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High-Performance and Light-Emitting n-Type Organic Field-Effect Transistors Based on Dithienylbenzothiadiazole and Related Heterocycles

Takahiro Kono,[†] Daisuke Kumaki,[†] Jun-ichi Nishida,[†]
Tomo Sakanoue,[‡] Motoyasu Kakita,[§] Hirokazu Tada,[§]
Shizuo Tokito,[⊥] and Yoshiro Yamashita*[,†]

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan, Department of Structural Molecular Science, The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, Japan, NHK Science and Technical Research Laboratories, Kinuta, Setagaya-ku, Tokyo 157-8510, Japan, and Division of Materials Physics, Graduate School of Engineering Science, Osaka University, Machikaneyama, Toyonaka 560-8531, Japan

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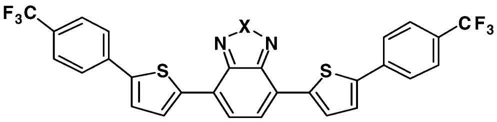
Organic field-effect transistors (OFETs) have attracted much attention for electronic applications,[1] and even light-emitting OFETs have recently been developed.[2] For the progress in this field, development of new organic semiconductors are very important. Although a lot of p-type semiconductors such as pentacenes[3] and thiophene oligomers[4] are reported, the number of n-type ones is still limited and the performance is not satisfactory. In the case of light-emitting FETs, the number of n-type ones are very few.[5] For the high-performance FETs, high mobilities, high on/off ratios, low threshold voltages, and high air stability are required. Recently, we have found that thiazolothiazole[6] and bithiazole[7] derivatives containing trifluoromethylphenyl groups exhibit high electron mobilities and high on/off ratios. However, they show high threshold voltages and instability to air. To overcome these disadvantages, we lowered the LUMO levels of the semiconductors by using strongly electron-accepting heterocyclic units. For this purpose, 2,1,3-benzothiadiazole is an attractive heterocycle that has a high electron affinity.[8] The synthesis and modification of the ring system are easy. Introduction of thienyl groups can afford donor−acceptor compounds that are expected to be self-assembled by intermolecular charge-transfer interactions. Furthermore, they seem to be promising semiconductors for light-emitting n-type FETs because the dithienylbenzothiadiazole derivatives are known to be efficient fluorophores and have small HOMO−LUMO gaps.[9] We report here the high performance n-type FET characteristics and light-emitting properties of a dithienylbenzothiadiazole with trifluoromethylphenyl groups and the corresponding benzoselenadiazole and quinoxaline derivatives.



1: X = S
2: X = Se
3: X = CH =CH

The benzothiadiazole derivative **1** was prepared by the Stille coupling reaction of 2-(tributylstannyl)-5-(4′-trifluoromethylphenyl)thiophene with 4,7-dibromo-2,1,3-benzothiadiazole. The benzoselenadiazole derivative **2** and quinoxaline derivative **3** were similarly obtained from the corresponding dibromo compounds. The yields of **1**−**3** are 19, 12, and 20%, respectively. Differential scanning calorimetry (DSC) measurements showed a sharp melting endotherm peak at 254−257 °C for **1**, 260−263 °C for **2**, and 293−295 °C for **3**. The absoption maxima, emission maxima, fluorescence quantum yields, and differential pulse voltammetry (DPV) data of **1**−**3** are summarized in Table 1. The reduction potentials of five-membered heterocycles **1** and **2** are higher than that of the quinoxaline derivative **3**, indicating that **1** and **2** have higher electron affinity than **3**. The LUMO levels were calculated from the reduction potentials. Because their oxidation potentials could not be measured, the HOMO levels were estimated from the LUMO levels and the HOMO−LUMO gaps, which were obtained from the absorption onset in the thin films (Table 1). These compounds **1**−**3** show strong fluorescence even in the solid state. The emission maxima in the solid state are observed at longer wavelengths than those in solution by 48−65 nm, indicating the existence of the strong intermolecular interactions in the solid state.

