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Organic Semiconductor Molecules with Nonaromatic Core of 1,4-Dithiin

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Novel thiophene-condensed 1,4-dithiin derivatives having styryl or phenyl groups were synthesized, and their spectroscopic and electrochemical properties were investigated. Organic field-effect transistor (OFET) devices using these derivatives exhibited typical p-type FET characteristics, though the core units of both molecules were not aromatic compounds.

π-Conjugated thiophene derivatives offer great potential for applications in organic electronics.[1–4] The incorporation of thiophene rings into molecules has been utilized to provide good stability against air oxidation and strong intermolecular interactions.[5,6]

In this context, we have introduced the nonaromatic 1,4-dithiin framework into organic semiconductor molecules, because this framework will contribute to a lower HOMO energy level, which is favorable for the fabrication of air-stable materials. The most well-known 1,4-dithiin derivative, thianthrene (dibenzo-1,4-dithiin), is known to have a bent structure in the neutral state but a planar structure in the radical cation state.[7–9] In our previous study, the 1,4-dithiin analog fused to two benzo[*b*]thiophenes on both sides, bisbenzo[*b*]thieno[2,3-*b*:3′,2′-*e*]-1,4-dithiin (**BBTD-*syn***) (Figure 1), was reported to be a candidate as an organic semiconductor, having a bent nonaromatic 1,4-dithiin structure like a butterfly.[10] However, it was difficult to fabricate OFET devices through vacuum deposition onto SiO_2 substrates, since the **BBTD-*syn*** evaporates easily owing to the radiant heat. Therefore, we needed to design more suitable 1,4-dithiin derivatives with higher evaporation temperatures. Recently, Videlot-Ackermann et al. reported thiophene derivatives such as 5,5′-distyryl-2,2′-bithiophene (**DS2T**), which showed a relatively high hole mobility of $\mu = 2.0 \times 10^{-2}$ $cm^2\,V^{-1}\,s^{-1}$.[11–13] The hole mobility was maintained for more than 100 days under ambient conditions. Thus, they focused on the styryl groups in terms of endcap substituents that offer a planar structure and moderate solubility. Consequently, we designed two novel types of organic semiconductor molecules, i.e., 2,6-distyryldithieno[2,3-*b*;3′,2′-*e*]-1,4-dithiin (**DSDTD**), which has the 1,4-dithiin framework and styryl groups as wing moieties, and 2,6-diphenyldithieno[2,3-*b*;3′,2′-*e*]-1,4-dithiin (**DPDTD**), in order to increase the molecular weight by altering the chemical structure from condensed phenyl to linked phenyl groups (Figure 2). In this paper, we report the first synthesis, spectroscopic and electrochemical properties, and FET characteristics of the novel 1,4-dithiin derivatives **DSDTD** and **DPDTD**.

The novel 1,4-dithiins **DSDTD** and **DPDTD** were synthesized through the procedure shown in Scheme 1. Bis(2-trimethylsilylthien-4-yl)sulfide (**2**) was synthesized by the Stille coupling reaction between 4-bromo-2-trimethylsilylthiophene

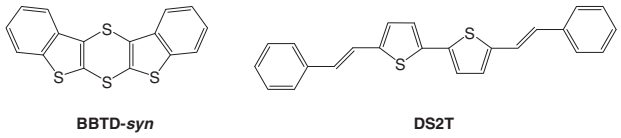


Figure 1. Structures of **BBTD-*syn*** and **DS2T**.

