

n-Type Field-effect Transistors Based on Thieno[3,2-*b*]thiophene-2,5-dione and the Bis(dicyanomethylene) Derivatives

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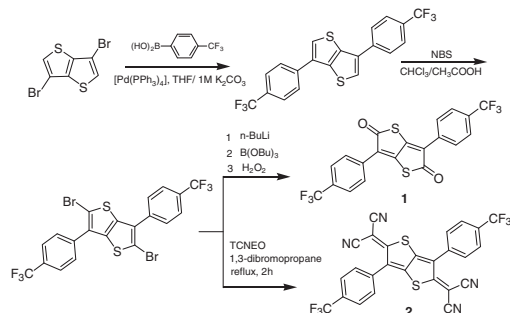
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Two new compounds, 3,6-bis(4-trifluoromethylphenyl)thieno[3,2-*b*]thiophene-2,5-dione (**1**) and 2,5-bis(dicyanomethylene)-3,6-bis(4-trifluoromethylphenyl)thieno[3,2-*b*]thiophene (**2**), were synthesized and characterized. The crystal structure of **1** was determined by single-crystal X-ray structure analysis. Organic field-effect transistors (OFETs) showed a relatively good mobility up to $0.039 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in **1** and a better air stability in **2**.

Organic field-effect transistors (OFETs) have been attracting increasing attention due to their potentials as low-cost, large-area, and flexible organic electronic devices.¹ During the past few years, remarkable progress has been made in developing p-type semiconducting materials such as pentacene,² rubrene,³ and poly(3-hexylthiophene) (P3HT).⁴ Their device performances have been comparable to those of amorphous silicon transistors. However, compared to the high performances of p-channel OFETs, the device performance of n-channel has been unsatisfactory^{1a} and development of novel n-type semiconductors remains a great challenge.

n-Type semiconductors have generally been prepared from electron-accepting π systems. Introduction of fluorine-containing substituents such as fluoroalkyl, pentafluorophenyl, trifluoroacetyl, and trifluoromethylphenyl groups to π -conjugated systems has been proven to be a good way to obtain n-channel OFETs with good performance.⁵ Cyano groups have also been widely used in n-type materials.⁶ We have used thiazolothiazole as electron-accepting π core to give high-performance n-type semiconductors.⁷ As an extension of this work, we have now focused on thieno[3,2-*b*]thiophene-2,5-dione for the following reasons. First, thieno[3,2-*b*]thiophene is a rigid heterocyclic system which has often been used in high-performance p-type semiconductors. Second, the dione unit is electron-accepting and the electron affinity can be further enhanced by substitution with dicyanomethylene groups. Third, by introduction of aryl substituents it is relatively easy to tune the physical properties. These considerations show that novel n-type organic semiconductors would be produced by introducing electron-accepting groups to the thieno[3,2-*b*]thiophene-2,5-dione core. We report herein the synthesis and characterization of dione **1** and the dicyanomethylene compound **2** with trifluoromethylphenyl groups (Scheme 1) and the OFETs based on them.

The synthetic approach of compounds **1** and **2** is outlined in Scheme 1. First, 3,6-dibromothieno[3,2-*b*]thiophene⁸ reacted with 4-trifluoromethylphenylboronic acid through palladium-catalyzed Suzuki coupling reaction under reflux for 24 h in deaerated aqueous K_2CO_3 solution and tetrahydrofuran (THF). The white solid 3,6-bis(4-trifluoromethylphenyl)thieno[3,2-*b*]thiophene was obtained and further purified by column



Scheme 1. Synthetic route to compounds **1** and **2**.

chromatography in a good yield of over 90%. Bromination with NBS afforded the corresponding dibromide as a white solid in a high yield of 95%. According to the method reported by Tiecco et al.,⁹ compound **1** was obtained in a yield of 75% as an orange solid. Compound **2** could be obtained by reaction of 2,5-dibromo-3,6-bis(4-trifluoromethylphenyl)thieno[3,2-*b*]thiophene with TCNEO (tetracyanoethylene oxide) in 1,3-dibromopropane in a yield of 62%.¹⁰ The two target compounds were characterized by mass spectrometry (MS), ¹HNMR, and elemental analysis. Although the number of hydrogens of **1** is the same as those of **2**, the chemical shifts in **2** show an obvious change relative to those of **1**. The significant shifting is attributed to the shielding caused by the close proximity of the cyano groups in **2**. The thermal properties of **1** and **2** were determined by DSC measurements (Figure S1¹⁴). They both exhibit excellent thermal stability with relatively high melting points at 258 and 378 °C, respectively. In addition, facile sublimation of the molecules allowed the deposition to give uniform thin films by vacuum evaporation for the fabrication of OFETs.

