Novel Field-effect Transistors Based on Bis(1,3-dithiol-2-ylidene) Compounds with a Conjugated Spacer Group

Yosuke Morioka, Jun-ichi Nishida, Eiichi Fujiwara,[†] Hirokazu Tada,[†] and Yoshiro Yamashita*
Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering,
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502
[†]*Institute for Molecular Science, Myodiaji, Okazaki 444-8585*

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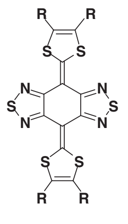
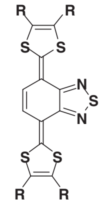
Bis(1,3-dithiol-2-ylidene) derivatives were used as active layers of organic field-effect transistors and the relationship between the structure and properties was investigated. A compound containing a dihydronaphthothiadiazole unit as a spacer group and the related heterocyclic compounds exhibited clear p-type transistor performances.

Organic field-effect transistors (OFETs) have recently attracted much attention from viewpoints of application purposes for electronic devices as well as basic interest in the mechanism of charge transportation.[1] For the progress of this field, development of new materials is particularly important. Typical examples showing FET characteristics are thiophene oligomers[2] and acene molecules like pentacene,[3] which have been extensively studied. Recently, tetrathiafulvalene (TTF) derivatives were reported to show excellent FET performances in single crystals.[4] This result suggests that bis(1,3-dithiol-2-ylidene) compounds with a conjugated spacer group, which are π-extended TTF analogues, are attractive candidates for OFETs. Bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT) **1a** belongs to this class of compounds and was found to show a good conductivity as a single component.[5] Since this molecule showed a high hole mobility in a single crystal,[5b] it was used as an active layer of a FET device and was found to exhibit notable FET performances.[6] As an extension of this work, we have now examined FET properties of related compounds of BTQBT to investigate the relationship between the structure and FET properties, and develop a new type of OFETs.



1a: R = H (BTQBT)
1b: R, R = benzo



2a: R = H
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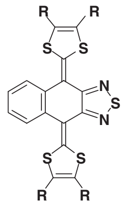
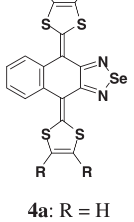
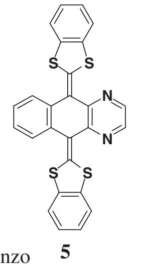


3a: R = H
3b: R, R = benzo



4a: R = H
4b: R, R = benzo



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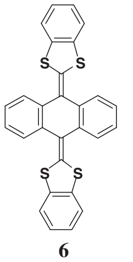

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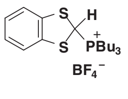

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BTQBT **1a** can be modified by introduction of substituents at the 1,3-dithiole ring and replacement of the fused thiadiazole ring with other groups. We chose the dibenzo derivative **1b** and bis(1,3-dithiol-2-ylidene) compounds with different π-spacer groups **2–6** for this study. The syntheses of them except for **5** have already been reported.[5,7] The pyrazine derivative **5** was prepared using the Wittig reaction of the corresponding dione with a phosphonium salt **7**.[8] FET devices were fabricated on SiO_2/Si substrates by a high-vacuum (ca. 10^{-5} Pa) evaporation method with bottom contact geometries at room temperature. The Au electrodes were prepared according to a previous method.[6b] The films were deposited on the electrodes with the thickness of ca. 80 nm. The FET measurements were carried out in situ. The mobilities were calculated by the values in the saturated region. The mobilities and on/off ratios measured under the same conditions are summarized in Table 1.

DibenzoBTQBT **1b** showed a lower mobility compared with BTQBT **1a**. This may be related to the insufficient intermolecular interactions in **1b** since the high FET performances of **1a** were attributed to the strong intermolecular interactions resulting in large transfer integral between molecules[6] and such interactions in crystals were observed only in the non-substituted derivative **1a**.[5a] It is noteworthy here that the on/off ratio of **1b** is still large (10^4). This is attributable to the electron-withdrawing property of the thiadiazole ring which can stabilize the highly electron-donating bis(1,3-dithiol-2-ylidene) skeleton.

Compounds **2** containing only one fused thiadiazole ring are much stronger electron donors than **1** owing to its quinoid structure as well as the less number of the electron-withdrawing ring.[7a] The non-substituted derivative **2a** did not show FET characteristics, whereas the less electron-donating dibenzo derivative **2b**[9] exhibited FET characteristics with a low mobility and a small on/off ratio. This result suggests that strong electron donors are not suitable as active layers of FET devices.

