Unique Molecular Arrangement in Semiconducting Layer and FET Characteristics of Thin Film Transistors Based on 2,6-Dialkylbenzo[1,2-*b*:4,5-*b*′]diselenophenes (C_n-BDSs)

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2,6-Dialkylbenzo[1,2-*b*:4,5-*b*′]diselenophenes developed as soluble organic semiconductors gave a unique molecular arrangement in bulk single crystals, where π-stacking dimeric pairs and monomeric molecules are arranged in a similar manner to herringbone packing. Such unique structure was preserved in thin films on Si/SiO_2 substrate, and the thin films fabricated by solution- or vapor-deposition acted as an active channel of field-effect transistors with mobility up to 8.4×10^{-2} cm^2 V^{-1} s^{-1} for solution- and 2.3×10^{-1} cm^2 V^{-1} s^{-1} for vapor-processed devices, respectively.

Recent intensive research efforts in developing new soluble organic semiconductors have contributed to significant improvements in the performance of solution-processed organic field-effect transistors (OFETs).[1] For example, OFETs using a novel thiophene–thieno[3,2-*b*]thiophene copolymer-based semiconductor[2] or modified pentacenes[3] have attained μ_{FET} as high as 1.0 cm^2 V^{-1} s^{-1}, which is almost comparable with those of vapor-processed OFETs based on molecular semiconductors such as pentacene.

We also recently reported another high-performance solution-processed OFET based on 2,7-dialkyl[1]benzothieno[3,2-*b*][1]benzothiophenes (C_n-BTBTs, Figure 1), which afforded one of the highest μ_{FET} (up to 2.8 cm^2 V^{-1} s^{-1}) among solution-processed OFETs ever reported.[4] Their structurally related materials, 2,6-dialkylbenzo[1,2-*b*:4,5-*b*′]dithiophenes (C_n-BDTs, Figure 1) were also found to be useful as soluble semiconductors, but the C_n-BDTs-based OFETs showed rather poor performances: μ_{FET} was up to 2.6×10^{-2} cm^2 V^{-1} s^{-1}, lower than those of the C_n-BTBT-based devices by two orders of magnitude.[5]

The poor performances of the C_n-BDT-based OFETs relative to C_n-BTBTs were rationalized by the difference of molecular arrangement in the thin-film state. Although both molecules form a well-defined lamella-like structure on the Si/SiO_2 substrate, molecular arrangement in the semiconducting layer is strikingly different: C_n-BDTs assume the one-dimensional π-stacking structure with less effective intermolecular interaction,[5] whereas C_n-BTBTs take the herringbone arrangement enabling two-dimensional interactive electronic structures.[4]

With these experimental results, we planned to replace the sulfur atoms in the BDT framework by selenium atoms to tune the solid-state structure of the C_n-BDT-based semiconducting layer, anticipating that not only the large atomic radius but the high polarizability of selenium atoms may contribute to enhance the intermolecular interaction and/or alter the molecular arrangement.[6] In this paper, we report the emerged unique molecular arrangement in the semiconducting layer of 2,6-dialkylbenzo[1,2-*b*:4,5-*b*′]diselenophenes (C_n-BDSs, $n = 8$, 10, and 12, Figure 1) and the FET characteristics of their thin film transistors.

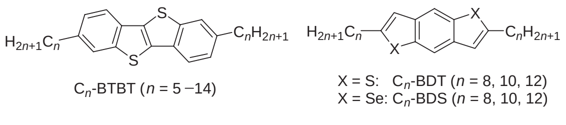

Figure 1. Molecular structures of C_n-BTBT, C_n-BDT, and C_n-BDS.

C_n-BDSs prepared analogously to the sulfur counterparts were characterized by spectroscopic as well as combustion elemental analyses (See Supporting Information).[7] In addition, their structures were fully elucidated by X-ray structural analysis. As a representative, molecular and crystal structure of C_{12}-BDS is depicted in Figures 2 and 3. Interestingly, the crystal contains two crystallographically independent molecules: one with a rather flat molecular structure (Figure 2a) forming π-stacking dimers in the BDS layer and the other with a doubly bent structure existing as monomeric molecules in the BDS layer (Figure 2b and Figure 3b). In the crystal structure, C_{12}-BDS molecules form the lamella-like structure along the crystallographic *c* axis direction (Figure 3a) as was observed in the molecular arrangements of C_{12}-BDT and C_n-BTBTs. The packing diagram in the semi-

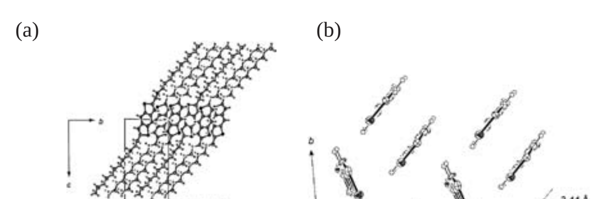

Figure 2. Molecular structures of C_{12}-BDS. Two crystallographically independent molecules are present in the bulk single crystal.

