ORGANIC
LETTERS

2012
Vol. 14, No. 18
4914–4917

Largely π-Extended Thienoacenes with Internal Thieno[3,2-*b*]thiophene Substructures: Synthesis, Characterization, and Organic Field-Effect Transistor Applications

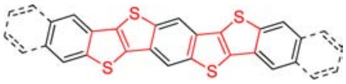
**Tatsuya Yamamoto,[†] Takeshi Nishimura,[†] Takamichi Mori,[†] Eigo Miyazaki,[†]
Itaru Osaka,[†] and Kazuo Takimiya*,[†,‡]**

*Department of Applied Chemistry, Graduate School of Engineering, Hiroshima
University, Higashi-Hiroshima 739-8527, Japan, and Emergent Molecular Function
Research Team, RIKEN Advanced Science Institute, Wako, Saitama 351-0198, Japan*

ktakimi@hiroshima-u.ac.jp

Received August 13, 2012

ABSTRACT



Two largely π-extended thienoacenes with internal thieno[3,2-*b*]thiophene substructures, *i.e.*, bis[1]benzothieno[2,3-*d*;2′,3′-*d*′]benzo[1,2-*b*;4,5-*b*′]-dithiophene (BBTBDT) and bis(naphtho[2,3-*b*]thieno)[2,3-*d*;2′,3′-*d*′]benzo[1,2-*b*;4,5-*b*′]dithiophene (BNTBDT), were synthesized, characterized, and evaluated as an active layer in thin-film organic field-effect transistors.

Thienoacene-based organic semiconductors have been intensively investigated during the past decade, and in fact they have contributed significantly in the development of high-performance organic field-effect transistors showing mobilities higher than 1.0 cm^2 V^{-1} s^{-1}.[1] Excellent air stability is another attractive advantage of such thienoacene-based organic semiconductors as [1]benzothieno[3,2-*b*]-[1]benzothiophene (BTBT)-[2] and dinaphtho[2,3-*b*;2′,3′-*f*]-thieno[3,2-*b*]thiophene (DNTT)-based materials[3] (Figure 1). The key structural feature in these materials is an internal thieno[3,2-*b*]thiophene substructure incorporated into a π-extended molecular framework, which significantly contributes to good stability by lowering the HOMO energy levels[4] and to high mobility in the solid state by effecting the intermolecular interaction via a nonbonded sulfur–sulfur interaction, which largely helps intermolecular orbital overlap.[1c] These apparent benefits from the internal thieno-[3,2-*b*]thiophene substructure in the π-extended systems have prompted synthetic chemists to develop related organic semiconductors with the thieno[3,2-*b*]thiophene substructure in largely extended π-systems with more than five fused-aromatic rings.[5] We have also been interested in such large π-systems with two thieno[3,2-*b*]thiophene

---

[†] Hiroshima University.

[‡] RIKEN Advanced Science Institute.

(1) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048. (b) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452–483. (c) Takimiya, K.; Shinamura, S.; Osaka, I.; Miyazaki, E. *Adv. Mater.* **2011**, *23*, 4347–4370. (d) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. *Chem. Rev.* **2012**, *112*, 2208–2267.

(2) (a) Takimiya, K.; Kunugi, Y.; Konda, Y.; Ebata, H.; Toyoshima, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2006**, *128*, 3044–3050. (b) Takimiya, K.; Ebata, H.; Sakamoto, K.; Izawa, T.; Otsubo, T.; Kunugi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 12604–12605. (c) Ebata, H.; Izawa, T.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H.; Yui, T. *J. Am. Chem. Soc.* **2007**, *129*, 15732–15733. (d) Izawa, T.; Miyazaki, E.; Takimiya, K. *Chem. Mater.* **2009**, *21*, 903–912.

(3) (a) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224–2225. (b) Yamamoto, T.; Shinamura, S.; Miyazaki, E.; Takimiya, K. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 120–130. (c) Kang, M. J.; Yamamoto, T.; Shinamura, S.; Miyazaki, E.; Takimiya, K. *Chem. Sci.* **2010**, *1*, 179–183. (d) Kang, M. J.; Doi, I.; Mori, H.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H. *Adv. Mater.* **2011**, *23*, 1222–1225. (e) Niimi, K.; Kang, M. J.; Miyazaki, E.; Osaka, I.; Takimiya, K. *Org. Lett.* **2011**, *13*, 3430–3433.

