Preparation, Characterization, and Field-effect Transistor Performance of Benzo[1,2-*d*:4,5-*d*′]bisthiazole Derivatives

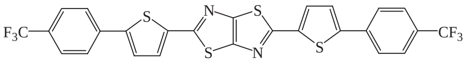
Masashi Mamada,[1] Jun-ichi Nishida,[1] Shizuo Tokito,[2] and Yoshiro Yamashita*[1]
[1]*Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering,*
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502
[2]*NHK Science and Technical Research Laboratories, Kinuta, Setagaya-ku, Tokyo 157-8510*

(Received April 25, 2008; CL-080435; E-mail: Yoshiro@echem.titech.ac.jp)

Benzo[1,2-*d*:4,5-*d*′]bisthiazole (BBT) derivatives were newly synthesized, and the crystal structure, optical and electrochemical properties were investigated. They were applied for organic field-effect transistors (OFET) as n-channel semiconductors. Although their thin films have relatively rough surface, the devices showed high-performance OFET characteristics. The thin film of **2** exhibited the electron mobility of 0.24 cm^2 V^{-1} s^{-1}.

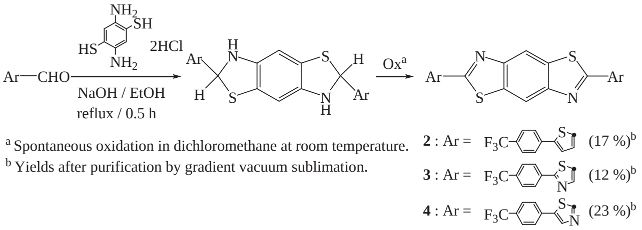
Organic thin-film transistors based on π-conjugated molecules continue to receive considerable attention for applications in the field of plastic electronics such as electronic papers, displays, organic light-emitting diodes, and radio frequency identification tags.[1–4] Development of new materials is very important to make progress in this field. We have reported organic semiconductors with a thiazolothiazole ring as core structure, whose devices exhibited high-performance p- and n-type FET characteristics.[5,6] The thiazolothiazole ring has advantages of a planar structure and large intermolecular π-overlap, leading to efficient π–π stacking. In addition, the nitrogen heterocycle enhances the electron affinity due to its electron-withdrawing property. This property is useful to enhance the air-stability in p-type semiconductors and decrease the barrier of electron injection in n-type semiconductors. For example, the derivative **1** (Figure 1) with trifluoromethylphenyl groups afforded a high-performance OFET device with a high electron mobility of 1.2 cm^2 V^{-1} s^{-1}.[7] As an extension of this work, we have now focused on a benzo[1,2-*d*:4,5-*d*′]bisthiazole (BBT) ring which is a π-extended system of thiazolothiazole. The π-extension is considered to be useful for increase in intermolecular interactions as well as decrease in Coulomb repulsion. Although a compound containing the BBT ring was reported to exhibit p-type semiconducting behavior very recently,[8] n-type behavior has not been reported so far. We report herein BBT derivatives affording n-type OFETs.

Scheme 1 shows the synthesis of BBT derivatives **2**–**4**, which were easily prepared by coupling reaction of commercially available 2,5-diamino-1,4-benzenedithiol dihydrochloride and the corresponding aldehydes.[9] The intermediate tetrahydro compounds were air-oxidized in chloroform to afford BBT derivatives. Theses compounds were purified by sublimation, and characterized by the spectroscopic data and elemental analysis.[10]



1

Figure 1. The chemical structure of **1**.



^{a} Spontaneous oxidation in dichloromethane at room temperature.
^{b} Yields after purification by gradient vacuum sublimation.

Scheme 1. Synthesis of BBT derivatives.

The electrochemical measurements of **2**–**4** were carried out in dichloromethane. The differential pulse voltamograms (DPV) of **2**–**4** exhibited one reduction peak at −1.40, −0.99, and −1.03 V vs. SCE, respectively. This result indicates that the LUMO levels of **3** and **4** are lower than that of **2** owing to the electron-accepting thiazole units. The absorption maxima of **2**–**4** were observed at 409, 400, and 407 nm, respectively. The HOMO–LUMO energy gaps estimated from the end absorptions were ca. 2.71, 2.71, and 2.70 eV, respectively. This result suggests that the intramolecular charge-transfer interaction between the electron-donating thienyl rings and the electron-withdrawing BBT ring is not significant in **2**. The emission maxima in the solid state were observed at longer wavelengths by 62 nm for **2**, 70 nm for **3**, and 77 nm for **4** compared to those in solution. These shifts can be attributed to the intermolecular interactions in the solid state.