The single crystals of **2** and **3** were obtained from slow sublimation. To investigate the molecular structures and intermolecular interactions in the solid state, we carried out

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[*] Corresponding author. E-mail: yoshiro@echem.titech.ac.jp.
[†] Tokyo Institute of Technology.
[‡] The Graduate University for Advanced Studies.
[§] Osaka University.
[⊥] NHK Science and Technical Research Laboratories.

(1) (a) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (b) Newman, C. R.; Frisbie, C. D.; da Silva Filho, D. A.; Brédas, J.-L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436. (c) Katz, H. E. *Chem. Mater.* **2004**, *16*, 4748.

(2) (a) Oyamada, T.; Uchiuzou, H.; Akiyama, S.; Oku, Y.; Shimoji, N.; Matsushige, K.; Sasabe, H.; Adachi, C. *J. Appl. Phys.* **2005**, *98*, 074506. (b) Sakanoue, T.; Fujiwara, E.; Yamada, R.; Tada, H. *Appl. Phys. Lett.* **2004**, *84*, 3037. (c) Swensen, J. S.; Soci, C.; Heeger, A. J. *J. Appl. Phys. Lett.* **2005**, *87*, 253511. (d) Zaumseil, J.; Friend, R. H.; Sirringhaus, H. *Nature Mater.* **2006**, *5*, 69.

(3) (a) Klauk, H.; Halik, M.; Zschieschang, U.; Schmid, G.; Radlik, W.; Weber, W. *J. Appl. Phys.* **2002**, *92*, 5259. (b) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986. (c) Tulevski, G. S.; Miao, Q.; Afzali, A.; Graham, T. O.; Kagan, C. R.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1788.

(4) (a) Halik, M.; Klauk, H.; Zschieschang, U.; Schmid, G.; Ponomarenko, S.; Kirchmeyer, S.; Weber, W. *Adv. Mater.* **2003**, *15*, 917. (b) Facchetti, A.; Letizia, J.; Yoon, M.-H.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Chem. Mater.* **2004**, *16*, 4715. (c) Takimiya, K.; Kunugi, Y.; Konda, Y.; Ebata, H.; Toyoshima, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2006**, *128*, 3044.

(5) Sakanoue, T.; Yamada, R; Tada, H. *Proc. SPIE* **2005**, 5940.

(6) Ando, S.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 5336.

(7) Ando, S.; Murakami, R.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14996.

(8) (a) Akhtaruzzaman, M.; Tomura, M.; Nishida, J.; Yamashita, Y. *J. Org. Chem.* **2004**, *69*, 2953. (b) Akhtaruzzaman, M.; Kamata N.; Nishida, J.; Ando, S.; Tada, H.; Tomura, M.; Yamashita, Y. *Chem. Commun.* **2005**, 3183.

(9) (a) Kato, S.; Matsumoto, T.; Ishi-i, T.; Thiemann, T.; Shigeiwa, M.; Gorohmaru, H.; Maeda, S.; Yamashita, Y.; Mataka, S. *Chem. Commun.* **2004**, 2342. (b) Raimundo, J.-M.; Blanchard, P.; Brisset, H.; Akoudad, S.; Roncali, J. *Chem. Commun.* **2000**, 939. (c) Aldakov, D.; Palacios, M. A.; Anzenbacher, P., Jr. *Chem. Mater.* **2005**, *17*, 5238.

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Table 1. Optical and Electrochemical Properties of 1−3a

	λ_{abs} (nm) (log ϵ)		λ_{em} (nm) (ϕ)						
compd	solution[a]	film[b]	solution[a]	solid[b]	E^1_{red}[c] (V)	E^2_{red}[c] (V)	HOMO (eV)	LUMO (eV)	E_g (eV)
1	256 (4.26), 348 (4.50), 480 (4.45)	330, 347, 475	616 (0.31)	667	−1.00	−1.52	5.38	3.38	2.00
2	251 (4.14), 355 (4.60), 512 (4.31)	339, 376, 544	670 (0.17)	735	−0.92	−1.46	5.21	3.45	1.76
3	272 (4.31), 351 (4.43), 457 (4.37)	295, 324, 452	598 (0.31)	646	−1.16	−1.60	5.34	3.21	2.13

