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Organic field-effect transistors based on heterocyclic co-oligomers containing a pyrazine ring†

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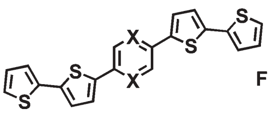
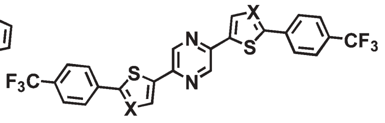
Received (in Cambridge, UK) 1st December 2006, Accepted 11th January 2007
First published as an Advance Article on the web 30th January 2007
DOI: 10.1039/b617573b

New oligomers containing a pyrazine unit have been prepared: the bithienyl derivatives afforded p-type FET devices whereas the trifluoromethylphenyl derivatives showed n-type FET behavior.

Much attention has recently been focused on organic field-effect transistors (OFETs) because of their possible applications to low-cost integrated circuits and flexible displays.[1–10] Development of new organic semiconductors is very important for the progress in this field. Pentacene and thiophene oligomers are typical semiconductors affording p-type FETs. However, they are air-sensitive and more stable materials have been strongly required. In order to enhance the air-stability, phenylene-thiophene co-oligomers have been designed.[11,12] However, those systems have non-planar geometry owing to the steric interactions between the neighboring rings, resulting in decreased carrier mobilities. In order to overcome this disadvantage, we have now introduced a pyrazine ring instead of the phenylene ring because it has no hydrogen atoms for steric repulsion. The pyrazine ring is an electron-accepting heterocycle, which would be useful to decrease the HOMO levels and enhance the air-stability in p-type FETs. Furthermore, we have also developed here novel n-type semiconductors containing a pyrazine ring because it decreases the LUMO levels leading to high electron affinity which is required for n-type semiconducting behavior.[3,13,14]



1: X = CH
2: X = N



3: X = CH
4: X = N

Pyrazine-containing co-oligomers **2–4** were prepared by the Stille coupling reaction of 2-bromo-5-iodopyrazine with the corresponding stannyl reagents in the presence of $Pd(PPh_3)_4$ in DMF in 8–25% yields. For comparison, benzene derivative **1** was also prepared.[15] The optical properties and redox potentials of co-oligomers **1–4** are shown in Table 1. Oxidation and reduction potentials of **1–4** were measured by cyclic voltammetry. Replacement of the benzene ring with a pyrazine ring in **2** increases the oxidation potentials a little and a reduction peak appears. This fact indicates that the introduction of the pyrazine ring decreases both the HOMO and LUMO levels. Replacement of the end-thienyl groups with trifluoromethylphenyl groups in **3** positively shifts the reduction potential, indicating that the LUMO level is lowered. The replacement of the thiophene groups with the electron-accepting thiazole rings in **4** induces a further positive shift of the reduction potential, indicating that **4** has the lowest LUMO level among them.

The absorption and emission maxima of the pyrazine derivative **2** are red-shifted compared to those of other compounds. This fact can be attributed to the intramolecular charge transfer from the electron-donating bithienyl group to the electron-accepting pyrazine group. All of the compounds **1–4** exhibited efficient fluorescence. The emission maxima are observed at longer wavelength in the solid state than those in solution, indicating the presence of the strong intermolecular interaction in the solid state.

Single crystals of **3** suitable for X-ray analysis were obtained by recrystallization from chloroform.‡ There exist two crystallographically independent molecules (molecules 1 and 2) each of which lies about an independent inversion centre. The molecules are a little twisted (Fig. 1), where the dihedral angles between the thiophene ring and the pyrazine ring are 4.9° (molecule 1) and 14.7° (molecule 2), and those between the thiophene ring and the trifluoromethylphenyl group are 16.1° (molecule 1) and 7.8° (molecule 2). It should be noted that the molecules have a definite geometry, with the nitrogen of the pyrazine ring and the sulfur of the thiophene located at the same direction. This is attributed to an electrostatic interaction between the electron-negative N atom and the electron-positive S atom, and short contacts between the N and S atoms of 2.9 Å are observed for both molecules 1 and 2. Such a

Table 1 Optical properties and redox potentials of co-oligomers **1–4**

	Solution[a]		Solid		
Compound	λ_{abs}/nm	λ_{em}/nm	λ_{em}/nm	$E_{ox}{}^{b}$/V	$E_{red}{}^{b}$/V
1	391	445	511, 545	+0.72	—
2	426	482	572	+0.78	−1.96
3	407	453	508, 542	—	−1.86
4	391	430	539	—	−1.76

[a] In CH_2Cl_2. [b] 0.1 M $n\mathrm{Bu_4NPF_6}$ in DMF, Pt electrode, scan rate 100 mV/s, V vs Fc/Fc^+.

