiophene and 5,5‴-dibromo-2,2′:5′,2″:5″,2‴-quaterthiophene were synthesized following the literature [17]. 3,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,3⁗⁗-sexithiophene(β6T) [16] and 2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗⁗-sexithiophene (α6T) [18] were synthesized following the previously reported methods. The purification of sexithiophenes was performed by sublimation using the same glassware as described earlier [14].

Analyses

Differential scanning calorimeter (DSC) measurements were performed with a Perkin-Elmer PYRIS Diamond differential scanning calorimeter. All the measurements were done under nitrogen at a heating and cooling rate of 5°C/min. Measurement was done in the temperature range between 50°C and 350°C for α6T and between 50°C and 360°C for β6T. Melting points were estimated at the extrapolated onset of each transition peak.

Liquid crystalline behavior was observed using a Nikon S-Ke polarizing microscope equipped with a Japan Hightech LK-600PM hot stage. UV/vis spectra were obtained using a Hitachi U-4100 Spectrophotometer. Chloroform was used as a solvent.

Device Fabrication and Characterization

Top contact type OFETs were constructed on highly doped n-type silicon wafers covered with 300-nm-thick silicon dioxide with a capacitance per unit area (C_{ins}) of 10 nF cm^{-2}. Prior to the deposition of oligothiophenes, the substrate was soaked to the ethanol for 20 min in an ultrasonic bath, immersed in a neat 1,1,1,3,3,3-hexamethyldisilazane, then rinsed with chloroform in an ultrasonic bath for 5 min. Oligothiophene films were deposited on the substrate surface by thermal evaporation at a base pressure of 10^{-6} Torr and a deposition rate of c.a. 0.03 nm s^{-1}. During the evaporation, the substrate temperature was held at 120°C. The resulting film thickness was approximately 100 nm. Finally, gold source-drain electrodes were evaporated on top of the oligothiophene films through a shadow mask, defining the channel length of $L = 20\,\mu m$ and channel width of $W = 5$ mm. The OFET devices were characterized using computer-controlled two-source measure units (Keithley 6430 and 2400 source meters) at

room temperature in an ambient condition. The mobility (μ) and the threshold voltage (V_T) were calculated in a saturation regime (drain voltage V_D of -50 V) using the equation $I_D = (WC_{ins}/2L)\mu(V_G - V_T)^2$, where I_D is the source-drain current and V_G is the gate voltage.

RESULTS AND DISCUSSION

Physical Properties of Sexithiophenes

α6T was obtained as shell-like deep-orange crystals and β6T as platelet orange crystals, the color of the latter being pale compared with that of the former. Figure 1 shows DSC thermograms of sexithiophenes. α6T is reported to exhibit nematic liquid crystalline phase at high temperature [19,20]. Our DSC and polarizing microscopic investigations reproduced the reported results. Moreover, a small endothermic peak corresponding to the mesophase-isotropic liquid transition was observed at 335°C, which was not detected in the earlier works. On the other hand, liquid crystalline phase was not observed for β6T. The melting point of β6T is ca. 349°C, which is more than 30 degrees higher than that of α6T (312°C) and is almost same as that of the longer analogue, α-septithiophene (α7T) [14]. The higher melting point of β6T than that of α6T indicates stronger intermolecular interaction between neighboring molecules.

Figure 2 shows UV/vis spectra of sexithiophenes in chloroform. Both of the compounds are hardly soluble, and β6T seems to be even less soluble than α6T, which is in good agreement with its higher melting point (stronger molecular interaction) compared with that of α6T. The wavelength of absorption peak of β6T (413 nm) is shorter than that of α6T (435 nm), suggesting its shorter π-conjugation length.

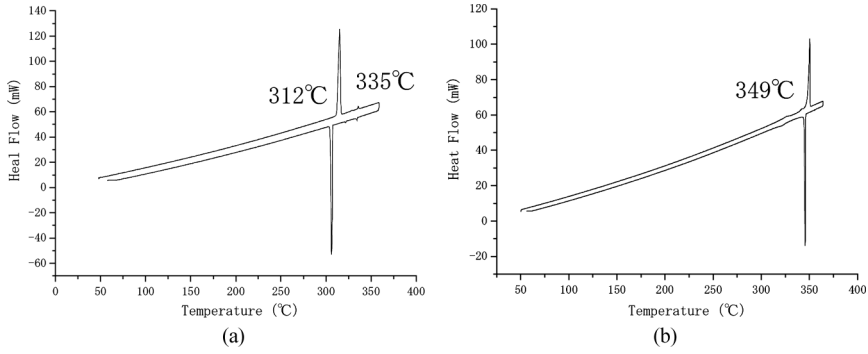

FIGURE 1 DSC thermograms of (a) α6T and (b) β6T.