[a] In CH_2Cl_2. [b] 50 nm thick on a quartz plate. [c] In DMF (0.1M $TBAPF_6$), Pt electrode, scan rate 20 mV s^{-1}, V vs SCE. The fluorescence quantum yields were obtained by using 9,10-diphenylanthracene (λ_{ex} = 365 nm, ϕ_f = 0.90 in cyclohexane) as a standard.

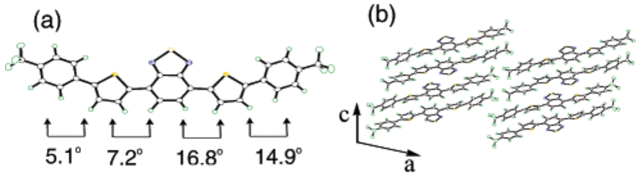

Figure 1. (a) Molecular and (b) crystal structure of **2**.

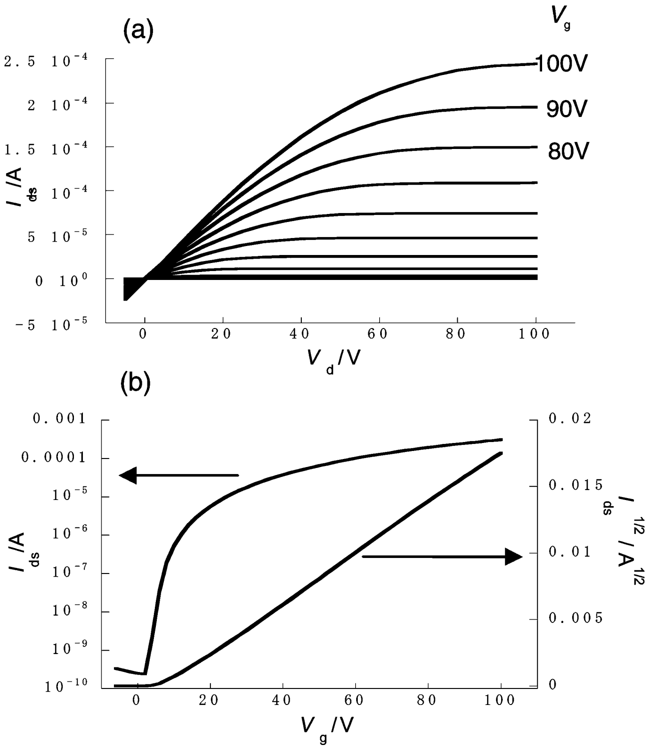

Figure 2. (a) Output characteristics and (b) transfer characteristics of **1** at T_{sub} = 80 °C on top contact geometry.

Table 2. Field-Effect Transistor Characteristics of 1

T_{sub} (°C)	mobility (cm^2 V^{-1} s^{-1})	on/off	threshold (V)
25	0.04	1×10^5	39
50	0.08	1×10^5	30
80	0.19	1×10^6	3

X-ray structure analyses. The molecule **2** has a little deformed strucure (Figure 1a) in which the dihedral angles between the component rings are 5.1−16.8°. An important feature is that a short contact between the S atom of the thiophene ring and the N atom of the selenadiazole ring (2.9−3.0 Å) exists and no disorder caused by the thienyl ring rotation is observed. In the crystal structure (Figure 1b), the molecule forms a columnar structure in which the average interplanar distance is 3.40 Å. A short heteroatom contact between the two columns (S···Se, 3.62 Å) is observed. Although the molecular structure of **3** is similar to that of **2**, it forms a dimer structure that is packed in a herringbone manner (see the Supporting Information).

