New n-Type Field-effect Transistors Based on Pyrimidine-containing Compounds with (Trifluoromethyl)phenyl Groups

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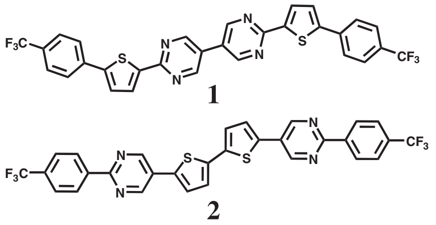
New co-oligomers containing pyrimidine units were prepared. The planar molecular and π-stacking structures were revealed by X-ray structure analysis. The FET devices based on them showed good n-type performance.

Organic thin-film transistors (OTFTs) based on π-conjugated molecules are of great interest for applications to plastic electronics such as organic light-emitting diodes (OLEDs), displays, e-paper and radio-frequency identified tags (RFID tags). They have advantages of low cost, lightness, flexibility, and disposability.[1,2] Many p- and n-type organic OFETs have been reported, and some of these materials show high hole or electron mobility comparable to amorphous Si.[3–9] However, the number of n-type OFETs is still limited and the performance is not satisfactory yet. To achieve high electron mobility, lower LUMO levels are necessary. For this purpose, electron-withdrawing groups have been introduced into well-known p-type semiconductor cores such as acenes or oligo-thiophenes.[10,11] We have also used electron-accepting nitrogen-heterocycles such as thiazole and pyrazine to lower the LUMO levels.[12,13]

We have now designed new oligomers **1** and **2** containing pyrimidine rings (Scheme 1). The heterocycle is a stronger electron-acceptor than thiazole. The pyrimidine ring also has an advantage of reducing steric repulsion between the neighboring rings. Planar geometry of the molecule is important for strong intermolecular interactions leading to high mobility. On the other hand, nitrogen heterocycles have a disadvantage in that the nitrogen atoms interact with the SiO_2 substrate leading to a molecular arrangement lying on the substrate. Some oligomers containing nitrogen heterocycles are known to lie on the SiO_2 substrate,[14] and such an arrangement is unfavorable for high mobility. The control of the molecular arrangement is crucial for high-performance FETs. We have found here that the FET performances of **1** and **2** were greatly improved by the substrate treatment.

Pyrimidine-containing co-oligomers **1** and **2** were prepared by the Stille or Suzuki–Miyaura coupling reaction in the presence of Pd catalyst in DMF or toluene in 15 and 12% yields, respectively. These compounds were purified by sublimation. Their structures were determined by the spectral data along with elemental analysis.[15]



Scheme 1.

A single crystal of **2** suitable for X-ray structure analysis was obtained by sublimation. The molecule **2** was found to be almost planar, where the dihedral angles between the phenylene and pyrimidine rings and between the pyrimidine and thienylene rings are 0.6 and 1.5°, respectively. This molecule forms π-stacking as shown in Figure 1.[16]

The optical properties and reduction potentials are shown in Table 1. The reduction potentials of **1** and **2** were measured by differential pulse voltammetry. These values were similar to each other, indicating that the position of the pyrimidine units is not related to the reduction potentials. The absorption maximum of **2** in solution is red-shifted by 23 nm compared to that of **1**, indicating that the intramolecular charge transfer from the electron-donating bithiophene unit to the electron-accepting pyrimidine takes place more effectively in **2** than in **1**. Although the absorption and emissions maxima of **1** and **2** are blue-shifted in films compared to those in solution, the end absorptions of them are red-shifted. This fact suggests the presence of the intermolecular interactions in the solid state (Figure S1).[15]

FET devices based on **1** and **2** were fabricated by a vapor-deposition method with bottom contact geometry on SiO_2/Si substrates which are bare or treated with HMDS. Cr (10 nm)/Au (20 nm) electrodes forming channels of 25-μm length (L) and 294-mm width (W) were photolithographycally defined. The semiconductor layer was evaporated on the electrode/dielectric surface, where the SiO_2 layer was 300-nm thick. The FET performances are summarized in Table 2. In the case of bare substrates, the electron mobilities of both **1** and **2** decreased drastically at the substrate temperature of 80 °C. The on/off ratio also decreased at the high temperature. On the other hand, in the

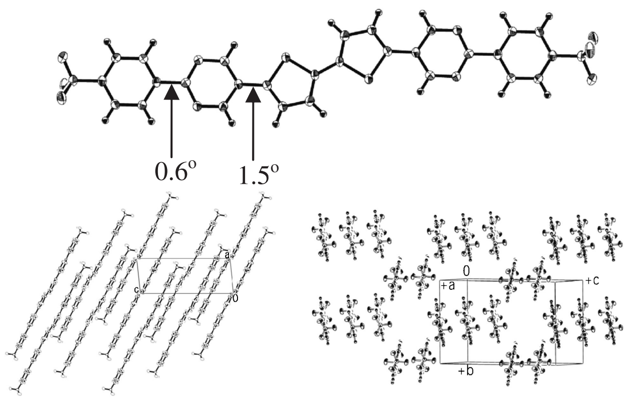


Figure 1. ORTEP and packing structure of **2**.