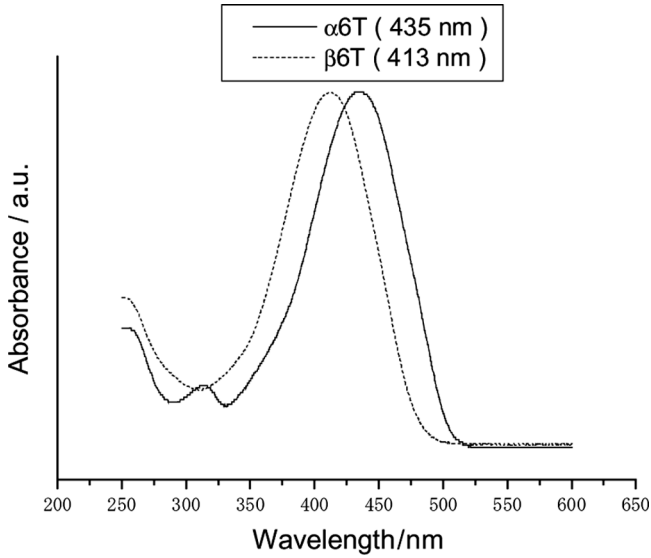

FIGURE 2 UV/vis absorption spectra of α6T and β6T in $CHCl_3$.

Indeed, sp^2 carbons of both ends of β6T molecule are not involved in the π-conjugation (Scheme 1) while all carbons of α6T participate in the π-conjugation.

FET Characteristics of Sexithiophenes

Figure 3 shows drain current–drain voltage (I_D–V_D) characteristics of α6T and β6T films at room temperature. Both films showed excellent

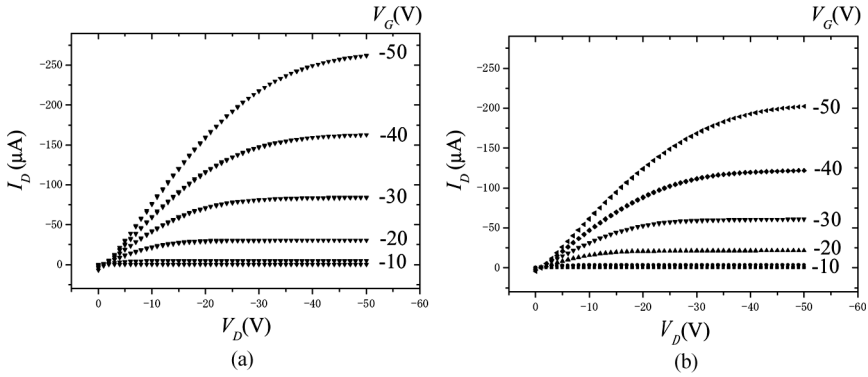

FIGURE 3 I_D–V_D characteristics of a) α6T and b) β6T.

TABLE 1 Field-Effect Mobilities (μ), Threshold Voltages (V_T) and on/off Current Ratios (I_{on}/I_{off}) of α6T and β6T

	μ (cm^2/Vs)	V_T (V)	I_{on}/I_{off}
α6T	0.154	−8.43	1.5×10^4
β6T	0.102	−10.42	7×10^4

p-type characteristics with linear raise of I_D at smaller value of V_D and well-developed saturation regime at larger V_D value (pinch-off). Histeresis was hardly seen for increasing and decreasing scans of V_D, suggesting the formation of uniform, good thin films with negligible number of trap sites such as structural defects and impurities.

The hole mobility obtained for α6T film is 0.15 cm^2/Vs ($V_T = -8.4$V) which is higher compared with literature values [4,7–10,15]. It is probably because of high purity of our sample as well as good film fabrication condition. For instance, DSC measurement of the commercially available α6T without further purification showed a broad transition peak with an onset at ca. 288°C. On the other hand, the melting point of the sample that we synthesized and purified was estimated to be 312°C.

The hole mobility of β6T film was calculated to be 0.10 cm^2/Vs ($V_T = -10$ V) which is lower compared with that of α6T. X-ray single crystal structure analyses showed that the molecular packing manner of these two compounds is almost same [16]. We therefore consider that the difference in mobility is attributed to the π-conjugation length: while the two compounds are structural isomers of each other, the absorption wavelength of β6T is shorter than that of α6T, i.e., π-conjugation length of β6T is shorter (Fig. 2). Relationship between conjugation length and charge mobility has also been reported for α-oligothiophenes and oligoacenes with different molecular lengths [15,21].

CONCLUSIONS

Physical and electrical properties of newly synthesized sexithiophene, β6T, were compared with those of its structural isomer, α6T. Together with the difference in π-conjugation length of the molecules, big difference was seen in charge mobility. It was revealed that π-conjugation length of the molecule considerably influences the FET characteristic. The findings obtained in this research will help the molecular design of organic semiconductor materials with high mobility. Further improvement of organic transistors is anticipated.

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