Electronegative Oligothiophenes Having Difluorodioxocyclopentene-annelated Thiophenes as Solution-processable n-Type OFET Materials

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Solution-processable electronegative oligothiophenes bearing difluorodioxocyclopentene-annelated thiophenes have been synthesized. The electronic properties of the oligomers were investigated by absorption spectroscopy and electrochemical measurements. Their films fabricated by spin-coating showed typical n-channel OFET behavior.

Much attention has been focused on the development of superior materials for organic field-effect transistors (OFETs) due to their potential for low cost, large area, and flexible electronic devices.[1] The majority of such research has been devoted to p-type organic semiconductors, and oligo- and polythiophenes are one of the most studied π-conjugated systems.[1a,1b,2] On the other hand, the investigation of n-type π-conjugated semiconductors, which are an essential component for the realization of organic complementary circuits, has been falling behind.[3–7] We have recently reported that difluorodioxocyclopenta[*c*]thiophene (**C**) and difluorodioxocyclopenta[*b*]thiophene (**B**) units effectively contribute to increasing the electronegative character of oligothiophenes, and hence the vacuum-deposited film of BTTB (Figure 1) exhibited high field-effect electron mobility.[8] Another important aspect is the development of OFET materials sufficiently soluble in organic solvents, because their active layers can be fabricated by solution techniques such as spin-coating and drop-casting.[9] However, solution-processable n-type-OFET materials are still rare owing to the difficulty of adjusting the electron-withdrawing nature, solubility, and film morphology.[7b,10,11] In this communication, we report on the synthesis, properties, and FET performance of electronegative oligothiophenes having difluorodioxocyclopentene-annelated thiophenes (**B** and **C** units) as well as 3-hexylthiophene (**H** unit) to ensure solution processability (Figure 1).

Novel oligothiophenes BHHB, BHTHB, and BHCHB were synthesized, similarly to the recently reported BTTB,[8] from stannyl compounds **1** and **2** (Figure 2) with the corresponding central units by Stille couplings followed by acidic ketal deprotection. Unlike BTTB, these oligomers are soluble in common organic solvents such as THF, chloroform, and toluene. Thus, the products could be purified by silica-gel column chromatography and preparative gel-permeation liquid chromatography. Detailed synthetic procedures are given in Supporting Information.[12]

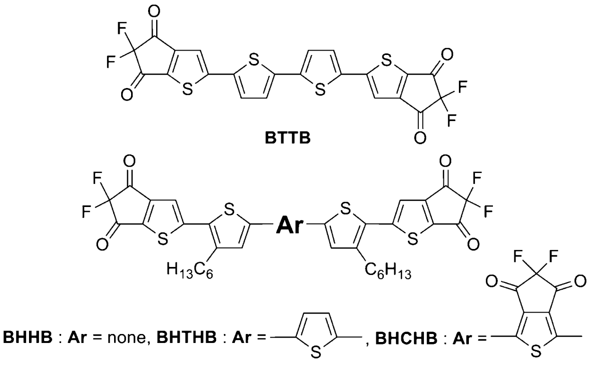
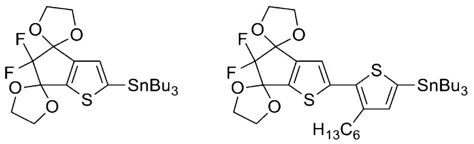


Figure 1. Chemical structures of BTTB, BHHB, BHTHB, and BHCHB.



1 **2**

Figure 2. Chemical structures of **1** and **2**.

The electronic properties of the oligothiophenes were investigated by UV–vis absorption spectra and cyclic voltammetry (CV) measurements (Figure S1),[12] and the data were summarized in Table 1. Compared with the absorption maximum of BTTB (463 nm in THF),[8] the introduction of hexyl groups causes a slight blue shift of 5 nm for BHHB. On the other hand, the replacement of the thiophene unit in BHTHB with the **C** unit results in 36-nm red shift for BHCHB. As we have previously reported, this is attributable to the enhancement of a donor (**H** unit) and acceptor (**B** and **C** units) alternative configuration.[8] In CV measurements, all the oligomers showed a reversible reduction wave, reflecting electrochemical stability of their radical anions. Moreover, the reduction potential of BHCHB is positively shifted largely compared with those of BHHB and BHTHB, indicating that the **B** unit as well as the **C** unit effectively lowers the LUMO energy levels (Table 1)[13] and thus enhances the electronegativity of oligothiophenes.