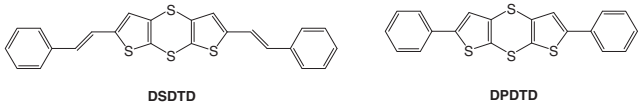
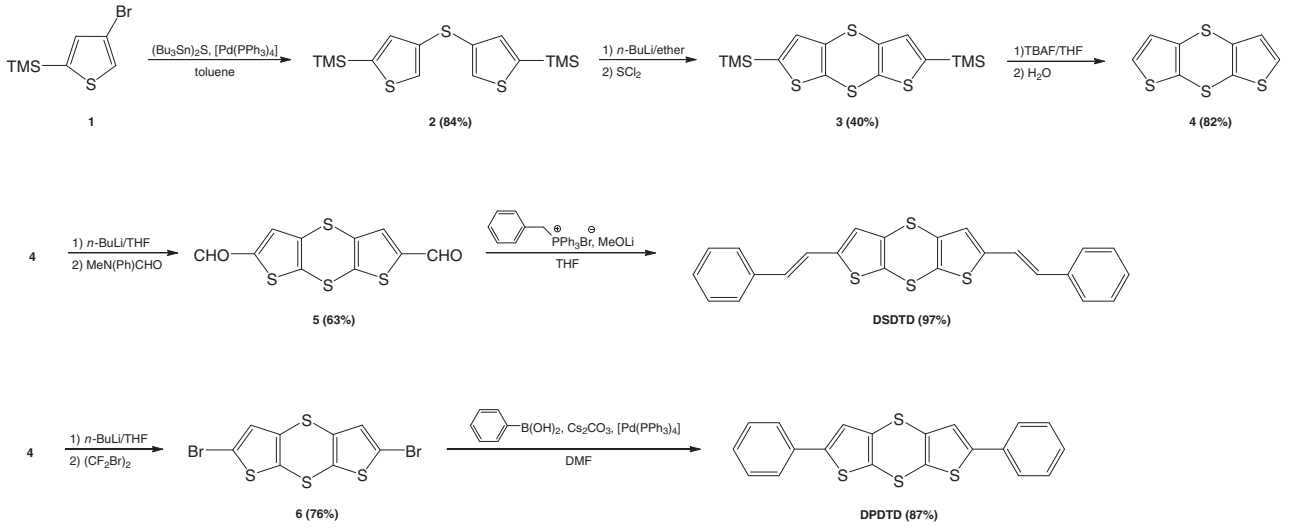


Figure 2. Structures of **DSDTD** and **DPDTD**.

(**1**) and $(Bu_3Sn)_2S$ with $[Pd(PPh_3)_4]$ in an autoclave.[14] The formation of the 1,4-dithiin ring was achieved by the reaction of compound **2** with *n*-BuLi following SCl_2 to produce 2,6-bis(trimethylsilyl)dithieno[2,3-*b*;3′,2′-*e*]-1,4-dithiin (**3**). The resulting compound was converted into dithieno[2,3-*b*;3′,2′-*e*]-1,4-dithiin (**4**) by a deprotection reaction with tetrabutylammonium fluoride (TBAF).[15–17] 2,6-Diformyldithieno[2,3-*b*;3′,2′-*e*]-1,4-dithiin (**5**) was then prepared from compound **4** with *n*-BuLi following MeN(Ph)CHO, and **DSDTD** was synthesized through the Wittig reaction in 97% yield as an orange solid. Meanwhile, 2,6-dibromodithieno[2,3-*b*;3′,2′-*e*]-1,4-dithiin (**6**) was also prepared from compound **4** using *n*-BuLi following $(CF_2Br)_2$, and **DPDTD** was synthesized through the Suzuki–Miyaura coupling in 87% yield as a yellow solid.

Both compounds are soluble and stable in organic solvents; therefore, the HOMO energy levels and transition energies were estimated from their optical and electrochemical measurements. Furthermore, DFT calculations at the B3LYP/6-311+G(d,p) level were also performed to explore the HOMO–LUMO energy levels, and these results are summarized in Table 1.[18] The calculated HOMO showed that the orbital distribution exists mainly on the 1,4-dithiin ring.

The UV–vis absorption spectra of target molecules were measured, as shown in Figure 3a. Focusing on the maximum absorption wavelength, λ_{max}, in CH_2Cl_2, **DSDTD** (377 nm) and **DPDTD** (341 nm) showed a more red-shifted absorption compared to **BBTD-*syn*** (309 nm), depending on the terminal substitutions. The transition energies, E_g, obtained from λ_{max} were estimated to be 3.29 eV for **DSDTD** and 3.64 eV for **DPDTD**, which indicated indirectly that the styryl groups elongate the π-conjugation length more than the phenyl groups, as expected. Furthermore, focusing on the λ_{max} values of both spectra from the deposited films on quartz glass, they showed a 27-nm red shift compared to the solution spectra owing to the intermolecular interactions between molecules in the films.



Scheme 1. Synthetic routes to **DSDTD** and **DPDTD**.

