ORGANIC
LETTERS

2012
Vol. 14, No. 13
3300–3303

Dibenzoannelated Tetrathienoacene: Synthesis, Characterization, and Applications in Organic Field-Effect Transistors

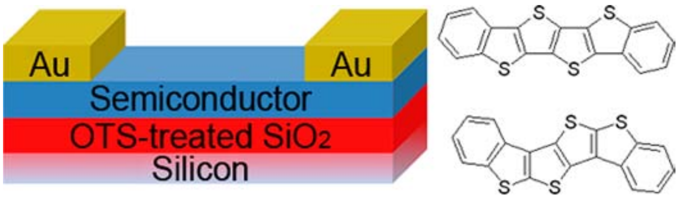
**Jianyao Huang,[†,‡] Hao Luo,[†,§] Liping Wang,[*,§] Yunlong Guo,[†] Weifeng Zhang,[†]
Huajie Chen,[†,‡] Minliang Zhu,[†,‡] Yunqi Liu,[†] and Gui Yu[*,†]**

*Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese
Academy of Sciences, Beijing 100190, P. R. China, Graduate University of Chinese
Academy of Sciences, Beijing 100049, P. R. China, and School of Materials Science and
Engineering, University of Science and Technology Beijing, Beijing 100083, P. R. China*

yugui@iccas.ac.cn; lpwang@mater.ustb.edu.cn

Received May 8, 2012

ABSTRACT



Two structural isomers of six-fused-ring sulfur-containing molecules were synthesized as active materials for *p*-type organic field-effect transistors, and their optical and electrochemical properties were characterized. Field-effect transistors based on these compounds were fabricated to investigate the relationships between structures and semiconductor properties.

In the course of development of suitable π-conjugated molecules used as *p*-channel organic semiconductor materials, many ladder-type molecules have been intensively studied, particularly acene- and thienoacene-based molecules.[1] Recently, different isomers of thienoacenes have received considerable attention because of their topology of planar frameworks and highly delocalized electronic structures, which make them good candidates for applications in organic field-effect transistors (OFETs).[2] Structure variations of these molecules by changing substituents or extending rings would be an effective way to build a series of sulfur-containing π-conjugated systems.[3] As derivatives of thienoacenes, benzoannelated fused oligothiophenes aroused our interest because of the synthetic challenge and strong intermolecular interactions ($C-H\cdots\pi$, $\pi\cdots\pi$, and $S\cdots S$ interactions, etc.). Dialkylated or diphenyl[1]benzothieno[3,2-*b*]benzothiophene,[4] dibenzo[*d*,*d′*]thieno[3,2-*b*:4,5-*b′*]dithiophene,[5] and benzoannelated pentathienoacene,[6] which contain four, five, and seven fused rings, respectively, have been explored fairly good performances as *p*-channel semiconductors in previous works. However, six-fused-ring systems, dibenzotetrathienoacenes

---

[†] Institute of Chemistry.

[‡] Graduate University of Chinese Academy of Sciences.

[§] University of Science and Technology Beijing.

(1) (a) Takimiya, K.; Shinamura, S.; Osaka, I.; Miyazaki, E. *Adv. Mater.* **2011**, *23*, 4347. (b) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. *Chem. Rev.* **2011**, *112*, 2208. (c) Liu, Y.; Yu, G.; Liu, Y. *Sci. China Chem.* **2010**, *53*, 779.

(2) Li, R.; Dong, H.; Zhan, X.; Li, H.; Wen, S.-H.; Deng, W.-Q.; Han, K.-L.; Hu, W. *J. Mater. Chem.* **2011**, *21*, 11335.

(3) (a) Liu, Y.; Wang, Y.; Wu, W.; Liu, Y.; Xi, H.; Wang, L.; Qiu, W.; Lu, K.; Du, C.; Yu, G. *Adv. Funct. Mater.* **2009**, *19*, 772. (b) De, P. K.; Neckers, D. C. *Org. Lett.* **2012**, *14*, 78. (c) Niimi, K.; Shinamura, S.; Osaka, I.; Miyazaki, E.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 8732. (d) Sokolov, A. N.; Atahan-Evrenk, S.; Mondal, R.; Akkerman, H. B.; Sánchez-Carrera, R. S.; Granados-Focil, S.; Schrier, J.; Mannsfeld, S. C. B.; Zoombelt, A. P.; Bao, Z.; Aspuru-Guzik, A. *Nat. Commun.* **2011**, *2*, 437. (e) Liu, Y.; Di, C.-a.; Du, C.; Liu, Y.; Lu, K.; Qiu, W.; Yu, G. *Chem.—Eur. J.* **2010**, *16*, 2231.