(4) Takimiya, K.; Yamamoto, T.; Ebata, H.; Izawa, T. *Sci. Tech. Adv. Mater.* **2007**, *8*, 273–276.

(5) Huang, J.; Luo, H.; Wang, L.; Guo, Y.; Zhang, W.; Chen, H.; Zhu, M.; Liu, Y.; Yu, G. *Org. Lett.* **2012**, *14*, 3300–3303.

10.1021/ol302243t © 2012 American Chemical Society
Published on Web 09/10/2012

substructures and focused on two thienoacenes with seven or nine fused aromatic rings, namely bis[1]benzothieno[2,3-*d*;2′,3′-*d*′]benzo[1,2-*b*;4,5-*b*′]dithiophene (BBTBDT) and bis(naphtho[2,3-*b*]thieno)[2,3-*d*;2′,3′-*d*′]benzo[1,2-*b*;4,5-*b*′]-dithiophene (BNTBDT) (Figure 1). Here, we report their synthesis featured by a double iodine-promoted thienothiophene formation reaction, characterization by means of single crystal X-ray analysis, UV−vis absorption spectra, photoelectron spectroscopy in air (PESA), and their thin-film-based organic field-effect transistor (OFET) characteristics.

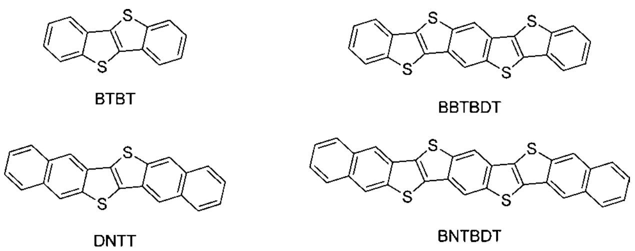


Figure 1. Thienoacene-based organic semiconductors with internal thieno[3,2-*b*]thiophene substructure(s).

The synthesis of BBTBDT and BNTBDT are outlined in Scheme 1, where the iodine-promoted thienothiophene formation from *o*-bis(methylthio)stilbenes, originally developed for the synthesis of DNTT, is employed at the final step. For the synthesis of appropriate precursors for BBTBDT and BNTBDT, the Wittig−Horner reaction was found to be very useful. Thus, a key intermediate in the synthesis is 2,5-bis(methylthio)terphthalaldehyde (**1**), which was reacted with a 2-fold amount of dimethyl 2-(methylthio)benzylphosphonate (**2**)[6] or dimethyl ((3-(methylthio)naphthalen-2-yl)methyl)phosphonate (**4**) to give the corresponding tetrakis(methylthio)-1,4-di((*E*)-styryl)benzene derivatives (**3** or **5**) in good yields. The subsequent iodine-promoted thienothiophene formation gave the desired thienoacene, BBTBDT or BNTBDT, respectively, in modest yields. It should be noted that, although the yields of the final steps are not very high, the present approach to large thienoacenes is quite efficient, as such highly π-extended thienoacenes as BNTBDT with nine aromatic rings in a linear manner can be conveniently synthesized. As expected from the highly π-extended, rigid, and planar structures without any substituents at the periphery, BBTBDT and BNTBDT are not soluble in common organic solvents, and thus their characterizations were done with mass spectroscopy and combustion elemental analysis. For BBTBDT, single crystal X-ray analysis affords definite structural confirmation (Figure 2).

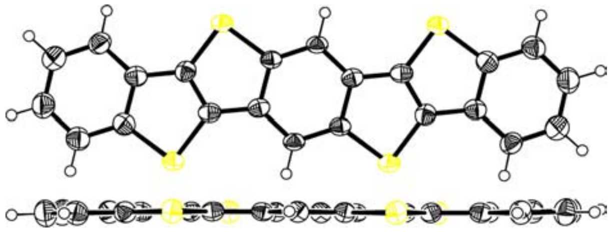
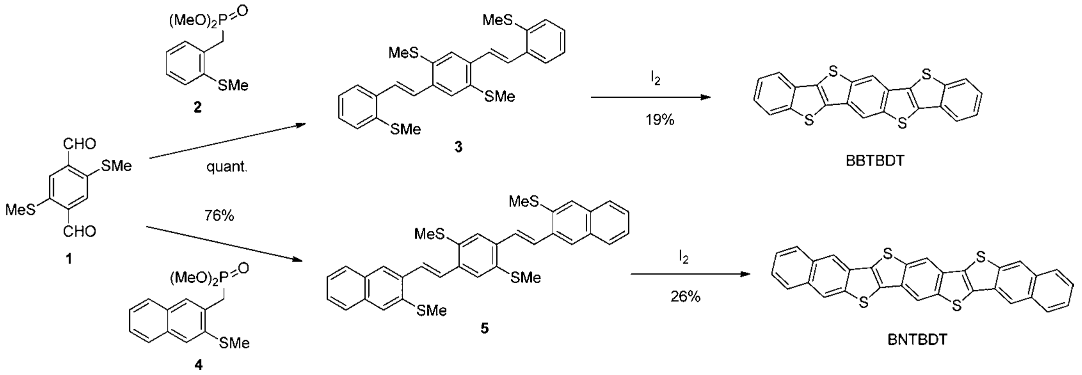