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† Electronic supplementary information (ESI) available: Synthesis of co-oligomers, FET device fabrication and performance data, and molecular structure. See DOI: 10.1039/b617573b

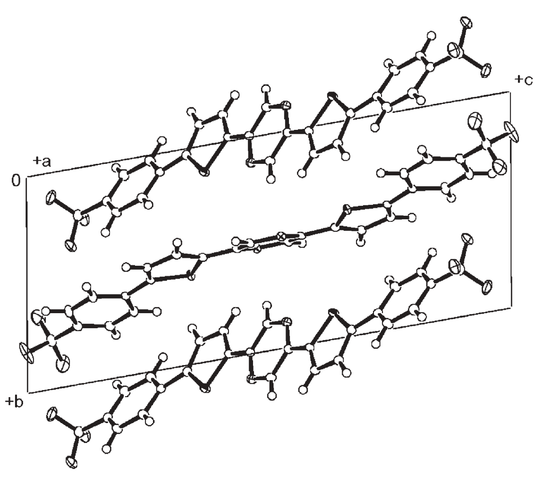


Fig. 1 A view of the crystal packing of compound **3**.

Table 2 Field-effect characteristics of **1–4** films on bottom contact geometry at different temperatures

Compound	Type	T_{sub}/°C	Mobility/ $\mathrm{cm^2\ V^{-1}\ s^{-1}}$	On/off ratio	Threshold/V
1	p	r.t	3.1×10^{-6}	4.0×10^{3}	−141
		50	1.1×10^{-4}	5.1×10^{5}	−109
2	p	r.t	3.6×10^{-4}	9.3×10^{7}	−69
		50	1.0×10^{-3}	4.6×10^{6}	−126
3	n	r.t	2.9×10^{-4}	1.6×10^{6}	+108
		50	8.3×10^{-4}	2.8×10^{6}	+105
4	n	r.t	1.2×10^{-3}	2.7×10^{7}	+62
		50	3.0×10^{-3}	2.7×10^{7}	+41

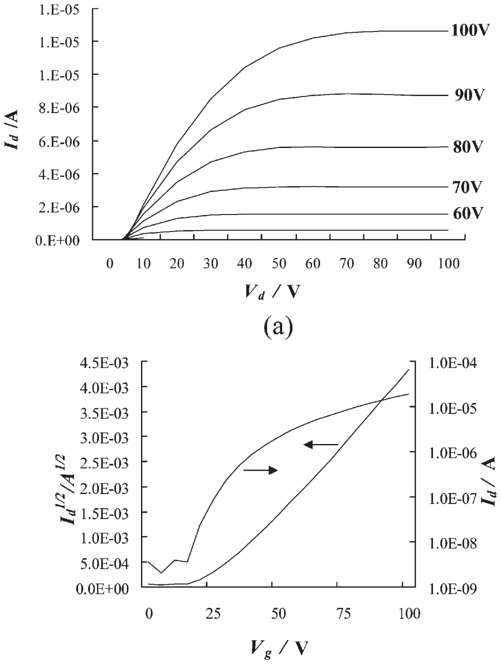
definite geometry is considered to be favorable for an ordered molecular arrangement. Those molecules are packed in a herringbone manner as shown in Fig. 1. On the other hand, the benzene derivative **1** is considered to have a disordered structure since the direction of the thienyl groups cannot be controlled.

FET devices based on **1–4** were fabricated on SiO_2/Si substrates by vapor-deposition with bottom contact geometry. Gold electrodes forming channels of 25 μm length (*L*) and 6 mm width (*W*) were photolithographically defined. The semiconductor layer was evaporated on the electrode/dielectric surface, where the SiO_2 layer was 600 nm thick. The FET performances are summarized in Table 2.