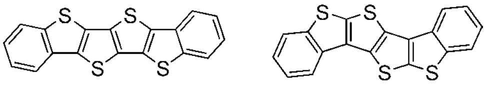
(4) Takimiya, K.; Ebata, H.; Sakamoto, K.; Izawa, T.; Otsubo, T.; Kunugi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 12604.

(5) Gao, J.; Li, R.; Li, L.; Meng, Q.; Jiang, H.; Li, H.; Hu, W. *Adv. Mater.* **2007**, *19*, 3008.

(6) (a) Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2005**, *7*, 5301. (b) Yamada, K. *Appl. Phys. Lett.* **2007**, *90*, 072102.

10.1021/ol3012748

(**DBTTA**s), have not been reported yet. In view of understanding that superacid-induced intramolecular cyclization reaction of aromatic methyl sulfoxides[7] would be accessible to various fused thiophene derivatives, we herein report a facile and effective way to synthesize two isomeric dibenzoannelated tetrathienoacenes: a linear ladder-type [1]benzothieno-[2″,3″:4′,5′]thieno[2′,3′:4,5]thieno[3,2-*b*][1]benzothiophene (**L-DBTTA**) and an S-shaped [1]benzothieno[3″,2″:4′,5′]-thieno[2′,3′:4,5]thieno[2,3-*b*][1]benzothiophene (**S-DBTTA**) (Figure 1). Compared with the axisymmetric odd-numbered fused oligothiophene rings, even-numbered ones with centrosymmetry might lead to interesting semiconductor properties.[8] To investigate structure–property relationships, molecular electronic structures and other physicochemical properties of both isomers were described.



L-DBTTA S-DBTTA

Figure 1. Molecular structures of compounds **L-** and **S-DBTTA**.

According to Takimiya's synthetic approach to obtain dinaphtho[2,3-*b*:2′,3′-*f*]thieno[3,2-*b*]thiophene (**DNTT**), thienothiophene could be formed by treating 1,2-bis-(*o*-(methylthio)aryl)ethane with an excess of iodine.[9] In analogy, **L-DBTTA** could be synthesizd through a derivative of benzo[*b*]thiophene. However, this route was not readily carried out because of the difficulty of separating the intermediate 3-(methythio)benzo[*b*]thiophene and corresponding aldehyde 3-(methylthio)benzo[*b*]thiophene-2-carbaldehyde. Therefore, we developed an effective procedure from the commercially available starting material thieno[3,2-*b*]thiophene (Scheme 1). 2,5-Bis(2-(methylthio)-phenyl)thieno[3,2-*b*]thiophene (**1**) was obtained with a moderate yield by Suzuki cross-coupling reaction before oxidation to 2,5-bis(2-(methylsulfinyl)phenyl)thieno[3,2-*b*]thiophene using 30% aqueous hydrogen peroxide. Cyclization of the methyl sulfoxide gave the target product with a yield of 75%. The synthesis of **S-DBTTA** was attempted to employ the similar method from 3,6-dibromothieno[3,2-*b*]thiophene initially, which was not successful because the highly reactive hydrogens at 2,5-positions resulted in complex byproducts. Instead, we tried to prepare 2,5-bis (methylthio)-3,6-diphenylthieno-[3,2-*b*]thiophene (**4**). The synthesis of 3,6-dibromo-2,5-bis(methylthio) thieno[3,2-*b*]thiophene (**3**) was previously reported,[10] while a modified method was employed here. To avoid the byproducts, 2,5-bis(methylthio)thieno[3,2-*b*] thiophene (**2**) was synthesized using *n*-butyllithium and dimethyl disulfide, followed by ready bromination to obtain the desired compound **3** with a high yield. Then, **4** was readily synthesized via Suzuki reaction of the compound **3** with phenylboronic acid. Unlike the corresponding precursor of **L-DBTTA**, **4** is insoluble in common solvents including ether, ethanol, acetone, and dichloromethane. Poor solubility led to an increase of reaction time and temperature of the next oxidation step. The optimized conditions were stirred at 40 °C for over 24 h. **S-DBTTA** was obtained via a similar method with **L-DBTTA** with a yield of over 70% (two steps). Both **L-** and **S-DBTTA** show a poor solubility in common solvents because of their rigid structures and strong intermolecular interactions. They were fully characterized with spectroscopic and elemental analyses (see the experimental procedures, Supporting Information).