Figure 2. Molecular structure of BBTBDT.

Owing to their poor solubility and good film forming property, evaluation of electronic structures of BBTBDT and BNTBDT was done by using their vacuum-deposited thin films. As depicted in Figure 3a, ionization potentials (IPs), closely related to the HOMO energy levels, of both compounds are determined to be 5.2 eV, whereas the optical band gap estimated from the absorption edge are 2.8 eV for BBTBDT and 2.4 eV for BNTBDT, respectively (Figure 3b). In general, extension of the π-electron system tends to elevate the HOMO energy level, i.e., lower the IP, and reduce the HOMO−LUMO gap. The experimental IPs for the compounds are not the case, and in fact, calculated HOMO energy levels using the DFT methods[7] are 5.51 eV for BBTBDT and 5.16 eV for BNTBDT, respectively, below the vacuum level (Figure S3). This can be partially interpreted by the fact that the present evaluation was done in the thin film state, where the electronic structure can be influenced by intermolecular interaction; in this context, BBTBDT may have strong intermolecular interaction in the

Scheme 1. Syntheses of BBTBDT and BNTBDT



solid state. In any case, these IPs in the thin film state are thought to be suitable as a p-channel organic semiconductor for OFET application in terms of both facile hole injection from the source electrode and good stability in air.[8]

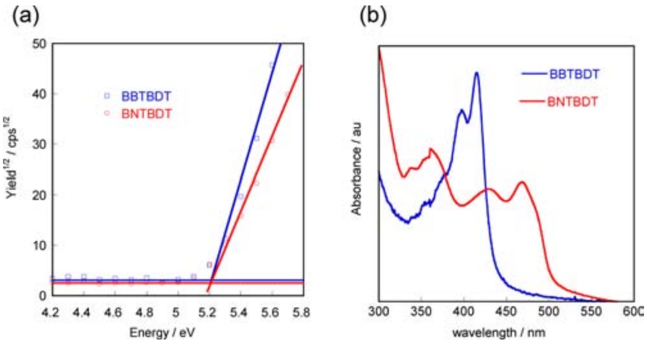


Figure 3. Characterization of evaporated thin films: (a) ionization potentials (IPs) determined by photoelectron yield spectroscopy in air and (b) UV−vis absorption spectra.

OFET characteristics of BBTBDT and BNTBDT were evaluated by using vapor-deposited thin films on Si/SiO$_2$ substrates modified with octyltrichlorosilane (OTS)- or octadecyltrichlorosilane (ODTS)-SAM with a top-contact, bottom-gate device configuration. Typical output and transfer curves of the BBTBDT- and BNTBDT-based devices are shown in Figure 4, and the mobility extracted from the saturation regime with other device characteristics are summarized in Table S1.

It is interesting to note that the extracted mobilities of BBTBDT-based devices are not significantly affected by the device fabrication conditions; regardless of the surface treatment and substrate temperature during deposition (T_{sub},), the mobilities are on the order of 10^{-2} to 10^{-1} cm^2 V^{-1} s^{-1} and the maximum mobility obtained was 0.14 cm^2 V^{-1} s^{-1}. Compared to the mobilities of other related π-extended thienoacene-based OFETs, the present values are rather modest. This could be partially attributed to the packing structure in the solid state. XRD patterns of the BBTBDT thin film for both out-of-plane and in-plane measurements indicate that the film is nicely crystalline, and all the XRD peaks that appeared are indexed by the bulk single crystal structure (Figure S4). This means that packing structures both in the thin film state and in the bulk single crystals are identical, and thus the electronic structure in the solid state can be discussed by using the crystal structure elucidated by the single crystal structural analysis. Figure 5 shows the crystal structure of BBTBDT, in which a typical molecular lamella structure along the crystallographic *a*-axis is observed (Figure 5a). In the BBTBDT layer in the crystallographic *bc*-plane (Figure 5b), π-stacking columns with face-to-face molecular overlap exist, which is in sharp contrast to related thienoacene-based organic semiconductors such as BTBT[2] and DNTT derivatives[3] as well as acenedithiophene derivatives,[9] which generally crystallize into the herringbone packing structure affording strongly interactive, two-dimensional electronic structures. To gain further insight into the intermolecular interaction, we calculated intermolecular transfer integrals (orbital coupling) of the HOMO (t_{HOMO}) in the *bc*-plane.[10] The calculated t_{HOMO}s are relatively small (~22 meV) compared to the ones observed for DNTT and BTBT derivatives (up to 80 meV),[1c] which qualitatively agrees well with the lower mobility of the present BBTBDT-based OFETs.