Table 1. Summary of optical and electrochemical properties, and calculated MO energies for **DSDTD** and **DPDTD**

	UV–vis		CV			Experimental		Theoretical[a]		
	λ_{max} (solution) /nm	λ_{max} (film) /nm	E_{pa} /V	E_{pc} /V	$E_{1/2}$ /V	$E_{HOMO}{}^{elec}$ /eV[b]	E_g /eV[c]	$E_{HOMO}{}^{calc}$ /eV	$E_{LUMO}{}^{calc}$ /eV	$E_g{}^{calc}$ /eV
DSDTD	377	404	0.70	0.59	0.65	−5.41	3.29	−5.47	−2.17	3.30
DPDTD	341	368	0.74	0.60	0.67	−5.46	3.64	−5.63	−1.72	3.91
BBTD-*syn*	309	—	0.94	0.83	0.89	−5.65	4.01	−5.76	−1.56	4.20

[a]The MO energies were calculated using the Gaussian09 program with the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d). [b]$E_{HOMO}{}^{elec}$ values are relative to the Ag/Ag^+ (4.71 V) reference electrode.[18] [c]Estimated from λ_{max}.

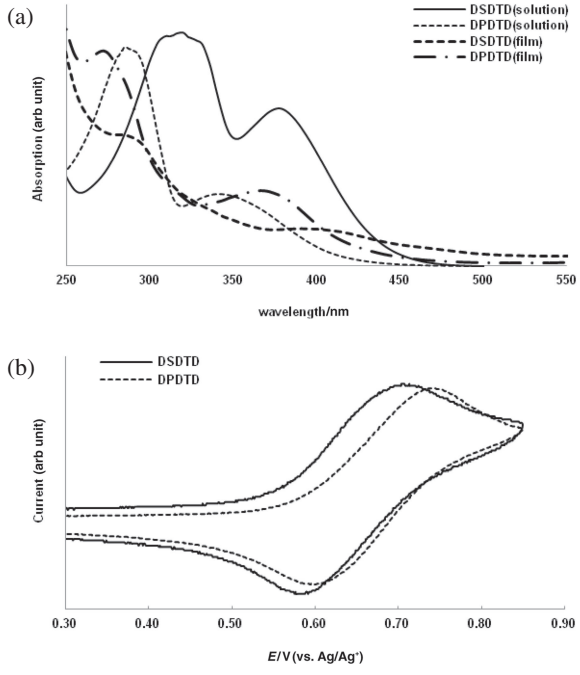


Figure 3. (a) Normalized UV–vis absorption spectra for **DSDTD** and **DPDTD** in CH_2Cl_2 and on quartz at room temperature. (b) Normalized cyclic voltammograms for **DSDTD** and **DPDTD**.

The electrochemical properties of the target molecules were examined through cyclic voltammetry (CV) measurements, as shown in Figure 3b. The anodic peak potential, E_{pa}, cathodic peak potential, E_{pc}, half-wave potential, $E_{1/2}$, and HOMO energy ($E_{HOMO}{}^{elec}$) are summarized in Table 1.[19] Reversible redox waves were seen for both compounds, indicating that the radical cations of these molecules are stable in CH_2Cl_2.

The $E_{1/2}$ values of **DSDTD** (0.65 V) and **DPDTD** (0.67 V) were shifted cathodically compared to that of **BBTD-*syn*** (0.89 V), and the $E_{HOMO}{}^{elec}$ values were estimated to be −5.41 eV for **DSDTD** and −5.45 eV for **DPDTD**. Since the $E_{HOMO}{}^{elec}$ values were quite negative, both molecules also have the potential for fabrication as air-stable FETs similarly to **DS2T**.

Top-contact bottom-gate-type OFET devices based on **DSDTD** or **DPDTD** were fabricated through vacuum deposition. Although **BBTD-*syn*** was sublimed easily by the radiant heat, we succeeded in fabricating thin-film devices using **DSDTD** and **DPDTD**. On the basis of the FET characteristic measurements, both devices showed typical p-type FET characteristics under ambient conditions (Figures S1 and S2).[20] The hole mobilities of these devices were $2.4 \times 10^{-3}\,cm^2\,V^{-1}\,s^{-1}$ ($I_{on/off} = 2 \times 10^3$, $V_{th} = 2.8$ V) for **DSDTD**, and $4.6 \times 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$ ($I_{on/off} = 4 \times 10^3$, $V_{th} = -2.2$ V) for **DPDTD**, which are the typical values of more than ten devices. In particular, the devices with **DPDTD** were unusual as they had a high hole mobility even though the core unit was not an

