

n-Type Organic Field-Effect Transistors with Very High Electron Mobility Based on Thiazole Oligomers with Trifluoromethylphenyl Groups

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n-Type organic field-effect transistors (OFETs) are envisioned as key components of organic p–n junctions, bipolar transistors, and complementary integrated circuits leading to flexible, large-area, and low-cost electronic applications.¹ Compared to the p-type semiconductors, such as pentacene, n-type semiconductors are still not fully developed, and the performances are not satisfactory. Thus, pentacene afforded a thin film FET with the highest hole mobility of 3.0 cm²/Vs,² whereas the highest electron mobility was reported to be 0.62 cm²/Vs using a perylene diimide derivative.³ To obtain the high electron mobility, the organic semiconductor layer should be highly ordered with strong intermolecular interactions and should also have a proper LUMO energy level near the work functions of source/drain electrodes.⁴ Recently, high performance n-type organic semiconductors have been obtained by introducing fluoro or fluoroalkyl substituents into pentacene and oligothiophene derivatives, which are known as hole-transporting systems.⁵ However, they still have disadvantages of insufficient intermolecular π – π overlap⁶ and inefficient electron injection.⁴ These disadvantages were expected to be overcome by using electron-accepting heterocycles as core π -electron systems and a trifluoromethylphenyl group as an end substituent. Actually, we have recently succeeded in fabricating an n-type OFET with a high electron mobility of 0.30 cm²/Vs based on a thiazolothiazole derivative with trifluoromethylphenyl groups.⁷ In this context, we have now turned our attention to thiazole oligomers⁸ and designed regioselectively linked thiazole oligomers **1**–**3** and thiazole/thiophene co-oligomers **4** and **5** with 4-trifluoromethylphenyl groups for high performance n-type organic semiconductors. We report herein their synthesis, characterization, and structures along with those of thiophene oligomer **6**. OFETs based on them have been constructed, and their very high electron mobilities are presented here.

5,5'-Bithiazole **1** was prepared by the homo-cross-coupling reaction of 5-bromo-2-(4-trifluoromethylphenyl)thiazole with Fe(C₅H₇O₂)₃ in THF in 30% yield. 2,2'-Bithiazole **2** was obtained by the Suzuki coupling reaction of 5-bromo-2-(5-bromothiazol-2-yl)thiazole and 4-trifluoromethylphenylboronic acid with Pd(PPh₃)₄ in refluxing toluene in 14% yield. Other derivatives **3**–**6** were prepared using the Stille coupling reactions of the corresponding dibromo precursors and stannyl reagents with Pd(PPh₃)₄ in refluxing toluene in 6–18% yields. All of compounds **1**–**6** were purified by sublimation, and the structures were determined by the spectral data along with elemental analysis.

The reduction potentials of **1**–**6** measured by differential pulse voltammetry are as follows: bis(4-trifluoromethylphenyl)bithiophene⁷

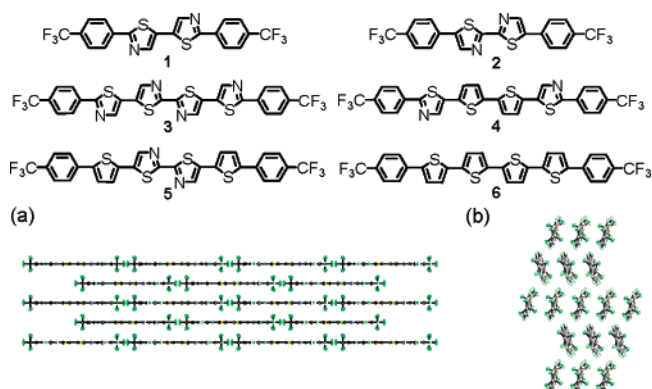


Figure 1. X-ray structure of **1** and **2**. (a) Stacking structure of **1** along the *c*-axis. (b) Stacking structure of **2**.

