High-performance n-Type Organic Field-effect Transistors Based on Co-oligomers Containing a Trifluoromethylphenylthiazolyl Group and a Biphenylene Core

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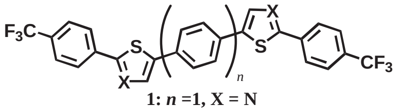
New co-oligomers containing trifluoromethylphenylthiazolyl and phenylene units were prepared. The derivative with thiazolyl and biphenyl units showed high-performance n-type FET behavior.

Organic semiconductors have attracted much attention for electronic and optical applications such as organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs) since they have advantages of low-cost, lightness, mechanical flexibility, and disposability.[1,2] Various p-type OFETs have been reported, which are based on acenes such as pentacene or oligomers such as oligothiophenes. Some of these materials show high hole mobility comparable to amorphous Si (≈1.0 $cm^2 V^{-1} s^{-1}$).[3–6] In contrast, the number of n-type OFETs is still limited and the performance is not satisfactory.[7–11]

We have reported that a 4-trifluoromethylphenyl group effectively induces n-type FET behavior.[12,13] Particularly, a bithiazole derivative with trifluoromethylphenyl groups, 2,2′-(4-trifluoromethylphenyl)-5,5′-bithiazole (Scheme 1), showed the highest electron mobility of $1.83 cm^2 V^{-1} s^{-1}$,[14] suggesting that the trifluoromethylphenylthiazolyl group is favorable for affording high-performance n-type semiconductors. On the other hand, most of n-type OFETs are generally unstable in air and the devices based on the trifluoromethylphenyl derivatives were also very air-sensitive.[12–14] To enhance the stability, introduction of phenylene units seemed favorable because they have wide HOMO–LUMO energy gap. In this context, we have now designed co-oligomers **1** and **2** containing trifluoromethylphenylthiazolyl and phenylene units and have investigated their FET behavior.

The syntheses of **1** and **2** were accomplished by using the Stille coupling reaction of 1,4-diiodobenzene or 4,4′-diiodobiphenyl with the corresponding stannyl reagent in the presence of $Pd(PPh_3)_4$ in DMF in 42 and 32% yields, respectively. For comparisons, co-oligomer **3** with thiophene units was synthesized by using the Suzuki–Miyaura coupling reaction of 4,4′-diiodobiphenyl with the corresponding boronic acid in the presence of $Pd(PPh_3)_4$ in a mixture of toluene and water (10:1) in 55% yield.[15] All of compounds **1**–**3** were purified by sublimation, and their structures were determined by the spectral data along with elemental analysis.



1: *n* =1, X = N
2: *n* =2, X = N
3: *n* =2, X = CH

Scheme 1.

The reduction potentials measured by differential pulse voltammetry and optical properties of **1**–**3** are shown in Table 1. The properties of **1** and **2** are similar to each other, indicating that the number of the phenylene unit affords no significant effect on their HOMO and LUMO energies. In contrast, the physical properties of **3** are greatly different from those of **1** and **2**. Thus, the absorption and emission maxima of **3** are red-shifted and the reduction potential was negatively shifted compared to those of **1** and **2**. This fact indicates that the thiazolyl derivatives **1** and **2** have lower LUMO energy levels and larger HOMO–LUMO energy gaps than **3**. This can be attributed to the stronger electron-accepting property of the thiazolyl unit than that of thienyl one. Additionally, the thiazolyl group has no hydrogen atom on the nitrogen atoms, which is favorable for planar geometry owing to the decrease in the steric repulsion between the thiazolyl and trifluoromethylphenyl rings.

The FET devices based on **1**–**3** were fabricated on SiO_2/Si substrates by a vapor-deposition method with bottom contact geometry.[15] The FET characteristics are summarized in Table 2. All of the devices showed n-type FET behavior. The electron mobility and on/off ratio of **2** were the highest among them. It should be noted here that the electron mobility greatly increases by the replacement of the phenylene core in **1** by the biphenylene core in **2**. Since the LUMO energy is not changed by the replacement, this enhancement can be attributed to the stronger intermolecular interactions in **2**. On the other hand, the comparison of **2** and **3** indicates that the thiazolyl group is favorable for decreasing the threshold voltages as well as increasing the electron mobilities. This is considered to be due to the higher electron affinity of **2** leading to the easier electron injection. In addition, the device of **2** showed fairly good air-stability. Thus, after standing in air for 8 h, the mobility of the bottom contact device was $5.7 \times 10^{-5} cm^2 V^{-1} s^{-1}$ in air and the mobility was recovered to $5.2 \times 10^{-3} cm^2 V^{-1} s^{-1}$ under the vacuum

Table 1. Optical properties and redox potentials of co-oligomers **1**–**3**

Compound	Solution[a]		Solid	E_{red}/V^b
	λ_{abs}/nm	λ_{em}/nm	λ_{em}/nm	
1	371	421, 433	471	−1.49, −1.73
2	367	422, 442	463, 492	−1.57, −1.80
3	401	463, 490	504, 521	−1.85

[a] In CH_2Cl_2. [b] 0.1 M nBu_4NPF_6 in DMF, Pt electrode, scan rate 100 mV/s, V vs. Fc/Fc^+.