aromatic compound. The morphologies of the deposited thin films of the target molecules were investigated by XRD (Figure S3).[20] The *d*-spacings calculated from $\Delta 2\theta$ were 23.0 Å for **DSDTD** and 17.3 Å for **DPDTD**. These values were slightly higher than the molecular lengths as optimized by the DFT calculations (21.3 Å for **DSDTD** and 16.6 Å for **DPDTD**). Therefore, it is no longer our speculation that the active layers of these films may not be simple monolayers, and molecules do not line up perpendicularly to the Si/SiO_2 substrate, based on their bent structures. The AFM images of the thin films supported the *d*-spacings estimated from the orderly XRD patterns on the measurements of the step heights as follows: 23.5 Å for **DSDTD**, and 17.7 Å for **DPDTD**. Further studies on the morphologies, crystal structures, and configuration in the thin layers of **DSDTD** or **DPDTD** are now underway.

In summary, we have synthesized the novel thiophene-condensed 1,4-dithiin derivatives, **DSDTD** and **DPDTD**, which were characterized by optical and electrochemical studies. As a result, we were able to develop novel organic semiconductor molecules as air-stable OFETs with low HOMO energy levels by incorporating a nonaromatic compound into the core unit. We fabricated the OFETs with a top-contact bottom-gate structure, and found that the devices showed typical p-type FET characteristics. These are novel examples of the incorporation of molecules with core units that are not aromatic compounds as the active layers of OFETs; therefore, these results will serve as guidelines for future research on organic devices.

References and Notes

1 A. Facchetti, J. Letizia, M.-H. Yoon, M. Mushrush, H. E. Katz, T. J. Marks, *Chem. Mater.* **2004**, *16*, 4715.
2 M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891.
3 J. Zaumseil, H. Sirringhaus, *Chem. Rev.* **2007**, *107*, 1296.
4 K. Takimiya, S. Shinamura, I. Osaka, E. Miyazaki, *Adv. Mater.* **2011**, *23*, 4347.
5 A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107*, 1066.
6 R. S. Sánchez-Carrera, S. Atahan, J. Schrier, A. Aspuru-Guzik, *J. Phys. Chem. C* **2010**, *114*, 2334.
7 H. Bock, A. Rauschenbach, C. Näther, M. Kleine, Z. Havlas, *Chem. Ber.* **1994**, *127*, 2043.
8 T. Nishinaga, A. Wakamiya, K. Komatsu, *Tetrahedron Lett.* **1999**, *40*, 4375.
9 M. R. Bryce, A. K. Lay, A. Chesney, A. S. Batsanov, J. A. K. Howard, U. Buser, F. Gerson, P. Merstetter, *J. Chem. Soc., Perkin Trans. 2* **1999**, 755.
10 T. Yamamoto, S. Ogawa, R. Sato, *Tetrahedron Lett.* **2004**, *45*, 7943.
11 C. Videlot-Ackermann, J. Ackermann, H. Brisset, K. Kawamura, N. Yoshimoto, P. Raynal, A. E. Kassmi, F. Fages, *J. Am. Chem. Soc.* **2005**, *127*, 16346.
12 C. Videlot-Ackermann, J. Ackermann, K. Kawamura, N. Yoshimoto, H. Brisset, P. Raynal, A. E. Kassmi, F. Fages, *Org. Electron.* **2006**, *7*, 465.
13 Y. Didane, G. H. Mehl, A. Kumagai, N. Yoshimoto, C. Videlot-Ackermann, H. Brisset, *J. Am. Chem. Soc.* **2008**, *130*, 17681.
14 L. S. Miguel, W. W. Porter, III, A. J. Matzger, *Org. Lett.* **2007**, *9*, 1005.
15 M. G. Voronkov, A. N. Pereferkovich, *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 272.
16 H. Bock, B. Roth, *Phosphorus Sulfur Relat. Elem.* **1983**, *14*, 211.
17 H. Hiemstra, C. T. Kiers, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *35*, 1140.
18 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian09 (Revision B.01)*, Gaussian, Inc., Wallingford CT, **2010**.
19 M. E. Norako, M. A. Franzman, R. L. Brutchey, *Chem. Mater.* **2009**, *21*, 4299.
20 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