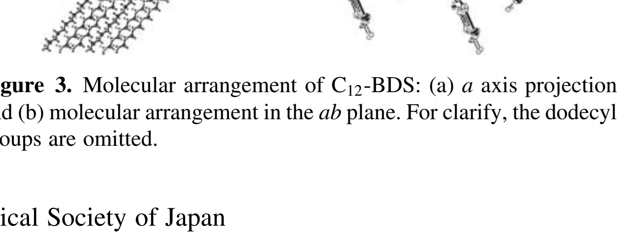

Figure 3. Molecular arrangement of C_{12}-BDS: (a) *a* axis projection and (b) molecular arrangement in the *ab* plane. For clarify, the dodecyl groups are omitted.

Table 1. FET characteristics of C_n-BDS-based devices[a]

Method	Compound	μ /$cm^2 V^{-1} s^{-1}$ [d]	I_{on}/I_{off}	V_{th} /V
Spin-coating[b]	C_8-BDS	3.9×10^{-2}	10^7	−4.3
	C_{10}-BDS	4.2×10^{-2}	10^6	−8.6
	C_{12}-BDS	8.4×10^{-2}[e]	10^7	−11
Vapor deposition[c]	C_8-BDS	1.9×10^{-1}	10^7	−15
	C_{10}-BDS	2.0×10^{-1}	10^6	−18
	C_{12}-BDS	2.3×10^{-1}	10^7	−19

[a] "top-contact" configuration with 50 µm and 1.5 mm of channel length and width, respectively, was used. [b] 0.8 wt% chloroform solution was used unless otherwise mentioned. [c] Fabricated on HMDS-treated Si/SiO_2 substrates. [d] Extracted from the saturation regime. [e] 1.2 wt% chloroform solution was used.

conducting BDS layer is however, quite different from those of C_{12}-BDT (π-stacking)[5] or C_n-BTBTs (herringbone),[4] where the π-stacking dimers and monomeric molecules are arranged in a similar manner to the herringbone packing resulting in a very unique molecular arrangement that can be classified as an in-between structure of the herringbone and the π-stacking (Figure 3b). A question thus posed was whether such molecular arrangement is suitable for the semiconducting channel in OFETs or not. To address this, we fabricated OFET devices on Si/SiO_2 substrate using vacuum deposition or spin-coating.

Summarized in Table 1 are the FET characteristics of C_n-BDSs-based OFETs evaluated under ambient conditions. The FET metrics of the solution-processed devices are slightly better than those for the C_n-BDT-based devices, but rather inferior to the C_n-BTBT-based ones. The FET performances of the vapor-processed devices were improved with a μ_{FET} higher than $0.1\,cm^2\,V^{-1}\,s^{-1}$, which however, is still lower by one order of magnitude than those obtained from the vapor-processed C_n-BTBT-based devices (up to $3.9\,cm^2\,V^{-1}\,s^{-1}$).[4]

Figure 4a shows the XRD pattern of the C_{12}-BDS thin film consisting of a series of peaks assignable to (00*l*) diffractions. The calculated interlayer spacing (*d*-spacing) is 32.5 Å, which is almost the same as that of the crystallographic *c* axis length of the bulk single crystal (32.962(8) Å), indicating that the molecular arrangements in both phases can be correlated to each other. We also took in-plane XRD of the C_{12}-BDS thin film (Figure 4a, inset): although the intensities of peaks are weak, five peaks assignable to the in-plane (*hk*0) diffractions are observed.