Table 2. Field-effect characteristics **1**–**3** on bottom contact geometry

Compound	SiO_2 treatment	T_{sub} /°C	Mobility /$cm^2 \cdot V^{-1} s^{-1}$	on/off ratio	Threshold /V
1	bare	r.t.	2.4×10^{-3}	5.1×10^4	+28
	bare	80	2.5×10^{-3}	1.1×10^5	+25
2	bare	r.t.	0.026	5.2×10^5	+29
	bare	80	0.080	6.9×10^4	+14
	bare	120	0.027	1.2×10^6	+24
	HMDS	80	0.092	7.8×10^5	+24
3	bare	r.t.	6.7×10^{-5}	1.9×10^4	+45
	bare	80	5.2×10^{-3}	5.8×10^6	+37
	HMDS	r.t.	1.0×10^{-3}	1.4×10^5	+52
	HMDS	80	0.029	4.0×10^5	+58

condition (Supporting Information).[15] This stability is noteworthy because the previous trifluoromethylphenyl derivatives did not exhibit the n-type FET behavior in air.[12–14]

To improve the FET performances the top-contact devices using **2** were fabricated. Gold electrodes were defined after 50 nm of semiconductor deposition at 80 °C by using shadow masks with W/L of 1.0 mm/100 µm. The SiO_2 gate dielectric was 200-nm thick and treated with HMDS or octadecyltrichlorosilane (OTS). The FET measurements were carried out at room temperature in a high vacuum chamber (10^{-5} Pa). The electron mobility was improved as expected (HMDS: 0.29 $cm^2 V^{-1} s^{-1}$, OTS: 0.40 $cm^2 V^{-1} s^{-1}$) (Table 3). The mobilities are in a class with the highest values reported so far.[3,8] The transfer and output characteristics of **2** on the OTS treated SiO_2 with the top contact geometry are depicted in Figure 1. With the higher substrate temperatures or treatment with HMDS, the peaks became sharper, indicating that the crystallinity in the film increases in such conditions. The d-spacing of **2** obtained from the first reflection peak is 2.60 nm ($2\theta = 3.44°$). Since the molecular length is 2.75 nm, the molecules are considered to be arranged nearly perpendicularly to the substrate. The film of **2** was also investigated by scanning electron microscope (SEM) (Figure 2). Interestingly, large grains with a fiber structure (≈1-µm size) were observed on both the substrate and the Au electrode. This finding suggests that electrons flow in the crystal fibers, and transport by hopping between them. This might be a reason for the high electron mobility in **2**. Forming such crystal fibers seems favorable for affording high-performance FETs.

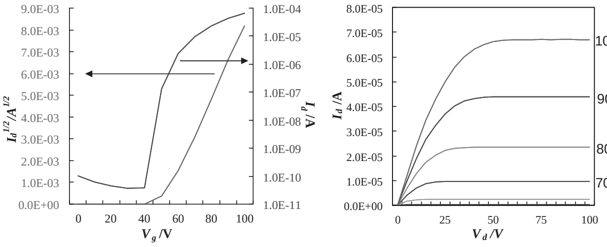
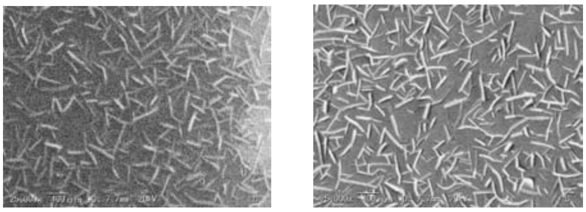


Figure 1. Transfer and output characteristics of **2** on top contact geometry.

Table 3. Field-effect characteristics of **2** on top contact geometry

Compound	SiO_2 treatment	T_{sub} /°C	Mobility /$cm^2 \cdot V^{-1} s^{-1}$	on/off ratio	Threshold /V
2	HMDS	80	0.29	1.7×10^5	+30
	OTS	80	0.40	1.2×10^5	+62



(a) (b)

Figure 2. SEM images of device **2**. (a) On the SiO_2 substrate. (b) On the Au electrode.

In summary, we have developed new co-oligomers containing trifluoromethylphenyl and phenylene units. The oligomer with the thiazolyl and biphenyl core showed the highest n-type FET performance. The introduction of the biphenylene unit was effective to increase the electron mobility as well as to enhance the air stability. The trifluoromethylthiazolyl group was favorable for inducing n-type FET behavior. Additionally, we could observe the formation of crystal fiber structure which would be suitable for carrier transportation.

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15 Details on preparation of **1**–**3**, fabrication of OFET devices, air stability of the device of **2** and X-ray diffractograms of thin films of **2** are available in Supporting Information which is available electrically on the CSJ-Journal website, http://www.csj.jp/journals/chem-lett/.