Table 1. Optical properties and reduction potentials of **1** and **2**

Compound	λ_{abs}/nm		λ_{em}/nm		E_{red}/V[b]
	Solution[a]	Film	Solution[a]	Solid	
1	379	352	429, 450	530	−1.47
2	402	373, 453	463, 487	516	−1.44

[a]In CH_2Cl_2. [b]0.1 M n-Bu_4NPF_6 in DMF, Pt electrode, scan rate 100 mV/s, V vs. SCE.

Table 2. Bottom-contact FET characteristics of **1** and **2**[a]

Compound	Condition	T_{sub} /°C	Mobility /$cm^2 V^{-1} s^{-1}$	On/off ratio	Threshold /V
1	bare	rt	5.7×10^{-5}	1×10^5	+44
	bare	50	5.8×10^{-6}	2×10^3	+41
	bare	80	2.0×10^{-8}	2×10^1	+28
	HMDS	rt	1.5×10^{-3}	1×10^5	+56
	HMDS	50	1.2×10^{-2}	2×10^5	+60
	HMDS	80	1.9×10^{-2}	1×10^5	+63
2	bare	rt	2.9×10^{-4}	5×10^4	+67
	bare	50	8.0×10^{-4}	6×10^4	+50
	bare	80	1.8×10^{-7}	7×10^1	+38
	HMDS	rt	1.6×10^{-3}	2×10^6	+44
	HMDS	50	1.0×10^{-3}	3×10^5	+37
	HMDS	80	8.0×10^{-3}	4×10^4	+57

[a]Electrode: Cr/Au = 10/20 nm, SiO_2/Si substrate, SiO_2: 300 nm, $L/W = 25/294000$ µm.

Table 3. Top-contact FET characteristics of **1** and **2**[a]

Compound	Condition	T_{sub} /°C	Mobility /$cm^2 V^{-1} s^{-1}$	On/off ratio	Threshold /V
1	HMDS	80	0.011	3×10^4	+56
2	HMDS	80	0.011	7×10^4	+35

[a]Au electrode: 50 nm, SiO_2/Si substrate, SiO_2: 200 nm, $L/W = 50/1000$ µm.

case of HMDS treatment substrates, the devices fabricated under the same conditions with those for the bare substrates showed good n-type FET behavior. The mobilities were better at 80 °C than those at room temperature in contrast to the case of the bare substrate. This result suggests that the morphology in the films of **1** and **2** is greatly affected by HMDS treatment.

Top-contact devices using **1** and **2** were fabricated to investigate the effect of contact between the source and drain electrodes and semiconductor layer. The FET measurements were carried out at room temperature in a high vacuum chamber (10^{-5} Pa). The electron mobilities were 0.011 $cm^2 V^{-1} s^{-1}$ for both **1** and **2** as shown in Table 3. Their output and transfer characteristics with top contact geometry are shown in Figure S2.[15] The small difference in the FET characteristics between the top and bottom devices suggests a good contact between the gold electrodes and the semiconductors **1** and **2**.

The films of **1** and **2** deposited on SiO_2/Si substrates were investigated by X-ray diffraction in reflection mode (XRD) (Figures S3 and S4).[15] Although a weak reflection peak was observed in the film of **1** ($2\theta = 4.94°$, d-spacing = 17.87 Å), no reflection peak was observed in the film of **2**. Disorder orientation of molecules in the crystal may be a reason why a weak or no reflection peak was observed in the XRD measurement.[15]

The films of **1** and **2** deposited on the bare or HMDS treatment SiO_2 substrate at 80 °C were investigated by atomic force microscope (AFM). Many small grains were observed in the films on the bare substrate as shown in Figure S5,[15] where the direction of crystal growth was not in order. On the other hand, the films deposited on the HMDS treated SiO_2 substrate showed larger grains (0.5–1.0 µm). Although the drastic effect of HMDS treatment seems related to the interaction of the semiconductors with the bare substrate, the detail is still puzzling.

In summary, we have developed two new co-oligomers containing pyrimidine units. Although these films have low crystallinity, the devices showed good n-type FET behavior. The HMDS treatment on the SiO_2 substrate was very effective to improve the FET performances.

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15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

16 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-708223.