Thermogravimetric analysis (TGA) data indicate weight loss (5%) only on heating above 340 °C (Figure S1, Supporting Information), suggesting good thermostabilities for both **DBTTA**s. Figure 2 shows the UV–vis absorption spectra of the two compounds in dilute solution of dichloromethane and in thin films. In solution, **S-DBTTA** has an absorption peak at 312 nm, and **L-DBTTA** shows three absorption peaks at 334, 348, and 366 nm, which contribute to the $\pi-\pi^*$ transitions. Compared with the spectra recorded in solution, a slight red shift was observed in the thin films of **S-DBTTA** ($\delta\lambda = 34$ nm). Similar phenomenon was found in the film of hexathienoacenene (**HTA**), suggesting a typical absorption of sulfur-rich linear thienoacenes.[3e] For solution and thin film of **L-DBTTA**, absoption spectra show longer absorption maxima than those of the compound **S-DBTTA**. The optical energy gaps are 3.18 and 3.35 eV for **L-** and **S-DBTTA,** respectively, determined by extrapolating the long-wavelength absorption edge in film phase with the equation $E_g = 1240/\lambda_{onset}$ eV. This suggests the linear isomer has better conjugation.

Cyclic voltammograms (CV) of **L-** and **S-DBTTA** were investigated at room temperatiure using vacuum-deposited thin films on indium tin oxide (ITO)-coated glass as a working electrode and Ag/AgCl as a reference electrode in dichloromethane solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as a supporting electrolyte. Their CV curves are shown in Figure 2b. The onset of the oxidation peaks were 1.22 and 1.30 eV versus Ag/AgCl for **L-** and **S-DBTTA**, respectively. The corresponding HOMO energy levels were estimated to be −5.62 and −5.70 eV using the equation $E_{HOMO} = -e(4.40 + E_{onset})$ eV. Their optical and electrochemical

---

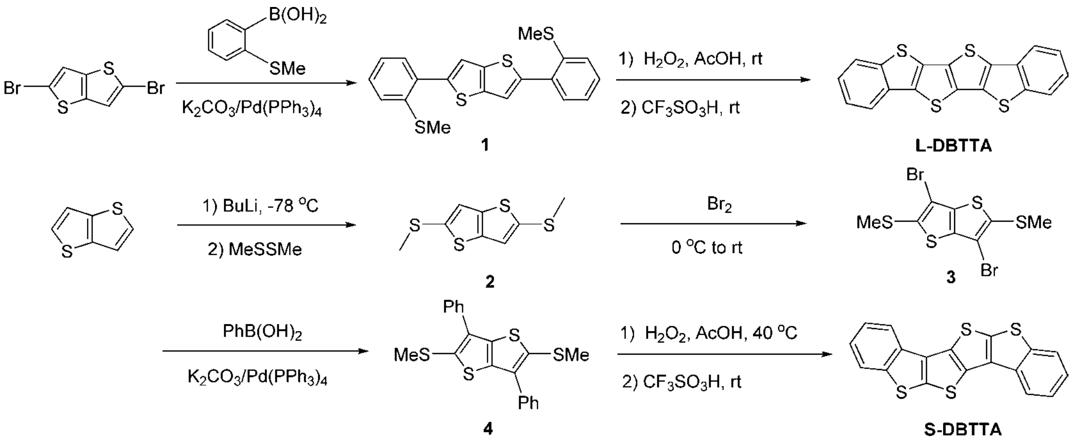
(7) (a) Sirringhaus, H.; Friend, R. H.; Wang, C. S.; Leuninger, J.; Mullen, K. *J. Mater. Chem.* **1999**, *9*, 2095. (b) Gao, P.; Beckmann, D.; Tsao, H. N.; Feng, X.; Enkelmann, V.; Pisula, W.; Mullen, K. *Chem. Commun.* **2008**, 1548. (c) Gao, P.; Beckmann, D.; Tsao, H. N.; Feng, X.; Enkelmann, V.; Baumgarten, M.; Pisula, W.; Müllen, K. *Adv. Mater.* **2009**, *21*, 213. (d) Du, C.; Ye, S.; Chen, J.; Guo, Y.; Liu, Y.; Lu, K.; Liu, Y.; Qi, T.; Gao, X.; Shuai, Z.; Yu, G. *Chem.—Eur. J.* **2009**, *15*, 8275. (e) Du, C.; Ye, S.; Liu, Y.; Guo, Y.; Wu, T.; Liu, H.; Zheng, J.; Cheng, C.; Zhu, M.; Yu, G. *Chem. Commun.* **2010**, *46*, 8573.