Bottom-contact OFET devices were fabricated on the gate electrode of p-doped silicon substrate. Source and drain gold electrodes with W/L of 294 mm/25 µm were prepatterned on a layer of SiO_2 dielectrics (300 nm). After HMDS treatment of the substrate, films of the oligomers with a thickness of 100 nm were prepared by spin-coating from 1.0 wt % chloroform solution at 1500 rpm for 1 min onto the substrate. Subsequently, under high vacuum, the OFET devices were annealed at 150 °C

Table 1. Absorption[a] and electrochemical data[b] of the oligomers

Oligomer	$\lambda_{max}{}^{a}$/nm	$E^{red}{}_{1/2}$/V	$E_{p.a}$/V	LUMO[c]/eV
BHHB	458	−1.72	+0.99	−3.08
BHTHB	482	−1.70	+0.96	−3.10
BHCHB	518	−1.26	+1.28	−3.54

[a]In THF. [b]In C_6H_5F, 0.1 M n-Bu_4NPF_6, V vs. Fc/Fc^+. [c]LUMO = $-(E^{red}{}_{1/2} + 4.8)$.

Table 2. Field-effect characteristics of the oligomers

Oligomer	μ/cm^2 V^{-1} s^{-1}	I_{on}/I_{off}	V_{th}/V
BHHB	no FET		
BHTHB	6.7×10^{-7}	1.1×10^3	30
BHCHB	1.9×10^{-4}	7.5×10^4	20

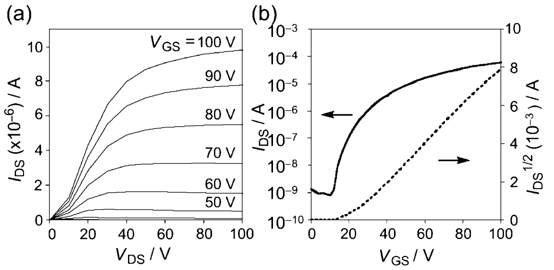


Figure 3. (a) Output characteristics of bottom-contact OFET of BHCHB and (b) transfer characteristics of the same device at 100 V of drain voltage.

for 30 min and then subjected to performance measurement at room temperature. The results are summarized in Table 2. The device based on BHHB showed no FET response. On the other hand, n-channel characteristics were observed on BHTHB film with low field-effect electron mobility. Moreover, the OFET performance of the BHCHB-based device was further enhanced, and its electron mobility reached up to 1.9×10^{-4} cm^2 V^{-1} s^{-1}, which is higher by three orders of magnitude relative to that of BHTHB, with an on/off current ratio of 7.5×10^4 and a threshold voltage of 20 V. Its output and transfer characteristics are shown in Figure 3.

Finally, to elucidate the observed large differences of the OFET performance, the morphology of the thin films on the HMDS-modified SiO_2 substrates was investigated by atomic force microscope (AFM) measurements. As shown in Figure 4a, unconnected islands were observed for the BHHB film, which clearly visualized the lack of charge-transporting pathways. The BHTHB film displayed needle-like isolated crystals, whereas the observation of the BHCHB film revealed that homogeneous-sized grains cover the substrate uniformly (Figures 4b and 4c).[14] These results indicate that network connections between the grains are responsible for the improved OFET performance of the BHCHB-based device compared with that of BHTHB, and therefore suggest that the presence of the **C** unit contributes to modulating the film growth suitable for OFETs.

In summary, we have accomplished the development of a new class of solution-processable n-type OFET materials by introducing both electronegative difluorodioxocyclopentene-annelated thiophenes and lipophilic hexyl groups into a π-conjugated oligomeric backbone. Our preliminary studies demonstrated that the combination of the **B** and **C** units is considerably improvement for n-channel OFET performance. It is important to note that this finding is in marked contrast to recently reported BCB-based OFET devices fabricated by a vacuum-deposition method,[8] where the nonstacking manner in the crystal has suggested the disturbance of its OFET behavior. Further design of related soluble π-conjugated systems for the application to the active layers of n-type OFET devices and photovoltaic devices is underway in our laboratory.