The single crystals of **2** suitable for the X-ray structure analysis were obtained by slow sublimation although those of **3** and **4** could not be obtained. The X-ray analysis revealed that the crystal of **2** is composed of one kind of molecule with a center of symmetry.[11] As shown in the side view (Figure 2a), **2** has a zigzag molecular structure with a little deformed geometry. The dihedral angles between the BBT and thiophene rings, and the thiophene and benzene rings are 9.79 and 4.44°, respectively. The zigzag shape may disturb the formation of

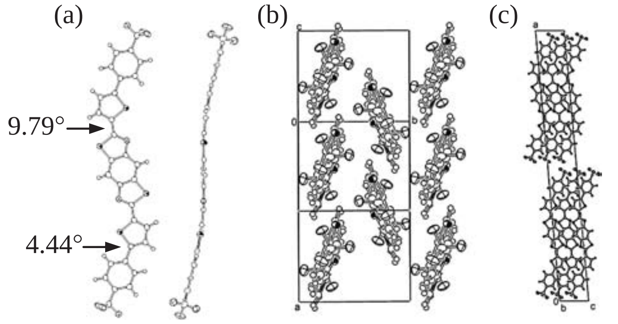


Figure 2. (a) Front view and side view of **2**. (b) The packing in **2** as seen down the long molecular axis. (c) *b* Axis projection.

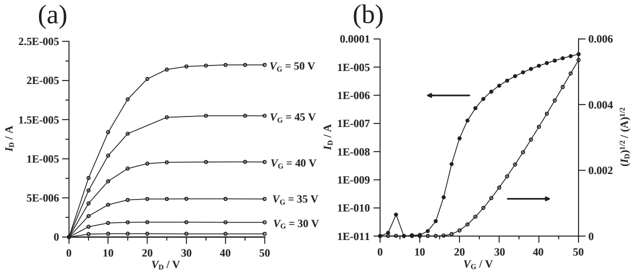


Figure 3. (a) Output characteristics of **2**. (b) Transfer characteristics of **2**.

π-stacking structure. The packing structure of **2** is a herringbone type as shown in Figure 2b, which is in contrast to the π-stacking in the corresponding thiazolothiazole derivatives.[6] The herringbone packing is effective for increasing of dimensionality as seen in pentacene, which leads to the highest performance in thin-film transistors.[12]

The orientation of vacuum deposited thin films of **2**–**4** was investigated by X-ray diffraction (XRD) analysis.[10] The XRD of the film of **2** deposited on SiO_2/Si substrates at rt showed a weak reflection peak. The *d*-spacing obtained from the first reflection peak ($2\theta = 6.30$) is 14.0 Å. The simulation pattern obtained from the single crystal data of **2** shows a (400) peak at $2\theta = 6.25$ with a very small (200) peak. Since the long axis of molecule is in the direction of *a* axis (56.8 Å) of the unit cell, molecule **2** may be perpendicular on the substrate. On the other hand, the films of **3** and **4** showed no clear peaks, suggesting amorphous or disordered structures on the substrate. These results indicate poor intermolecular interactions of these compounds on the substrate, which is unfavorable for the efficient carrier transport. The thin films deposited on octadecyltrichlorosilane (ODTS)-treated SiO_2/Si substrates have the similar XRD patterns to those on untreated substrates. Thus, the XRD of the films of **2** deposited on the ODTS-treated substrate at rt and 50 °C showed a reflection peak at ca. $2\theta = 6.70$ (13.2 Å). The films of **3** and **4** exhibited no peaks even at higher substrate temperatures.

The FET devices were fabricated with top contact configuration. Figure 3 shows the drain current (I_D) versus source–drain voltage (V_D) and gate voltage (V_G) at a drain voltage of 50-V characteristics for the n-channel OFETs of **2** deposited at $T_{sub} = 50$ °C on ODTS-treated substrates. The I_D–V_G curves showed no hysteresis behavior. The FET characteristics of **2**–**4** are summarized in Table 1. The mobilities of **2**- and **3**-based devices increased at higher substrate temperatures, whereas that of **4**-based device did not change. The device of **2** exhibited good mobility of 0.24 $cm^2\,V^{-1}\,s^{-1}$, on/off ratio of 2.9×10^6 and threshold voltage of 24 V. The mobility is a little lower than that of the thiazolothiazole derivative **1**. This is probably due to the difference in intermolecular interactions between molecules. On the other hand, the threshold voltage of **2**-based device is much decreased compared to that of **1** (67 V). This can be attributed to the better contact between the semiconductor and electrodes as well as the higher electron affinity. The devices based on **3** and **4** exhibited poorer characteristics than that of **2**, in particular as to the higher threshold voltages instead of the lower LUMO levels of **3** and **4**. This result can be attributed to their amorphous-like morphology as shown in the XRD study, resulting in large barrier in the charge carrier injection from the electrode to molecules.