(–1.81 V), **1** (–1.63 V), **2** (–1.46 V), **3** (–1.35 V), **4** (–1.62 V), **5** (–1.44 V). The reduction peak of **6** was not observed. As expected, the electron affinity increases with an increase in the number of thiazole rings. This is ascribed to the electron-withdrawing property of the thiazole ring. The electron affinity of 2,2'-bithiazole **2** is higher than that of 5,5'-bithiazole **1**. The reduction potential of **5** with 2,2'-bithiazole is also more positively shifted than that of **4**. This can be explained by the fact that the LUMO of **2** has large coefficients on the electron-negative nitrogen atoms, whereas the LUMO of **1** has almost no coefficient on the nitrogens (see Supporting Information). The HOMO–LUMO gaps obtained from the absorption onsets are 2.77 eV for bis(4-trifluoromethylphenyl)bithiophene, 2.90 eV for **1**, 2.83 eV for **2**, 2.57 eV for **3**, 2.44 eV for **4**, 2.42 eV for **5**, and 2.45 eV for **6**.

The single crystals of **1** and **2** were obtained by slow sublimation. To investigate the molecular structures and intermolecular interactions in the solid state, their X-ray structure analyses were carried out. Their crystal structures are shown in Figure 1. Both of the molecules have a torsion angle of 0° between the thiazole rings. Interestingly, the molecule of **1** has a completely planar geometry, as shown in Figure 1a, where the torsion angle between the thiazole and 4-trifluoromethylphenyl rings is also 0°. Moreover, the molecule forms a unique two-dimensional columnar structure, where one molecule bridges two others with an intermolecular short separation of 3.37 Å between the stacked molecules. The molecule **2** also affords a columnar structure, as shown in Figure 1b. However, two kinds of crystallographically independent molecules exist in the unit cell, and they have torsion angles of 1.6 and 10.4° between the thiazole and 4-trifluoromethylphenyl rings owing to the steric interactions between the hydrogen atoms. This result suggests that the 2-(4-trifluoromethylphenyl)thiazole unit is more effective for

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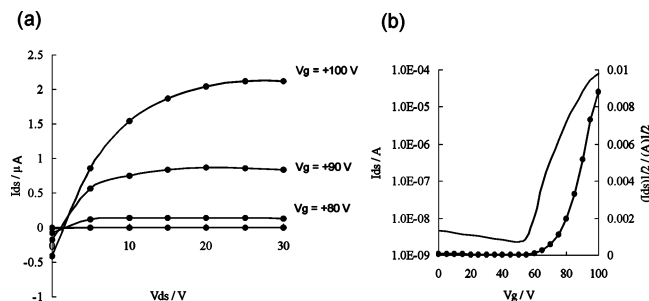


Figure 2. (a) Drain current (I_d) versus drain voltage (V_d) characteristics as a function of gate voltage (V_g) for **1** OFET on OTS-modified SiO_2 . (b) I_d and $I_d^{1/2}$ versus V_g plots for the same devices. The field-effect mobility calculated in the saturation regime is $1.83 \text{ cm}^2/\text{Vs}$.

Table 1. Field-Effect Transistor Characteristics Deposited with Various Conditions

compound	surface	T ($^{\circ}\text{C}$)	mobility (cm^2/Vs)	on/off ratio	threshold (V)
1	SiO_2	25	0.21	5×10^5	67
	SiO_2	50	0.045	2×10^4	55
	HMDS	25	0.52	5×10^5	59
	OTS	25	1.83	1×10^4	78
2	SiO_2	25	not observed		
3	SiO_2	25	0.0028	2×10^4	63
4	SiO_2	25	0.085	1×10^4	63
5	SiO_2	25	0.018	1×10^4	61
6	SiO_2	25	0.025	8×10^3	76

forming a closely packed columnar structure favorable for efficient intermolecular π - π interactions.