The optical properties of the molecules were examined by UV-vis spectroscopy in CH_2Cl_2 solution and in solid films shown in Figure 1. The data are summarized in Table 1. As shown in Figure 1, the spectrum of **1** in the film is significantly changed from that in solution, and the longest absorption band undergoes an obvious bathochromic shift of about 60 nm. However, the absorption intensity obviously decreased. This may be because the longest absorption band in solution can be attributed to intramolecular charge transfer (ICT), and in the solid film, the ICT may be decreased leading to the lower intensity of the band and instead, the intermolecular charge transfer takes place at lower energies. Further insight into the electronic properties of these compounds was given by cyclic voltammetry at room temperature. Figure 2 shows the reduction waves of the compounds **1** and **2**, and the data are listed in Table 1. They both exhibit good reversible cathodic reduction

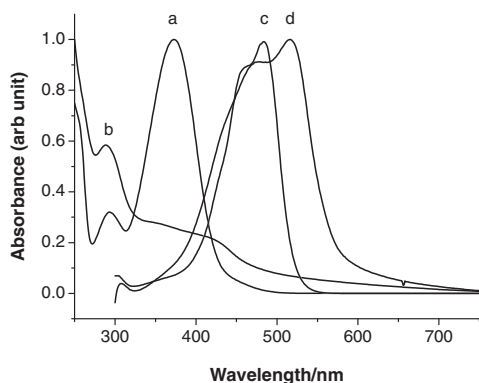


Figure 1. Normalized electronic absorption spectra of (a) **1** in CH_2Cl_2 , (b) **1** film, (c) **2** in CH_2Cl_2 , and (d) **2** film.

Table 1. The optical and electrochemical data of **1** and **2**

Compd	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$		$E_{1/2}^{\text{red}}/\text{V vs. SCE}$	HOMO/eV	LUMO/eV
	Solution	Film			
1	371	430	-0.50	-6.75 ^a	-3.84 ^a
			-0.91	-6.89 ^b	-3.66 ^b
2	483	516	0.10	-6.82 ^a	-4.44 ^a
			-0.27	-6.86 ^b	-4.51 ^b

^aCalculated from the optical and electrochemical characterization. ^bObtained from the DFT calculations (B3LYP/6-31G(d) level).

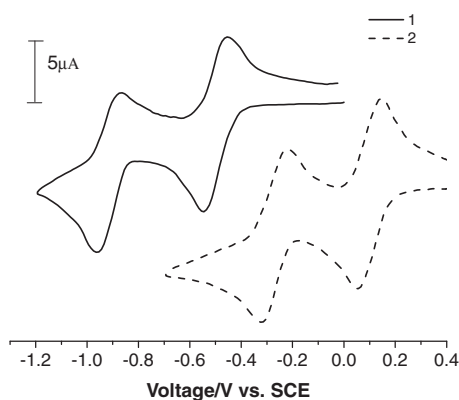


Figure 2. Cyclic voltammograms of **1** and **2** in 0.1 M $\text{Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$, scan rate 100 mV s^{-1} .

couples, suggesting that they have good electron-transport properties. In addition, the reduction potentials of **2** shift more positively than those of **1** because of the strongly electron-accepting cyano groups. The first reduction wave $E_{1/2}^{\text{red}}$ of **2** is about 0.1 V vs. SCE, which is very close to the value of TCNQ (0.13 V).¹¹ It indicates that compound **2** has potential as an electron acceptor for conducting charge-transfer complexes. Their energy levels were calculated using the ferrocene (E_{FOC}) value of -4.8 eV as a standard, while the E_{FOC} was calibrated to be 0.46 V vs. SCE in a CH_2Cl_2 solution of ferrocene. The electron affinity (EA) (LUMO level) for **1** and **2** derived from the first half-wave reduction potentials ($\text{EA} = (E_{1/2}^{\text{red}-1} + 4.34)$) are -3.84 and -4.44 eV , respectively. These values are very

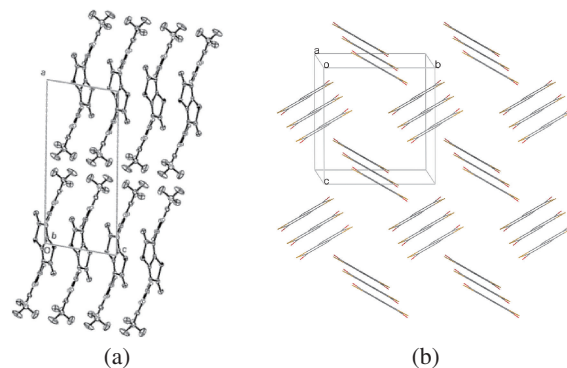


Figure 3. (a) Unit cell packing viewed along the b axis, (b) molecular arrangement in the unit cell. For clarity, trifluoromethylphenyl groups are omitted.

close to and far lower than -4.0 eV , the LUMO level that is advantageous for gaining air-stable n-channel FETs.¹² Based on the LUMO energy levels and the absorption onset in solution, the HOMO levels of **1** and **2** are estimated to be -6.75 and -6.82 eV , respectively. The results are very consistent with the levels obtained by density functional theory (DFT) calculations performed using the Gaussian 03 program at the B3LYP/6-31G(d) level.

