

## Solution-processable Oligothiophene Derivatives with Branched Alkyl Chains and Their Thin-film Transistor Characteristics

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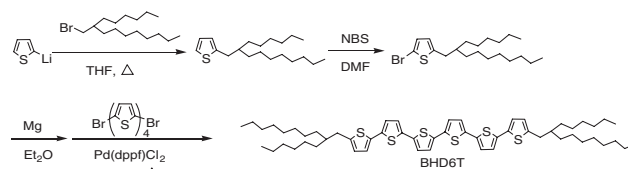
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Introduction of branched alkyl chains at the terminal positions of sexithiophene drastically improves the solubility of the compound, while still maintaining satisfactory charge carrier mobility. Field-effect transistors based on spin-coated films of the sexithiophene derivative exhibited p-type characteristics. Post thermal treatment enhanced crystallinity of the films and afforded a field-effect mobility of  $0.11\text{--}0.18\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  and an on/off ratio of  $10^4$ .



Scheme 1.

Solution-processed organic thin-film transistors (OTFTs) have been attracting considerable interest in recent years for their potential application to low-cost and large-area flexible electronics such as active-matrix displays and radiofrequency identification. As most  $\pi$ -conjugated semiconducting materials are insoluble themselves, various modified compounds such as substituted oligothiophenes,<sup>1</sup> acenes,<sup>1a,2</sup> fused heteroaromatics,<sup>3</sup> and fullerenes<sup>1a,4</sup> have been synthesized and applied to solution-processed OTFTs. Alkyl chain substitution is an effective way to solubilize aromatic compounds. Substitution, at the same time, affects molecular packing, and consequently can affect electronic properties of the compounds such as charge carrier mobility. In order to utilize substituted compounds for electronic devices, it is necessary to add substituents in an appropriate manner, i.e., without disturbing the electronic properties of the original  $\pi$ -conjugated core.

For oligothiophenes, which are among the most vigorously investigated class of semiconducting material, TFTs of evaporated films of the derivatives with *n*-alkyl substituents at the terminal ( $\alpha$ - and  $\omega$ -) positions afford comparable mobility to those of unsubstituted oligomers.<sup>5</sup> Alkyl substitution at the  $\alpha,\omega$ -position (substitution along the molecular long axis), however, does not improve much the solubility of the material. On the other hand, substitution at the  $\beta$ -position (substitution perpendicular to the molecular long axis) drastically improves the solubility while affording poor carrier mobility.<sup>1b</sup> Such phenomena can be correlated to the difference in molecular packing depending on the number and the position of alkyl-substituents.

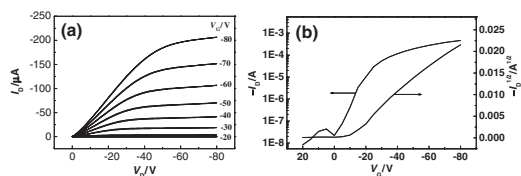
Aiming at the compatibility of high solubility and high carrier mobility of oligothiophene-based semiconducting materials, we have developed quinquethiophene and sexithiophene derivatives with branched alkyl chains (2-hexyldecyl chains), i.e., instead of *n*-alkyl chains, at both of the  $\alpha$ - and  $\omega$ -positions of the molecule.<sup>6</sup> In this paper, we report the synthesis, thin film fabrication and field-effect transistor (FET) characteristics of the sexithiophene derivative. Moreover, we demonstrate the improvement of hole mobility by annealing the films at an appropriate temperature.

The new thiophene-based material  $\alpha,\omega$ -bis(2-hexyldecyl)-sexithiophene (BHD6T) was successfully synthesized in good overall yield via simple steps from commercially available compounds (Scheme 1).<sup>12</sup> BHD6T solid can be dissolved at ca.  $20\text{ g L}^{-1}$  in chloroform at room temperature; it is a much better solubility compared to that of the sexithiophene derivative with *n*-hexyl chains at the  $\alpha,\omega$ -positions ( $\alpha,\omega$ -DH6T) ( $1\text{ g L}^{-1}$ )<sup>5b</sup> and comparable to that of  $\beta,\beta'$ -dihexyl-substituted sexithiophene ( $\beta,\beta'$ -DH6T) ( $10\text{ g L}^{-1}$ ),<sup>1b</sup> and is efficiently concentrated to fabricate TFTs by spin-coating. Good solubility also facilitates thorough purification of the synthesized compound using column chromatography.

