Characterization and Field-Effect Transistor Performance of Heterocyclic Oligomers Containing a Thiazolothiazole Unit

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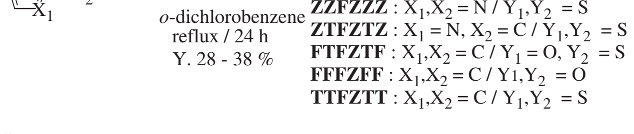
Novel mixed five-membered heterocyclic (furan, thiophene, and thiazole) oligomers containing a thiazolothiazole ring system have been investigated as active materials of organic field-effect transistors (OFETs). The field-effect moblities of 10^{-4}–10^{-3} cm^2/Vs were obtained for the furyl derivatives and their FET performances as p-type semiconductors are presented as the first examples of FET behavior of oligomers including furan rings.

Organic semiconductors have received significant attention because of their potential applications to flexible, light, and small electronic devices.[1,2] The most prominent organic semiconductors have been obtained by modification of thiophene oligomers and the properties have been tuned by introducing substituents in the π-conjugated system.[3–6] Among such thiophene oligomers, derivatives with thiazole units have shown high on/off ratio and enhanced stability to oxygen due to the electron-accepting property of thiazoly groups. In addition, these oligomers take a π-stacked structure which leads to strong intermolecular interactions.[7–9]

Recently, we have found that OFETs fabricated on thiazolothiazole-thiophene co-oligomers (**TTFZTT**) as active layer show good p-type characteristics with high stability to oxygen[10] and the field-effect mobilities are comparable with those of the corresponding alpha-6Ts[11] and are higher than those of thiophene/thiazole co-oligomers.[7,8] This result implies that the thiazolothiazole ring is a promising candidate as a core unit for high performance semiconductors. In this context, we have carried out the modification of **TTFZTT** by replacing with other five-membered heterocycles such as furan or thiazole. We report here the physical properties and the FET performances of novel thiazolothiazole/thiazole co-oligomers (**ZTFZTZ**, **ZZFZZZ**) and thiazolothiazole/furan co-oligomers (**FTFZTF**, **FFFZFF**).



Scheme 1. Synthesis of thiazolothiazole/heterocyclic oligomers.

Four new co-oligomers with a thiazolothiazole unit were easily prepared in 28–38% yields by one-step reaction of the corresponding aldehydes with dithiooxamide,[12] and purified by gradient sublimation (Scheme 1). They have satisfactory elemental analyses and mass spectra.[13] The thermal properties of these oligomers were investigated by differential scanning calorimetry (DSC) measurements. DSC of furan-containing co-oligomers (**FFFZFF** and **FTFZTF**) showed sharp melting endotherms at 252 and 279 °C, respectively, which are lower than that of thiazolothiazole-thiophene co-oligomer (**TTFZTT**: 280 °C). On the other hand, DSC measurements of thiazole-containing co-oligomers (**ZTFZTZ** and **ZZFZZZ**) showed higher melting endotherms at 377 and 398 °C, respectively, indicating that the oligomers with thiazole rings are thermally more stable than the corresponding oligomers with thiophene and/or furan rings.

The absorption and emission spectra and the cyclic voltammetry (CV) data of co-oligomers are summarized in Table 1. The absorption and emission maximum of **FFFZFF** are observed at 434 and 484 nm, respectively, which are slightly shifted to shorter wavelengths relative to those of **TTFZTT**. On the other hand, the absorption and emission maximum of **FTFZTF** are almost the same to those of **TTFZTT**. These results indicate that the energy gap of **FTFZTF** is similar to that of **TTFZTT**, while the energy gap of **FFFZFF** is larger than that of **TTFZTT**.

The CVs of thiazolothiazole-furan co-oligomers in CH_2Cl_2 exhibited irreversible oxidation waves at $+0.91$ V (**FTFZTF**) and $+1.02$ V (**FFFZFF**) vs SCE, respectively, which are slightly shifted to lower potentials relative to that of **TTFZTT** ($+1.12$ V). This result indicates that the HOMO levels of furan derivatives (**FFFZFF** and **FTFZTF**) are higher than that of **TTFZTT**. On the other hand, the CV of thiazolothiazole-thiazole co-oligomer (**ZZFZZZ**) in CH_2Cl_2 exhibited no oxidation wave and an irreversible reduction wave at -0.92 V vs SCE, indicating that **ZZFZZZ** would behave as electron acceptor.

Both bottom and top contact configurations were used to make the FET devices. The *n*-doped silicon substrate was used as gate. For the bottom contact, gold electrodes forming channels of 25 μm lengths (*L*) and 2.94 mm widths (*W*) were photolithographically defined. The semiconducor layer was then fab-

Table 1. Thermal, optical,[a] and electrochemical[b] properties of oligomers containing a thiazolothiazole unit

Oligomers	λ_{abs}/nm	λ_{em}/nm	E_1^{ox}/V	E_1^{red}/V
ZZFZZZ	433	521	—	-0.92
ZTFZTZ	442	492	—	—
FTFZTF	447	501	$+0.91$	—
FFFZFF	434	484	$+1.02$	—
TTFZTT[c]	445	502	$+1.12$	—

[a] In $CHCl_3$. [b] *E* vs SCE in CH_2Cl_2, 0.1 mol dm^{-3} *n*-Bu_4-NBF_4, Pt electrode, scan rate 100 mVs^{-1}. [c] Ref. 10.

ricated on the entire electrode/dielectric surface. The SiO_2 gate dielectric was 600-nm thick. For the alternate top contact geometry, gold electrodes were defined after semiconductor deposition by using shadow masks with W/L of 1.0 mm/100 µm and 1.0 mm/50 µm. The SiO_2 gate dielectric was 200-nm thick. The electrical characteristics were obtained at room temperature in both air and ultra high vacuum conditions using a semiconductor parameter analyzer.