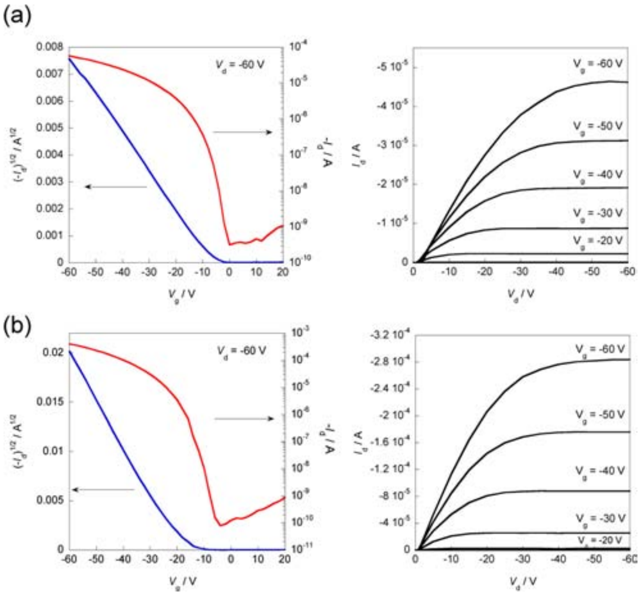


Figure 4. Transfer and output characteristics of OTFTs fabricated on ODTS-treated Si/SiO$_2$ substrate: (a) BBTBDT (T_{sub} = 60 °C) and (b) BNTBDT (T_{sub} = 150 °C).

In contrast to the modest OTFT characteristics of the BBTBDT-based devices, the BNTBDT-based ones showed a much enhanced mobility up to 0.94 cm^2 V^{-1} s^{-1}. It is interesting to note, however, that the device characteristics are largely influenced by T_{sub}s: at T_{sub}s higher than 100 °C, the mobility exceeds 0.1 cm^2 V^{-1} s^{-1}, whereas, at lower T_{sub}s, the mobilities are lower by more than 1 order of magnitude (Table S1). These results

---

(6) Niedermann, H.-P.; Eckes, H.-L.; Meier, H. *Tetrahedron Lett.* **1989**, *30*, 155–158.

(7) MO calculations were carried out with the DFT/TD-DFT method at the B3LYP/6-31g(d) level using the Gaussian 03 program package. Frisch, M. J. et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004. See Supporting Information for full reference.

(8) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Deliomeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5586–5608.

(9) (a) Takimiya, K.; Kunugi, Y.; Konda, Y.; Niihara, N.; Otsubo, T. *J. Am. Chem. Soc.* **2004**, *126*, 5084–5085. (b) Shinamura, S.; Osaka, I.; Miyazaki, E.; Nakao, A.; Yamagishi, M.; Takeya, J.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 5024–5035.

(10) (a) ADF2008.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com. (b) Senthilkumar, K.; Grozema, F. C.; Bickelhaupt, F. M.; Siebbeles, L. D. A. *J. Chem. Phys.* **2003**, *119*, 9809–9817. (c) Prins, P.; Senthilkumar, K.; Grozema, F. C.; Jonkheijm, P.; Schenning, A. P. H. J.; Meijer, E. W.; Siebbeles, L. D. A. *J. Chem. Phys. B* **2005**, *109*, 18267–18274.