(8) Shinamura, S.; Osaka, I.; Miyazaki, E.; Nakao, A.; Yamagishi, M.; Takeya, J.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 5024.

(9) (a) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224. (b) Kang, M. J.; Doi, I.; Mori, H.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H. *Adv. Mater.* **2011**, *23*, 1222. (c) Niimi, K.; Kang, M. J.; Miyazaki, E.; Osaka, I.; Takimiya, K. *Org. Lett.* **2011**, *13*, 3430.

(10) Fuller, L., S.; Iddon, B.; A. Smith, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3465.

Scheme 1. Synthesis of Dibenzoannelated Tetrathienoacenes



characteristics suggest both linear and kinked symmetrical thiophene-based fused-ring molecules have low-lying HOMO energy levels and relatively large energy gaps, which indicate good stability against oxygen under ambient conditions. Both **DBTTA**s have complete or partially phene-like electronic structures which would be stable delocalized at the neutral state, whereas injection of positive charge requires large deformation of molecular structure to result in a larger reorgnization energy (λ) than the acene-like structures.[1a,11] The kinked **S-DBTTA** was more obvious to have such effect due to the nonlinear structure. Although having similar HOMO energy levels, **L-** and **S-DBTTA** with different molecular structures show different energy gaps and energy levels of the lowest unoccupied molecular orbitals (LUMO). The LUMO energy levels were estimated to be about −2.44 eV for **L-DBTTA** and −2.35 eV for **S-DBTTA** from the optical band gap and HOMO energy level. These experimental data are in reasonable agreement with the theoretical studies (Table S1, Supporting Information).

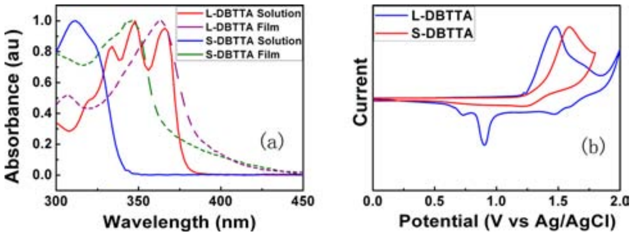


Figure 2. (a) UV−vis absorption spectra of **L-** and **S-DBTTA** in dilute dichloromethane solution and in thin films at room temperature. (b) Cyclic voltammograms of compounds **L-** and **S-DBTTA** in dichloromethane.

All devices fabricated by vapor deposition of **DBTTA**s on octadecyltrichlorosilane (OTS)-treated Si/SiO$_2$ (300 nm) substrates under different substrate temperatures with bottom-gate-top-contact configuration showed typical *p*-channel FET characteristics (Figure 3). The field-effect characteristics are summarized in Table 1. The best performance (a mobility of 0.15 cm^2 V^{-1} s^{-1} and a current on/off ratio of 10^6) was found for **L-DBTTA** at T_{sub} = 40 °C. This behavior correlates well with high crystallinity, as indicated by the relatively higher intensity in the corresponding X-ray diffraction (XRD) patterns and larger interconnected crystalline grains observed in the atomic force microscope (AFM) images. For the compound **S-DBTTA**, the best performance was obtained at T_{sub} = 50 °C with a mobility of 0.047 cm^2 V^{-1} s^{-1} and an on/off ratio of 10^6. Though AFM images showed larger grains were formed in the thin films of **S-DBTTA** deposited at 70 °C, their mobilities reduced to 0.032 cm^2 V^{-1} s^{-1}. One possibility is that, with the increase of the temperature, the morphologies of the films became worse owing to the increase of grain boundaries.