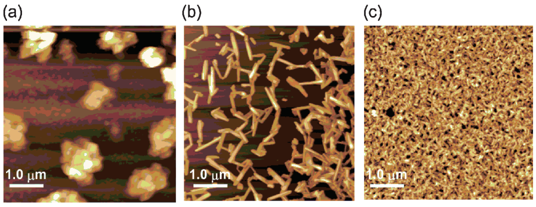


Figure 4. AFM images of thin films of BHHB (a), BHTHB (b), and BHCHB (c).

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References and Notes

1 a) A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107*, 1066. b) K. Takimiya, Y. Kunugi, T. Otsubo, *Chem. Lett.* **2007**, *36*, 578. c) J. E. Anthony, *Angew. Chem., Int. Ed.* **2008**, *47*, 452.

2 B. S. Ong, Y. Wu, Y. Li, P. Liu, H. Pan, *Chem.—Eur. J.* **2008**, *14*, 4766.

3 C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J.-L. Brédas, P. C. Ewbank, K. R. Mann, *Chem. Mater.* **2004**, *16*, 4436; A. Facchetti, M.-H. Yoon, T. J. Marks, *Adv. Mater.* **2005**, *17*, 1705.

4 A. Facchetti, Y. Deng, A. Wang, Y. Koide, H. Sirringhaus, T. J. Marks, R. H. Friend, *Angew. Chem., Int. Ed.* **2000**, *39*, 4547.

5 S. Ando, J. Nishida, H. Tada, Y. Inoue, S. Tokito, Y. Yamashita, *J. Am. Chem. Soc.* **2005**, *127*, 5336.

6 Y. Ie, M. Nitani, M. Ishikawa, K. Nakayama, H. Tada, T. Kaneda, Y. Aso, *Org. Lett.* **2007**, *9*, 2115; Y. Ie, Y. Umemoto, M. Nitani, Y. Aso, *Pure Appl. Chem.* **2008**, *80*, 589.

7 a) M.-H. Yoon, S. A. DiBenedetto, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.* **2005**, *127*, 1348. b) J. A. Letizia, A. Facchetti, C. L. Stern, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **2005**, *127*, 13476.

8 Y. Ie, Y. Umemoto, M. Okabe, T. Kusunoki, K. Nakayama, Y.-J. Pu, J. Kido, H. Tada, Y. Aso, *Org. Lett.* **2008**, *10*, 833.

9 S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, *Angew. Chem., Int. Ed.* **2008**, *47*, 4070.

10 S. Handa, E. Miyazaki, K. Takimiya, Y. Kunugi, *J. Am. Chem. Soc.* **2007**, *129*, 11684; H. Usta, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.* **2008**, *130*, 8580.

11 H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin, A. Dodabalapur, *Nature* **2000**, *404*, 478; A. Babel, S. A. Jenekhe, *J. Am. Chem. Soc.* **2003**, *125*, 13656; B. A. Jones, M. J. Ahrens, M.-H. Yoon, A. Facchetti, T. J. Marks, M. R. Wasielewski, *Angew. Chem., Int. Ed.* **2004**, *43*, 6363; R. Schmidt, M. M. Ling, J. H. Oh, M. Winkler, M. Könemann, Z. Bao, F. Würthner, *Adv. Mater.* **2007**, *19*, 3692; Z. Wang, C. Kim, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.* **2007**, *129*, 13362; H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dötz, M. Kastler, A. Facchetti, *Nature* **2009**, *457*, 679.

12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

13 The LUMO levels are calculated under the premise that the energy level of ferrocene/ferrocenium (Fc/Fc$^+$) is −4.8 eV below the vacuum level. A. J. Bard, L. R. Faulkner, *Electrochemical Methods-Fundamentals and Applications*, Wiley, New York, **1984**.

14 X-ray diffraction measurement of BHCHB films did not show clear diffraction peaks, indicating that the amorphous or less ordered films are formed on the SiO_2 substrates.