The films of **ZTFZTZ**, **FTFZTF**, and **FFFZFF** exhibited p-type semiconducting behavior. Table 2 summarizes the mobilities and on/off ratios for these films deposited at different temperatures. The replacement of thiazole with furan leads to good p-type semiconducting behavior (**FTFZTF**; 1×10^{-3} cm^2/Vs, $T_{sub} = 70\,°C$). **TTFZTT** film did not show FET characteristic over 40 V of gate voltage, while **FTFZTF** and **FFFZFF** films exhibited the characteristic at even higher gate voltages. This result indicates that furan-containing co-oligomers are more stable under electric fields. On the other hand, the FET characteristic was not observed in the films of **ZZFZZZ**. In addition, the difference in the mobilities between top-contact and bottom-contact configurations was observed. This is probably due to the difference in the grain size of the molecules caused by the two different conditions of surface.

Table 2. Field-effect characteristics of oligomers containing a thiazolothiazole unit deposited at different temperatures

Oligomers	T_{sub}/°C	Mobility [cm^2/Vs][a]	On/off ratio[a]
ZZFZZZ	20	Not FET	—
ZTFZTZ	20	Not FET/1×10^{-7}	—/10^3
FTFZTF	20	$2 \times 10^{-4}/1 \times 10^{-5}$	$10^3/10^2$
	50	7×10^{-4}/—	10^3/—
	70	1×10^{-3}/—	10^2/—
FFFZFF	20	$7 \times 10^{-4}/1 \times 10^{-7}$	$10^2/10^2$
	50	$4 \times 10^{-4}/1 \times 10^{-5}$	$10^3/10^4$
TTFZTT[b]	20	$5 \times 10^{-3}/3 \times 10^{-5}$	$10^3/10^3$
	50	2×10^{-2}/—	10^4/—

[a] top-contact / bottom-contact. [b] Ref. 10.

The films of these oligomer deposited on SiO_2/Si substrates were investigated by X-ray diffraction in reflection mode. Although **FTFZTF** films showed sharp and strong reflections, the **FFFZFF** film showed two weak reflection peaks. This result suggests that **FTFZTF** molecules have a higher degree of lamellar ordering film than **FFFZFF** molecules. Since the intermolecular interactions strongly affect the carrier mobilities of the organic semiconductors,[14] the difference in the mobility between **FTFZTF** and **FFFZFF** can be attributed to the difference in the molecular orientation. Moreover, the **ZTFZTZ** film showed almost no reflection peak, suggesting a disorder orientation on the Si/SiO_2 substrate which indicates a poor π–π intermolecular intraction. This result indicates that the field-effect mobility is strongly influenced by the orientation of the molecules. Compared to **TTFZTT**, **FTFZTF** with a smaller size of furan is expected to have stronger intermolecular interactions. On the other hand, less polarizable furan is expected to increase Columbic repulsion and decrease electronic interactions between the molecules. Therefore, a little decreased mobility of **FTFZTF** compared with **TTFZTT** may be related to be the electronic contribution. Although the electron accepting **ZZFZZZ** was expected to show n-type semiconducting behavior, no FET property was observed. This may be attributed to the improper molecular geometry in the thin film.

In summary, the OFETs using novel thiazolothiazole/five-menbered heterocyclic co-oligomers as active layers have been successfully fabricated and their OFETs showed p-channel characteristics. The FET performance was found to be dependent on five-menbered heterocycles, which affect the molecular orientation on the substrate. **FTFZTF** and **FFFZFF** showed FET performances as p-type semiconductors, which are the first examples of FET behavior of oligomers including furan rings.

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13 All oligomers were characterized by elemental analysis and mass spectrometry. **ZZFZZZ**: mp 383–384 °C. Anal. (Calcd) for $C_{16}H_6N_6S_6$: C 40.73 (40.49), H 1.37 (1.27), N 17.68 (17.71), S 38.75 (40.53). MS/EI (70 eV): 474 [M^+]. **ZTFZZT**: mp 377–378 °C. Anal. (Calcd) for $C_{18}H_8N_4S_6$: C 45.89 (45.74), H 1.63 (1.71), N 11.86 (11.85), S 40.41 (40.70). MS/EI (70 eV): 472 [M^+]. **FTFZTF**: mp 277–279 °C. Anal. (Calcd) for $C_{20}H_{10}N_2O_2S_4$: C 55.05 (54.77), H 2.52 (2.30), N 6.54 (6.39), S 29.08 (29.25). MS/EI (70 eV): 438 [M^+]. **FFFZFF**: mp 251–252 °C. Anal. (Calcd) for $C_{20}H_{10}N_2$ O_4S_2: C 55.05 (59.10), H 2.52 (2.48), N 6.54 (6.89), S 29.08 (15.78). MS/EI (70 eV): 406 [M^+].

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