FET devices with bottom contact geometry were constructed by vapor-deposition on SiO_2/Si substrate. FET measurements were carried out at room temperature in a vacuum chamber without exposure to air. All of them showed n-type behavior. The FET characteristics on bottom contact device are summarized in Table S6 (see the Supporting Information). The electron mobilities increase at higher substrate temperatures. The performance of **1** and **2** is similar. On the other hand, the quinoxaline derivative **3** showed a little lower mobility. This fact may be attributed to the inefficient intermolecular interaction in **3** as deduced from the single-crystal X-ray analysis. The films of **1**−**3** deposited on the SiO_2/Si substrate were investigated by X-ray diffraction in the reflection mode (XRD) (see the Supporting Information). The intensity and the number of the peaks increased with an increase in substrate temperatures. This finding indicates that the molecules are more highly ordered upon higher temperatures. The FET performance of **1** was optimized by fabricating the device with top contact geometry, where gold electrodes were defined after 50 nm of semiconductor deposition by using shadow masks with W/L of 1.0 mm/200, 100, 50 μm. The SiO_2 gate insulator was 200 nm thick and treated with hexamethyldisilazan (HMDS). The FET measurements were carried out in a high-vacuum chamber (1×10^{-5} Pa). Figure 2 shows the drain current (I_d) versus voltage (V_d) characteristics for the FET device of **1**. The FET characteristics on top contact geometry at different substrate temperatures are summarized in Table 2. The electron mobility calculated in the saturation regime was 0.19 cm^2 V^{-1} s^{-1} at 80 °C. It should be noted here that the threshold voltage is very low (3 V), which is much lower than those of previously reported bis(trifluoromethylphenyl) substituted semiconductors (55−78 V).[6,7] The low threshold voltage is of importance for the appreciations. This may be related to the high electron affinity and suitable morphology of **1**.

Next, light-emitting FET devices based on the semiconductors **1**−**3** were fabricated by using interdigital electrodes of Cr (10 nm)/Au (20 nm) with the W/L of 38 mm/5 μm on bottom contact geometry. The thin film of **1** was prepared by vapor deposition in a vaccum chamber (1×10^{-5} Pa) at the substrate temperature of 80 °C. After deposition, the device was exposed to air to be transferred to another vacuum chamber (1×10^{-3} Pa) equipped with a glass window from which light emission can be measured with a spectrogram and CCD system. The film was found to have air stability enough for the transfer in air. The device of **1** showed emission with a maximum of 661 nm, which is close to the fluorescence in the thin film (662 nm). The emission spectra

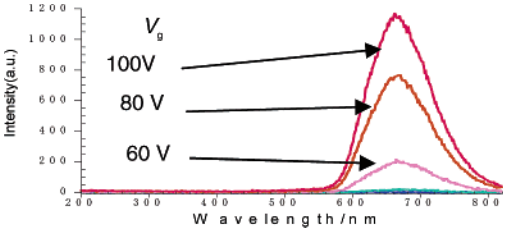

Figure 3. LFET spectra depending on V_g of the device of **1**.

were measured with the drain voltage of 100 V and the gate voltages were varied from 20 to 100 V. The emission intensity increased with an increase in gate voltage (Figure 3). The emission intensity also increased with an increase in drain voltages because of the increased carrier recombination. The emission was observed near the drain electrode side because the device has only an n-channel.[5] The successful light-emitting observation can be attributed to the small HOMO−LUMO gap. The FET devices based on **2** and **3** showed similar light-emitting behavior.

In conclusion, we have developed new semiconductors composed of donor−acceptor compounds including electron-accepting benzothiadiazole and related heterocycles. The FET devices based on them showed high n-type performance. Using the benzothiadiazole unit, we found the threshold voltage to be greatly reduced to 3 V. The devices showed n-type light-emitting FET characteristics, where the emission intensity was strongly dependent on the gate voltages.

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Supporting Information Available: Synthesis, absorption and emission spectra, CVs, LFET details of **1**−**3**, X-ray crystallographic data for **2** and **3** in CIF format, field-effect characteristics on bottom contact geometry, and XRD data. This material is available free of charge via the web site at http://pubs.acs.org.

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