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High Performance n-Type Organic Field-Effect Transistors Based on π-Electronic Systems with Trifluoromethylphenyl Groups

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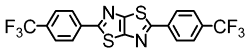
Organic field-effect transistors (OFETs)[1] based on organic semiconductors have attracted much attention for applications, such as flexible displays, low-cost electronic papers, and smart memory/sensor elements. There are many hole-transporting (p-type) semiconductors, such as pentacene[2] and oligothiophenes.[3] However, the numbers of n-type semiconductors are still limited, and the FET performances are not satisfactory.[4] The development of superior n-type semiconductors is crucial for the fabrication of organic p−n junctions, bipolar transistors, and complementary integrated circuits.[4c,5] Perfluoroalkyl groups have been reported to induce the n-type semiconducting behavior in the thiophene oligomers.[6] To develop n-type semiconductors, we have used a trifluoromethylphenyl group since it can be easily introduced in π-electronic systems. On the other hand, planar molecules are considered to be favorable for large transfer integral between molecules and less reorganization energy upon ionization, which are required for high performances of OFETs.[2b] Therefore, we have now designed planar molecules with trifluoromethylphenyl groups **1**−**3** to achieve high n-type performances. The thiazolothiazole unit was used in a p-type semiconductor (**TTFZTT**), where a planar geometry with efficient intermolecular interactions was observed.[7] The use of the heterocycle was also expected to enhance the electron affinity owing to its electron-withdrawing property. We report herein the synthesis, characterization, and structures of **1**−**3**. The OFETs based on them have been constructed, and their performances as n-type semiconductors are presented here.

Thiazolothiazole derivatives **1** and **2** were easily prepared in 54 and 18% yields, respectively, by one-step reaction of the corresponding aldehydes with dithiooxamide. Bithiophene derivative **3** was obtained by the Suzuki coupling reaction of 2,6-dibromobithiophene and 4-trifluoromethylphenylboronic acid with $Pd(PPh_3)_4$ in refluxing toluene in 58% yield. They were purified by sublimation, and the structures were determined by the spectral data along with elemental analysis and X-ray crystallography. Differential scanning calorimetry (DSC) measurements of **1** showed distinct crystal-to-liquid crystal (LC) transition at 214 °C and LC-to-isotropic transition at 267 °C. On the other hand, DSC of **2** and **3** exhibited a sharp melting endotherm peak at 298 and 261 °C, respectively.

The HOMO−LUMO energy gaps obtained from the end absorptions are 2.37 eV for **TTFZTT**, 2.48 eV for **2**, 2.77 eV for **3**, and 3.06 eV for **1**. The lower energy gaps observed in **TTFZTT** and **2** can be attributed to the intramolecular charge transfer from the thiophenes to the thiazolothiazole unit.



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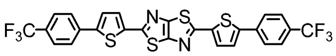

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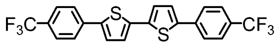

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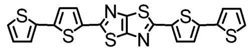

TTFZTT

Interestingly, **1**−**3** exhibited strong photoluminescence in the solid state (λ_{max} **1**, 481 nm; **2**, 554 nm; **3**, 546 nm). The emission maxima are observed at longer wavelengths than those in solution (67−87 nm red-shift), indicating the presence of strong intermolecular interactions in the solid state.

The electrochemical measurements of **1**−**3** were performed in dichloromethane.[8] The differential pulse voltammogram (DPV) of **2** exhibited two oxidation peaks (+1.28 V, +1.55 V vs SCE) and two reduction peaks (−1.48 V, −1.68 V vs SCE). Both the oxidation and reduction potentials of **2** are a little higher than those of **TTFZTT** ($E_{ox} = +1.07$ V, $E_{red} = -1.54$ V, −1.84 V vs SCE). This can be attributed to the electron-withdrawing effect of the trifluoromethylphenyl group. Reduction peaks of **3** (−1.81 V, −1.93 V vs SCE) are negatively shifted compared to that of **2** owing to the absence of the thiazolothiazole unit. The HOMO−LUMO energy gaps obtained from the redox peaks are 2.61 eV for **TTFZTT**, 2.71 eV for **2**, 3.04 eV for **3**, and 3.39 eV for **1**, whose order is consistent with the result from the end absorptions.

The single crystals of **1**−**3** 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. All of the molecules have a nearly planar geometry. Two thiophene rings of **2** and **3** take an all-trans conformation. Their crystal structures are shown in Figure 1. It should be noted here that the thiazolothiazole derivatives **1** and **2** have stacking structures, whereas the bithiophene derivative **3** has herringbone packing. Thus, the thiazolothiazole derivative **1** has a stacking structure with two kinds of columns, which grow in nearly orthogonal directions. The compound **2** also forms a columnar structure with separation of 3.53 Å between the stacked molecules. An intermolecular short S···S contact of 3.25 Å is observed between the S1 and S2 atoms of the thiazolothiazole ring. The columns of **2** are uniformly arranged to afford a sheetlike structure along with the *c*-axis with a distance of 22.1 Å. In contrast, as shown in Figure 1b, the bithiophene derivative **3** has herringbone packing with a tilt angle of ca. 66°, like usual oligothiophenes.[9] This result indicates that the introduction of the thiazolothiazole unit is effective to form stacking structures leading to efficient intermolecular π−π interactions.