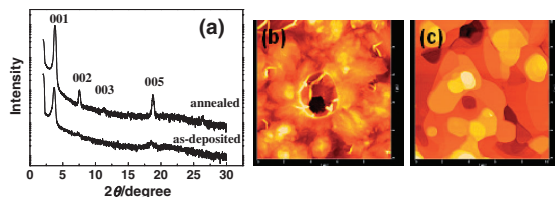
The result of differential scanning calorimetry (DSC) measurements shows that BHD6T turns into liquid at  $133\text{ }^\circ\text{C}$ , which is considerably lowered compared to the case of  $\alpha 6\text{T}$  ( $>300\text{ }^\circ\text{C}$ ). This can be attributed to the introduction of long branched alkyl chains that decrease molecular interaction. In the heating DSC scan of BHD6T, two endothermic phase transitions were observed at  $123$  and  $133\text{ }^\circ\text{C}$ . Polarizing microscopic observations at the temperature between the two phase transitions for BHD6T afforded a characteristic platelet-like texture that is reminiscent of some smectic phase. Such mesophases at higher temperature are often observed for oligothiophene derivatives with highly anisotropic molecular structure.<sup>1d,5c,6,8</sup> The existence of smectic-like mesophase for BHD6T indicates that the molecules are likely packed with their long molecular axis parallel to one another, so that the neighboring oligothiophene cores come close to one another, which is advantageous for carrier transport.

Bottom-contact FET devices were fabricated using spin-coated films from a  $5\text{ mg mL}^{-1}$  chloroform solution of BHD6T. The devices exhibited typical p-channel characteristics.<sup>9</sup> The representative values of hole mobility and on/off ratio of the BHD6T-TFTs were calculated to be  $7.5 \times 10^{-3}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  and  $10^4$ , respectively.

To improve the film performance, the devices were annealed at  $115\text{ }^\circ\text{C}$  for 1–2 h. Figure 1 shows the drain current ( $I_D$ )–drain voltage ( $V_D$ ) and the  $I_D$ –gate voltage ( $V_G$ ) characteristics of the same device after annealing at  $115\text{ }^\circ\text{C}$  for 1.5 h in a  $\text{N}_2$



**Figure 1.** (a)  $I_D$ - $V_D$  and (b)  $I_D$ - $V_G$  characteristics of the BHD6T-TFT after annealing at 115 °C for 1.5 h.



**Figure 2.** (a) XRD patterns of BHD6T-TFTs before and after annealing at 115 °C for 2 h. (b) AFM Images ( $10\ \mu\text{m} \times 10\ \mu\text{m}$ ) of BHD6T thin films before and (c) after annealing at 115 °C for 1.5 h.

atmosphere. The hole mobility increased to  $0.11\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ , and on/off ratio  $10^4$ , i.e., more than 10 times larger mobility than that of the same device before annealing.<sup>10</sup> By using trichlorooctadecylsilane instead of hexamethyldisilazane for surface treatment of the dielectric layer, the mobility even reached  $0.18\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ . Considering the fact that the hole mobility of the evaporated films of the parent material, i.e., unsubstituted  $\alpha$ 6T, was  $0.07$ – $0.15\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$  by our own experiments,<sup>7,11</sup> it can be deduced that introduction of branched alkyl chains does not disturb the favorable packing and arrangement of the active moiety.

To investigate the crystallinity and orientation of BHD6T molecules in thin films, X-ray diffraction (XRD) analyses were performed (Figure 2a). Only the (001) and the (005) diffraction peaks were observed for the film before annealing, while the (002) and the (003) peaks clearly appeared by annealing. In addition, the half-width of the (001) peak becomes smaller by annealing. These results indicate that the crystallinity of the film is improved by annealing, which can be correlated with the observed improvement of carrier mobility. The primary diffraction peak is observed at  $2\theta = 3.80^\circ$ , which corresponds to a layer  $d$ -spacing of 2.32 nm. When assuming a fully extended linear structure of the molecule, BHD6T shows a molecular length of some 5 nm. The XRD result thus shows that the molecular long axis seems to be considerably tilted from the surface normal.

Atomic force microscopic (AFM) studies allowed us to gain deeper insights into the film structures of BHD6T. The as-deposited films show stacks of small flake-like grains (Figure 2b), while the films after annealing show well-developed terraces (Figure 2c). Annealing longer or at higher temperature afforded structureless morphology. Note that the annealing temperature, 115 °C, is still below the transition temperature of BHD6T, so that one can avoid the drastic change in packing manner of neighboring molecules and the change in the crystal volume due to a phase transition that could cause cracks in the film. The height of a step is 2.5–3.0 nm, which substantially corresponds with the result of XRD.

In summary, introduction of branched alkyl chains at the  $\alpha$ - and  $\omega$ -positions of sexithiophene drastically improves the

solubility of the compound, while still maintaining satisfactory FET hole mobility. Moreover, after being annealed, the hole mobility of the thin film increased by one order of magnitude, which can be attributed to the molecular rearrangement toward the more developed crystalline nature of the film. The present results provide a new perspective on the molecular design of functionalized  $\pi$ -conjugated semiconducting materials.

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