Top contact OFETs were fabricated by vapor-deposition onto SiO_2 (200 nm), followed by Au deposition through shadow masks with W/L of 1.0 mm/100 or 50 μm . Although **2** did not show FET characteristics, **1** and **3–6** exhibited good n-type performances, which were not observed in air. The FET characteristics are summarized in Table 1. The electron mobility of **1** was found to be $0.21 \text{ cm}^2/\text{Vs}$ and was 3 times as high as that of the trifluoromethylphenylbithiophene derivative under the same conditions.⁷ This is attributed to the π -stacking structure leading to stronger intermolecular interactions.⁹ The two-dimensional structure of **1**, as shown in Figure 1, may play an important role in the high mobility. The thiazole derivative **4** also showed good n-type performance. The mobility of $0.085 \text{ cm}^2/\text{Vs}$ is about 3 times as high as that of the quaterthiophene derivative **6**, indicating that the 2-(4-trifluoromethylphenyl)thiazole unit is more effective for electron transport than the 2-(4-trifluoromethylphenyl)thiophene unit. All the threshold voltages of these oligomers were relatively high, probably due to their low electron affinities. However, the threshold voltages of thiazole derivatives **1** and **3–5** were ca. 10 V lower than those of the corresponding thiophene derivatives. This is attributed to the electron-withdrawing property of the thiazole ring as revealed by the DPV measurements. On the other hand, **2** did not show FET behavior, and the mobilities of 2,2'-bithiazole derivatives **3** and **5** were lower than those of the corresponding bithiophene derivatives **4** and **6**, indicating that the 2,2'-bithiazole unit is not suitable for affording high performance FETs. Furthermore, to improve the FET performance of **1**, the devices were fabricated by increasing the substrate temperature or treating SiO_2 substrate with hexamethyldisilazane (HMDS) or octadecyltrichlorosilane (OTS). Although the mobility decreased with an increase of temperature, the treatment of the substrate brought about drastic enhancement of the electron mobility. Figure 2 shows the drain current (I_d) versus drain voltage (V_d) characteristics for the FET

device of **1** fabricated on the OTS-treated substrate. The highest mobility of $1.83 \text{ cm}^2/\text{Vs}$ is 3 times as high as the highest value reported so far.³

The four kinds of films of **1** deposited under various conditions were investigated by X-ray diffraction in reflection mode (XRD) and AFM study. Sharp reflections up to the second order were observed in all films, indicating formation of lamellar ordering and crystallinity on the substrate. The d -spacing obtained from the first reflection peak (200) is ca. 9.68 Å. Since the molecular length of **1** obtained from the single-crystal X-ray analysis is 19.1 Å, the molecule of **1** is considered to be perpendicular to the substrate. On the other hand, the AFM study reveals that the growth of grains depends significantly on the substrate temperature and surface conditions. Although the grain size deposited on SiO_2 at 25 and 50 $^{\circ}\text{C}$ was almost similar and small, the larger boundary gap between the grains was observed in the film deposited at 50 $^{\circ}\text{C}$. The lower mobility observed at 50 $^{\circ}\text{C}$ can be attributed to the large boundary distance, which is unfavorable for the hopping of carriers at the grain boundaries. In contrast, the grain size deposited on HMDS or OTS-treated substrates dramatically increased in the order HMDS > OTS, where smooth layer-by-layer structures were also observed. Therefore, the highest electron mobility of $1.83 \text{ cm}^2/\text{Vs}$ observed at the OTS-treated film could be attributed to the film formation with a smooth surface and large size of grains.

In summary, we have developed new thiazole oligomers and thiazole/thiophene co-oligomers with trifluoromethylphenyl groups having strong intermolecular interactions and electron-accepting properties. Some FET devices based on them showed excellent n-type performances with high electron mobilities. A 5,5'-bithiazole with trifluoromethylphenyl groups has a two-dimensional columnar structure leading to a high performance n-type FET. The electron mobility was enhanced to $1.83 \text{ cm}^2/\text{Vs}$ on the OTS-treated substrate.

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Supporting Information Available: Experimental details, absorption and emission spectra, XRD, AFM, I_d versus V_d characteristics for compounds **1–6**, and X-ray crystallographic data for **1** and **2** in CIF format and LUMO of **1** and **2** calculated by the PM5 method. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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