To investigate the molecular arrangement and intermolecular interactions in the solid state, single-crystal X-ray analysis was carried out. Single crystals of **1** suitable for X-ray crystallography were grown by layer diffusion of hexane to a CH_2Cl_2 solution. On the other hand, crystals of **2** suitable for X-ray analysis could not be obtained. The molecule **1** has a somewhat deformed structure in which the dihedral angles between the phenyl rings and the thieno[3,2- b]thiophene ring are around 38° . It crystallizes in the monoclinic space group $P2_1/c$, and the unit cell packing viewed along the b axis is illustrated in Figure 3a. A typical herringbone arrangement shown in Figure 3b is observed which is favorable for two-dimensional carrier transport leading to high-performance OFET devices. Moreover, the benzene rings in the molecules arrange in an almost parallel manner with a close distance of about 3.63 \AA , suggesting the presence of the efficient intermolecular overlap between the molecules. In addition, short contacts of F-F (2.77 \AA) and S-S (3.79 \AA) are observed between the neighboring molecules.

The FET devices were fabricated with bottom-contact configuration. The SiO_2 gate dielectric was 300 nm thick and was treated with hexamethyldisilazane (HMDS). The organic semiconductors were deposited at a rate of $0.2\text{--}0.3 \text{ \AA s}^{-1}$ at room substrate temperatures. The FET measurements were carried out at room temperature in a high vacuum chamber (10^{-5} Pa). Figure S2¹⁴ shows the output and transfer characteristics of **1** and **2** on bare and HMDS-treated SiO_2 substrates. The FET performances of the devices for **1** and **2** are summarized in Table 2. The performance for the device of **1** on the HMDS-treated substrate is better than that on the bare SiO_2 substrate. However, the devices were not very stable in air. On the other hand, the FET performance of **2** is lower than that of **1**. However, introducing strongly electron-accepting dicyanomethylene groups obviously decreases the LUMO level. As a result, the air stability of the device obviously increases compared with

Table 2. Field-effect transistor characteristics of bottom contact devices for **1** and **2**^a

Compd	Substrate conditions	Measurement conditions	μ /cm ² V ⁻¹ s ⁻¹	I_{on}/I_{off}	V_{th} /V
1	Bare	Under vacuum	0.015	4×10^5	11
		In air (0 h)	—	—	—
	HMDS	Under vacuum	0.039	2×10^6	27
		In air (0 h)	—	—	—
2	Bare	Under vacuum	1.68×10^{-5}	1×10^3	12
		In air (0 h)	7.40×10^{-6}	61	6
		In air (24 h)	3.90×10^{-6}	57	6
	HMDS	Under vacuum	2.74×10^{-5}	4×10^2	21
		In air (0 h)	1.60×10^{-5}	48	16
		In air (24 h)	1.28×10^{-5}	28	17

^aSiO₂: 300 nm, active layer: 50 nm, $L/W = 25 \mu\text{m}/294000 \mu\text{m}$, S/D electrode: Au/Cr (20/10 nm).

that of **1**, although the mobility and on/off ratio decrease when exposed to air. The device performance did not change so much after 24 h in air (Table 2).

The XRD measurements in reflection mode for compounds **1** and **2** under various conditions were carried out. Figure S3¹⁴ shows the XRD patterns of 50-nm film deposited on untreated and HMDS-treated SiO₂ substrates of **1** at room temperature. As shown in Figure S3,¹⁴ the film for **1** shows a relatively sharp peak at $2\theta = 5.56^\circ$ corresponding to the d spacing of 15.9 Å, which is almost equal to the length of the unit-cell parameter a of the single crystal ($a = 16.1 \text{ \AA}$). Moreover, the molecular length is about 15.5 Å as given by X-ray single-crystal analysis, which is also in accordance with the value of the d spacing. This fact demonstrates that the a axis of the unit cell is oriented perpendicularly to the substrate, while the b axis and c axis are on the plane. This organization is supposed to be very favorable for transistor applications.¹³ However, the intensity of the peak in the film is relatively low. The FET properties of **1** may be improved by increasing the crystallinity of the film by decreasing the rate of the sublimation. Figure S4¹⁴ shows the XRD patterns of **2**. Compared to that of **1** shown in Figure S4,¹⁴ no obvious peak was observed on the XRD pattern of **2** regardless of the untreated or HMDS-treated substrates, which may be attributed to the unfavorable molecular arrangement, leading to the poor FET performance.

In summary, thieno[3,2-*b*]thiophene-2,5-dione and the bis(dicyanomethylene) derivatives with trifluoromethylphenyl groups were synthesized. Their electronic properties and structures were investigated by spectroscopic and electrochemical measurements and X-ray analysis. In addition, the preliminary FET properties were also examined. Good FET properties were obtained under vacuum for dione **1**. Although the electron mobility for dicyanomethylene **2** was not as high as that of **1**, the air stability of the device obviously increased. Further work to improve the FET performances by optimization of the FET device structure, the formation conditions of the films, and the modification of the molecules is in progress.

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