XRD measurements of the **DBTTA**s-based thin films at different substrate temperatures exhibit diffraction peaks at 2θ = 5.70, 11.42, and 23.06° (Figure S2, Supporting Information), which correspond to the primary, second-, and fourth-order diffraction peaks, respectively. The primary peak shows strong diffraction and determines the corresponding *d*-spacing of 1.55 nm, which is very close to

Table 1. OFET Characteristics of the **DBTTA**-Based Devices Fabricated on OTS-Treated Si/SiO$_2$ Substrates under Different Substrate Temperatures, L = 80 μm, W/L = 110

compd	temp (°C)	μ (cm^2 V^{-1} s^{-1})	$I_{\text{on}}/I_{\text{off}}$	V_{th} (V)
L-DBTTA	30	0.040	9.6×10^5	1
	40	0.15	5.9×10^6	9
	50	0.075	1.0×10^6	7
S-DBTTA	30	0.029	7.9×10^6	−8
	50	0.047	1.9×10^6	−7
	70	0.032	5.6×10^6	−11
	100	0.014	1.1×10^6	−12

---

[11] Yamamoto, T.; Shinamura, S.; Miyazaki, E.; Takimiya, K. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 120.

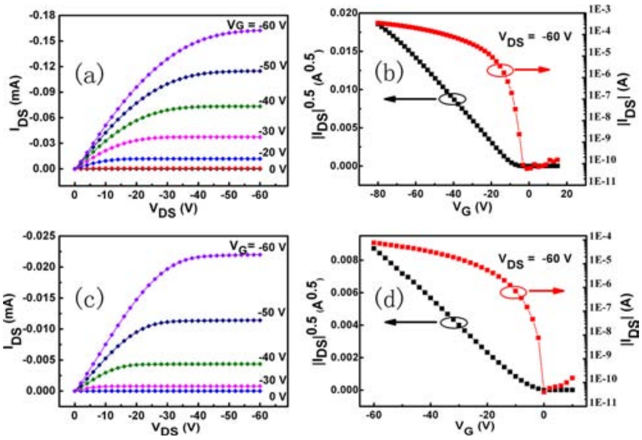


Figure 3. Electrical characteristics of the devices: (a) output and (b) transfer characteristics of the **L-DBTTA**-based OFETs; (c) output and (d) transfer characteristics of the **S-DBTTA**-based OFETs.

the length of the **L-DBTTA** molecule (1.498 nm, Supporting Information), indicating that the molecule was nearly perpendicular to the substrate and formed a perfectly packed structure. Being consistent with the direction of current flow, this orientation has been found favorable for achieving high mobility. However, the diffraction peaks of **S-DBTTA** show two strong peaks at 6.38 and 7.98° (Figure S3, Supporting Information), indicating *d*-spacing of 1.38 and 1.11 nm. These experimental data suggest a polymorphism in solid state which results in the formation of carrier trap sites and thus lowers the mobility.[1a]

In summary, we developed a successful strategy of synthesizing a new family of dibenzoannelated tetrathienoacenes as typical *p*-type organic semiconductors. Mobilities of 0.15 and 0.047 cm^2 V^{-1} s^{-1} were obtained for **L-** and **S-DBTTA**, respectively. For both C_2-symmetrical isomers, the linear one is a better candidate than the kinked one for fabricating organic field-effect transistors. Further investigation of the device optimization of **DBTTA**s is underway.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (20825208 and 21021091), the Major State Basic Research Development Program (2011CB808403 and 2011CB932303), and the Chinese Academy of Sciences.

Supporting Information Available. Experimental details, thermogravimetric analysis data and XRD for the synthesis and characterization of the compounds **L-** and **S-DBTTA**, device fabrication, and field-effect characteristics of the devices. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.