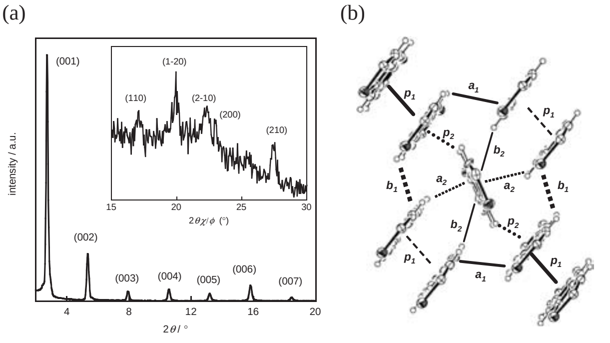

Figure 4. XRD pattern of spin-coated thin film of C_{12}-BDSs. Inset: In-plane-XRD ($2\theta\chi/\phi$ scan) (a), and calculated transfer integrals in the semicondcuting layer of C_{12}-BDS: $a_1 = 32.5$, $a_2 = -0.1$, $b_1 = -19.5$, $b_2 = -8.8$, $p_1 = 158.7$, $p_2 = -15.1$ meV, respectively (b).

On the basis of these thin film XRD data, we concluded that the packing structure of C_{12}-BDS both in the bulk single crystal and thin film are basically the same. To evaluate the electronic structure of C_{12}-BDS-based semiconducting channels, calculations of transfer integrals of HOMOs were carried out (Figure 4b).[8] As expected, very large orbital overlaps were confirmed in the dimeric pair of C_{12}-BDSs. On the other hand, relatively small orbital overlaps between the constituting units (the dimeric pair and monomeric molecules) were obtained. In particular, the transfer integrals around the monomeric unit are very small, which may deter the isotropic carrier migration in the thin film state.

In summary, we have synthesized and evaluated C_n-BDSs as new organic semiconductors. The C_n-BDS-based OFETs fabricated by both solution- and vapor-processes showed relatively high performances, but not among the best. XRD studies indicated that the molecular arrangement of C_n-BDS molecules in the thin film state is unique and can be classified as an in-between structure of herringbone and π-stacking. Calculation of transfer integrals in the BDS layer clarified that the present type of molecular arrangement is not necessarily suitable as the best semiconducting channel.

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References and Notes

1 Recent reviews on solution-processed OFETs, see: a) B. S. Ong, Y. Wu, Y. Li, P. Liu, H. Pan, *Chem.—Eur. J.* **2008**, *14*, 4766. b) I. Osaka, R. D. McCullough, *Acc. Chem. Res.* **2008**, *41*, 1202.

2 a) I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, M. F. Toney, *Nat. Mater.* **2006**, *5*, 328. b) B. H. Hamadani, D. J. Gundlach, I. McCulloch, M. Heeney, *Appl. Phys. Lett.* **2007**, *91*, 243512.

3 a) J. E. Anthony, J. S. Brooks, D. L. Eaton, S. R. Parkin, *J. Am. Chem. Soc.* **2001**, *123*, 9482. b) S. K. Park, T. N. Jackson, J. E. Anthony, D. A. Mourey, *Appl. Phys. Lett.* **2007**, *91*, 063514.

4 a) H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, T. Yui, *J. Am. Chem. Soc.* **2007**, *129*, 15732. b) T. Izawa, E. Miyazaki, K. Takimiya, *Adv. Mater.* **2008**, *20*, 3388.

5 T. Kashiki, E. Miyazaki, K. Takimiya, *Chem. Lett.* **2008**, *37*, 284.

6 Several selenophene-based semiconductors have been reported. a) Y. Kunugi, K. Takimiya, K. Yamane, K. Yamashita, Y. Aso, T. Otsubo, *Chem. Mater.* **2003**, *15*, 6. b) K. Takimiya, Y. Kunugi, Y. Konda, N. Niihara, T. Otsubo, *J. Am. Chem. Soc.* **2004**, *126*, 5084. c) K. Takimiya, Y. Kunugi, Y. Konda, H. Ebata, Y. Toyoshima, T. Otsubo, *J. Am. Chem. Soc.* **2006**, *128*, 3044. d) Y. M. Kim, E. Lim, I.-N. Kang, B.-J. Jung, J. Lee, B. W. Koo, L.-M. Do, H.-K. Shim, *Macromolecules* **2006**, *39*, 4081. e) K. Yamada, T. Okamoto, K. Kudoh, A. Wakamiya, S. Yamaguchi, J. Takeya, *Appl. Phys. Lett.* **2007**, *90*, 072102. f) T. Yamamoto, K. Takimiya, *J. Am. Chem. Soc.* **2007**, *129*, 2224. g) T. Izawa, E. Miyazaki, K. Takimiya, *Chem. Mater.* **2009**, *21*, 903.

7 All the new materials were fully characterized by spectroscopic and combustion elemental analyses. Physicochemical properties of C_n-BDSs and experimental details for XRD studies are also described in Supporting Information, available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

8 T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, H. Inokuchi, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 627.