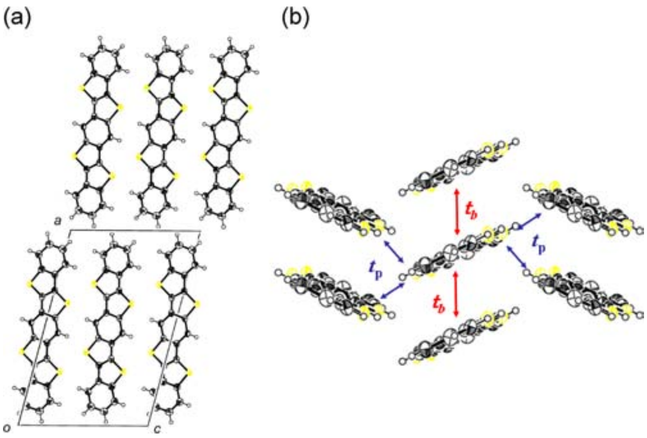


Figure 5. Packing structure of BBTBDT: (a) molecular lamella structure along the crystallographic *a*-axis direction, (b) π-stacking structure in the *bc*-plane. Calculated transfer integrals (t_{HOMO}s) are t_b = 12 meV and t_p = 22 meV.

can be qualitatively explained by considering the mechanism of crystal growth: during vacuum deposition, highly extended molecules such as BNTBDT tend to readily form crystal cores on the substrate at low temperature resulting in crystalline thin films with small crystallites.[11] Such a thin film thus has many grain boundaries, which in fact limit the charge transport in thin film transistors. In contrast, a higher T_{sub} can regulate crystal nucleation, resulting in thin films with larger grains. This speculation is supported by the surface observation by AFM (Figure S6): the BNTBDT thin film deposited at T_{sub} = rt has a surface without clear texture or consisting of very small grains less than 100 nm in size, whereas the film deposited at 150 °C clearly shows larger grains around 500 nm in size.

In summary, we have successfully synthesized highly π-extended thienoacenes, bis[1]benzothieno[2,3-*d*;2′,3′-*d*′]-benzo[1,2-*b*;4,5-*b*′]dithiophene (BBTBDT) and bis(naphtho-[2,3-*b*]thieno)[2,3-*d*;2′,3′-*d*′]benzo[1,2-*b*;4,5-*b*′]dithiophene (BNTBDT), with two internal thieno[3,2-*b*]thiophene substructures by featuring the iodine-promoted thienothiophene formation reaction. As expected from the molecular structures, these thienoacenes have suitable HOMO energy levels as p-channel organic semiconductors for OFET application. Although the device performances of the BBTBDT-based OTFTs were modest (up to 0.14 cm^2 V^{-1} s^{-1}), the BNTBDT-based OFETs gave relatively high mobilities close to 1.0 cm^2 V^{-1} s^{-1}. The present experimental results indicate that the largely π-extended thienoacenes cannot always afford good performances as organic semiconductors. Nevertheless, the BNTBDT-based OFETs showing mobilities close to 1.0 cm^2 V^{-1} s^{-1} are quite attractive, since recent OFET applications require many different material characteristics, not only high mobility and air stability but also thermal stability, for device integration and medical applications.[12] For the realization of thermally stable OTFTs, a largely π-extended organic semiconductor seems to be advantageous, since the thermal stability of the thin film state is generally good for large molecules. From this viewpoint, further optimization and application of BNTBDT-based OTFTs are now underway in our group.

Acknowledgment. This work was financially supported by Grants-in-Aid for Scientific Research (No. 23245041) from MEXT, Japan and a Founding Program for World-Leading R&D on Science and Technology (FIRST), Japan. HRMSs were carried out at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University.

Supporting Information Available. Synthetic details, characterizations data, and NMR spectra of materials, crystallographic information files (CIF) for BBTBDT, XRD patterns and AFM images of evaporated thin films, detailed FET characteristics, complete author list for ref 7. This material is available free of charge via the Internet at http://pubs.acs.org.

---

[11] (a) Sirringhaus, H.; H. Friend, R.; Wang, C.; Leuninger, J.; Mullen, K. *J. Mater. Chem.* **1999**, *9*, 2095–2101. (b) Niimi, K.; Shinamura, S.; Osaka, I.; Miyazaki, E.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 8732–8739.

[12] Kuribara, K.; Wang, H.; Uchiyama, N.; Fukuda, K.; Yokota, T.; Zschieschang, U.; Jaye, C.; Fischer, D.; Klauk, H.; Yamamoto, T.; Takimiya, K.; Ikeda, M.; Kuwabara, H.; Sekitani, T.; Loo, Y.-L.; Someya, T. *Nat. Commun.* **2012**, *3*, 723–1–7.

The authors declare no competing financial interest.