The FET devices were fabricated with top contact configuration. Gold electrodes were defined after semiconductor deposition (50

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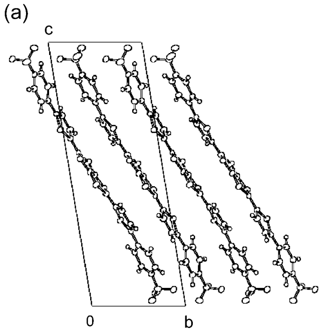

Figure 1. X-ray structure of **2** and **3**. (a) Stacking structure of **2** along with the *a*-axis. (b) Herringbone packing of **3**.

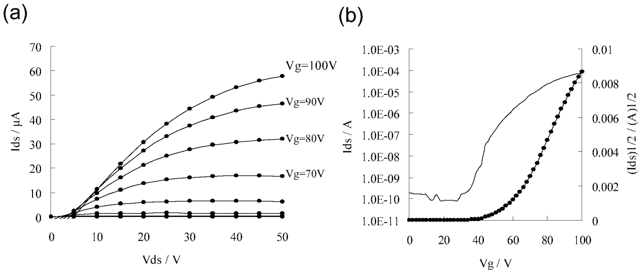

Figure 2. (a) Drain current (I_d) versus drain voltage (V_d) characteristics as a function of gate voltage (V_g) for OFET of **2** ($T_{sub} = 50$ °C). (b) I_d and $I_d^{1/2}$ versus V_g plots at $V_d = 50$ V for the same device. The field-effect mobility calculated in the saturation regime is 0.30 cm^2/Vs.

Table 1. Field-Effect Characteristics of Films **1**−**3** Deposited at Various Temperatures

compound	T_{sub} (°C)	mobility (cm^2/Vs)	on/off ratio	threshold (V)
1	25	not observed		
2	25	0.12	4×10^5	+55
	50	0.30	1×10^6	+60
	100	0.26	1×10^6	+57
3	25	0.07	1×10^5	+78
	50	0.18	3×10^5	+76

nm) by using shadow masks with W/L of 1.0 mm/100, 75, or 50 μm. The SiO_2 gate dielectric was 200 nm thick. The FET measurements were carried out at room temperature in a vacuum chamber (10^{-5} Pa) without exposure to air using a semiconductor parameter analyzer. Although **1** did not show FET characteristics, **2** and **3** exhibited high n-type performances. Figure 2 shows the drain current (I_d) versus drain voltage (V_d) characteristics for a FET device using **2** deposited at 50 °C. The electron mobilities of the film **2** calculated in the saturation regime were found to be 0.12−0.30 cm^2/Vs depending on the substrate temperature, as shown in Table 1. The mobilities are in a class with the highest values reported so far.[4] The on/off ratios were high values of 10^5−10^6. The thiophene derivative **3** also showed high n-type FET performances. The mobility of 0.18 cm^2/Vs at 50 °C is much higher than that of a perfluorooctylphenylbithiophene derivative recently reported,[6b] indicating the very effective nature of the trifluoromethylphenyl group. The fact that **2** showed the highest mobility may be related to the π-stacking structure leading to stronger intermolecular interactions.[10] The threshold voltage of **2** is ca. 20 V lower than that of **3**. This is attributed to the higher electron affinity of **2** as revealed by the DPV measurements. These findings indicate advantages of the thiazolothiazole unit to obtain high performance n-type OFETs.

The films of **1**−**3** deposited on SiO_2/Si substrates were investigated by X-ray diffraction in reflection mode. Sharp reflections up to the second or third order are observed, indicating formation of lamellar ordering and crystallinity on the substrate. The *d*-spacing of **2** obtained from the first reflection peak ($2\theta = 4.21$) is 2.39 nm. Since the molecular length of **2** obtained from the single-crystal X-ray analysis is 2.41 nm, the molecule of **2** is considered to be almost perpendicular on the substrate. This is an ideal molecular arrangement for charge transport. On the other hand, the *d*-spacing of **3** obtained from the first reflection peak ($2\theta = 4.21$) is 1.85 nm, and the molecular length is 1.93 nm, indicating that the molecule of **3** has ca. 16° declining orientation on the substrate. In contrast, the film of **1** showed almost no reflection peak, suggesting disorder orientation on the Si/SiO_2 substrate, which may be a reason for the no FET performance.

In summary, we have developed new π-electronic systems with trifluoromethylphenyl groups which were easily introduced using the Suzuki coupling reaction. Some FET devices based on them showed excellent n-type performances with high electron mobilities. The trifluoromethylphenyl group was found to be very effective in inducing n-type behavior. The thiazolothiazole unit was favorable for forming stacking structures leading to efficient intermolecular π−π interactions.

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Supporting Information Available: Experimental details, absorption and emission spectra, DPVs, I_d versus V_g characteristics for compounds **2** and **3**, and X-ray crystallographic data for **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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