Bithienyl derivatives **1** and **2** showed p-type FET characteristics. The hole mobility and on/off ratio of **2** are higher than those of **1**. In addition, the air-stability of the device of **2** was enhanced compared to that of **1**. These improved performances can be attributed to the introduced pyrazine ring as expected. On the other hand, the trifluoromethylphenyl derivatives **3** and **4** showed n-type FET behavior. The electron mobility was improved by replacing the thienyl unit with the thiazole one. This replacement also induces the reduction of the threshold voltage. This is considered to be due to the higher electron affinity of the thiazole ring as deduced from the higher reduction potential of **4**. Higher FET performances are generally observed with top contact geometry than with bottom contact one because of better contacts between the electrodes and semiconductors in the former. Therefore, top-contact devices using **2** and **4** were fabricated to improve the performances. Gold electrodes were defined after 50 nm of semiconductor deposition at 50 °C by using shadow masks with *W*/*L* of 1.0 mm/100, 50 μm. The SiO_2 gate electric was 200 nm thick and treated with hexamethyldisilazane (HMDS). The FET measurements were carried out at room temperature in a high vacuum chamber (10^{-5} Pa). The mobilities were improved as expected (**2**: p-type: 0.01 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$, **4**: n-type; 0.04 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$). At the same time, the threshold voltages were reduced (Table 3). The output characteristics of **4** with the top contact geometry are shown in Fig. 2.

Table 3 Field-effect characteristics of **2** and **4** on top contact geometry

Compound	Type	T_{sub}/°C	Mobility/ $\mathrm{cm^2\ V^{-1}\ s^{-1}}$	On/off ratio	Threshold/V
2	p	50	0.01	1.4×10^{4}	−35
4	n	50	0.04	5.1×10^{3}	+36



(a)

(b)

Fig. 2 Output characteristics (a) and transfer characteristics (b) of oligomer **4** FET.

The films of the co-oligomers **1–4** deposited on SiO_2/Si substrates were investigated by X-ray diffraction in reflection mode (XRD) (Fig. 3). Sharp reflections were observed in the **1–3** films, indicating the formation of lamella ordering and crystallinity on the substrate. However, the thin film of **4** which showed the highest electron mobility did not show clear XRD peaks. This point is still puzzling.

In summary, we have developed new co-oligomers containing a pyrazine unit. The bithienyl derivatives afforded p-type FET devices, where the introduction of the pyrazine ring was found to enhance the FET performance as well as the air-stability. The trifluoromethylphenyl derivatives showed n-type FET behavior and the introduction of the electron-accepting unit was effective to increase the electron mobility and decrease the threshold voltage.

This work was supported by The 21st Century COE program, a Grant-in Aid for Scientific Research on Priority Areas

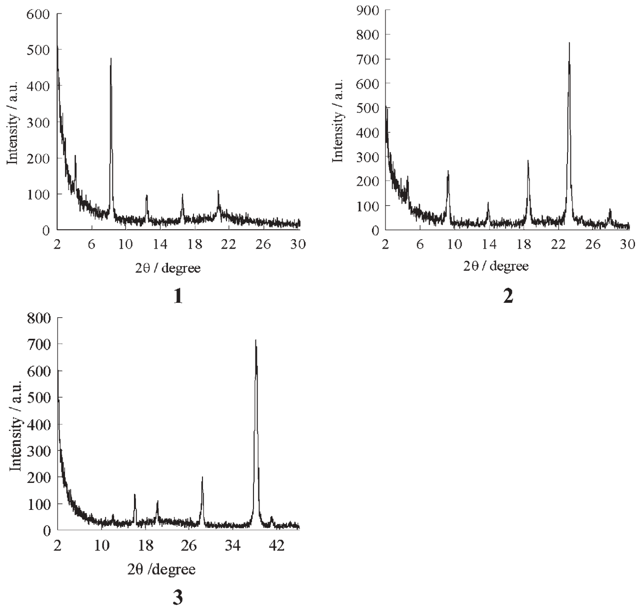


Fig. 3 X-Ray diffractograms of 50 nm films of **1–3** deposited on SiO_2 (T_{sub} = 50 °C).

(No. 15073212) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and The Asahi Grass Foundation.

Notes and references

‡ *Crystal data* for **3**. The measurement of **3** was made on a RAXIS-RAPID imaging plate diffractometer with Mo-Kα radiation (λ = 0.71075 Å) at −180.0 °C. The structure was solved by the direct method (SIR97) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at calculated positions. Absorption correction was applied using an empirical procedure. $C_{26}H_{14}N_2S_2F_6$ M = 532.52, crystal dimensions 0.70 × 0.60 × 0.05 mm, triclinic, space group $P\bar{1}$, a = 6.176(6), b = 9.17(1), c = 20.01(3) Å, α = 99.68(5), β = 89.06(5), γ = 105.91(4)°, V = 1074(7) Å^3, Z = 2, D_c = 1.646 g cm^{-3}, 9653 reflections collected, 4641 independent (R_{int} = 0.019), GOF = 1.31, R_1 = 0.044, wR_2 = 0.148 for all reflections. CCDC reference number 629009. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617573b

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