Table 1. FET characteristics of **2**-, **3**-, and **4**-based top contact devices on ODTS-treated substrates[a]

Compound	T_{sub}/°C	Mobility/$cm^2\,V^{-1}\,s^{-1}$	On/off ratio	Threshold/V
2	20	0.10	8×10^5	22
	50	0.24	3×10^6	24
3	20	0.01	3×10^4	32
	50	0.05	2×10^6	28
4	20	0.02	3×10^4	39
	50	0.02	1×10^4	39

[a] SiO_2: 200 nm, active layer: 30 nm, $L/W = 50/1000$, S/D electrode: 50-nm Au.

In summary, we have developed novel benzo[1,2-*d*:4,5-*d*′]-bisthiazole derivatives for n-channel OFETs. The herringbone packing was revealed in the crystal of **2** by the X-ray analysis. The field-effect electron mobility of the thin film of **2** was 0.24 $cm^2\,V^{-1}\,s^{-1}$, and the threshold voltage was much lower than the corresponding thiazolothiazole derivative **1**.

This work was supported by a Grant-in-Aid for Scientific Research (No. 19350092) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and Mizuho Foundation for the Promotion of Sciences.

References and Notes

1 a) C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99. b) H. Meng, M. Bendikov, G. Mitchell, R. Helgeson, F. Wudl, Z. Bao, T. Siegrist, C. Kloc, C.-H. Chen, *Adv. Mater.* **2003**, *15*, 1090. c) 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. d) H. E. Katz, *Chem. Mater.* **2004**, *16*, 4748. e) A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107*, 1066. f) J. Zaumseil, H. Sirringhaus, *Chem. Rev.* **2007**, *107*, 1296.

2 a) J. A. Rogers, Z. Bao, K. Baldwin, A. Dodabalapur, B. Crone, V. R. Raju, V. Kuck, H. Katz, K. Amundson, J. Ewing, P. Drzaic, *Proc. Nat. Acad. Sci. U.S.A.* **2001**, *98*, 4835. b) C. D. Sheraw, L. Zhou, J. R. Huang, D. J. Gundlach, T. N. Jackson, M. G. Kane, I. G. Hill, M. S. Hammond, J. Campi, B. K. Greening, J. Francl, J. West, *Appl. Phys. Lett.* **2002**, *80*, 1088.

3 a) R. A. Street, W. S. Wong, S. E. Ready, M. L. Chabinyc, A. C. Arias, S. Limb, A. Salleo, R. Lujan, *Mater. Today* **2006**, *9*, 32. b) L. Zhou, A. Wanga, S.-C. Wu, J. Sun, S. Park, T. N. Jackson, *Appl. Phys. Lett.* **2006**, *88*, 083502.

4 a) R. C. G. Naber, B. de Boer, P. W. M. Blom, D. M. de Leeuw, *Appl. Phys. Lett.* **2005**, *87*, 203509. b) M. Zirkl, A. Haase, A. Fian, H. Schön, C. Sommer, G. Jakopic, G. Leising, B. Stadlober, I. Graz, N. Gaar, R. Schwödiauer, S. Bauer-Gogonea, S. Bauer, *Adv. Mater.* **2007**, *19*, 2241.

5 a) S. Ando, J. Nishida, Y. Inoue, S. Tokito, Y. Yamashita, *J. Mater. Chem.* **2004**, *14*, 1787. b) S. Ando, D. Kumaki, J. Nishida, H. Tada, Y. Inoue, S. Tokito, Y. Yamashita, *J. Mater. Chem.* **2007**, *17*, 553.

6 a) S. Ando, J. Nishida, H. Tada, Y. Inoue, S. Tokito, Y. Yamashita, *J. Am. Chem. Soc.* **2005**, *127*, 5336. b) M. Mamada, J. Nishida, D. Kumaki, S. Tokito, Y. Yamashita, *Chem. Mater.* **2007**, *19*, 5404.

7 D. Kumaki, S. Ando, S. Shimono, Y. Yamashita, T. Umeda, S. Tokito, *Appl. Phys. Lett.* **2007**, *90*, 053506.

8 H. Pang, F. Vilela, P. J. Skabara, J. J. W. McDouall, D. J. Crouch, T. D. Anthopoulos, D. D. C. Bradley, D. M. de Leeuw, P. N. Horton, M. B. Hursthouse, *Adv. Mater.* **2007**, *19*, 4438.

9 T. Kawamoto, T. Konno, *Mol. Cryst. Liq. Cryst.* **2002**, *379*, 443.

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

11 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-685937.

12 a) J. Cornil, D. Beljonne, J.-P. Calbert, J.-L. Bredas, *Adv. Mater.* **2001**, *13*, 1053. b) T. W. Kelley, D. V. Muyres, P. F. Baude, T. P. Smith, T. D. Jones, *Mater. Res. Soc. Symp. Proc.* **2003**, *771*, 169.