Table 1. Mobilities and on/off ratios in the FET devices

Compound	Mobility/cm^2 V^{-1} s^{-1}	on/off
1a	2×10^{-2}	10^7
1b	3×10^{-4}	10^4
2a	Not Observed	—
2b	2×10^{-6}	50
3a	Not Observed	—
3b	8×10^{-5}	10^4
4a	Not Observed	—
4b	2×10^{-4}	10^4
5	6×10^{-7}	10^3
6	Not Observed	—

Benzo-fused derivatives **3** are weaker electron donors than **2** since the quinoid character is reduced in **3**.[7b] The molecules of **3** have a little twisted geometry due to a steric interaction between the sulfur and peri-hydrogen atoms. However, good π–π overlap between the molecules is expected since such an interaction was observed in the X-ray analysis of the single crystal of **3b**.[7b] The single crystal of **3b** shows a moderate conductivity as a single component,[7b] suggesting that **3** would exhibit FET performances. Although the non-substituted derivative **3a** did not show FET performances probably owing to the strong electron-donating property,[9] the less electron-donating dibenzo derivative **3b** exhibited clear FET properties. The output characteristics are shown in Figure 1. The channel conductance increases as the gate voltage becomes more negative, indicating the p-type semiconducting behavior. The mobility shown in Table 1 is similar to that of dibenzoBTQBT **1b**. The high on/off ratio (10^4) should be noted. The derivative has the following advantages. i) The solubility of **3b** in organic solvents is much better than that of **1b**, indicating that the film of **3b** can be formed by solution methods. ii) The syntheses is easy using the Wittig reaction of a readily available precursor quinone with **7**. iii) The fused benzene ring can be easily modified by introducing substituents to give its derivatives. These facts indicate that the bis(1,3-dithiol-2-ylidene) compounds containing a dihydronaphthothiadiazole unit as a spacer group would be candidates for active layers of FETs.

Recently a selenium-containing compound was reported to exhibit a higher mobility in the FET device than the corresponding sulfur material.[10] This reason was ascribed to the stronger intermolecular interaction resulting in larger transfer integral in the selenium compounds caused by the more polarized selenium atom. In this sense replacement of the thiadiazole ring by a selenadiazole ring was expected to enhance the FET performances. When we examined the FET behavior of the selenadiazole derivatives **4**, a little improvement of the FET performances was observed. Thus, dibenzo derivative **4b** showed a little higher mobility than that of **3b** although no FET property was observed in **4a**. The films of **3b** and **4b** deposited on SiO_2/Si substrates were investigated by X-ray diffraction in reflection mode. No clear reflection peaks were observed in both cases, suggesting a disorder orientation on the substrate.

Furthermore, for comparisons, FET behavior of pyrazine derivative **5** and dibenzo compound **6** was investigated. Although **5** showed a p-type semiconducting behavior, the mobility was low. Dibenzo derivative **6** did not show any FET properties. Since **6** is a butterfly-shaped molecule,[11] the nonplanar structure is considered to disturb efficient π–π intereactions between molecules, leading to no observation of FET characteristics. Although X-ray analysis of the pyrazine derivative **5** was not succeeded, the six-membered pyrazine ring is considered to cause a larger steric interaction than the five-membered thiadiazole ring. This structural factor may be one of the reasons for the low mobility of **5**.

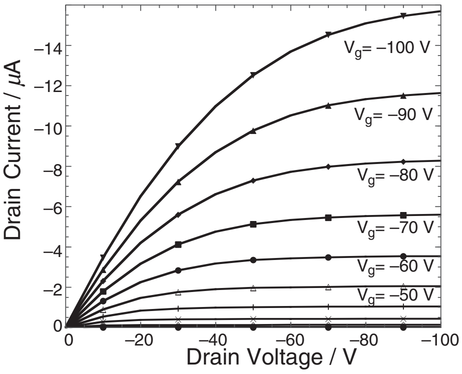

Figure 1. FET characteristics for the film of **3b** deposited at room temperature.

In conclusion, we have revealed the relationship between the structure and FET properties in a series of bis(1,3-dithiol-2-ylidene) compounds with a π-conjugated spacer. The moderate electron-donating properties of the molecules and efficient intermolecular interactions are essential for FET performances. The compounds with a dihydronaphthothiadiazole unit as a spacer and the corresponding selenium compounds become candidates for FET materials. Studies using the derivatives to improve the FET performances are currently in progress.

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8 **5**: mp 172–175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.5 (m, 2H, pyrazine), 6.91–7.20 (m, 12H, benzo); EIMS *m/z* 482 (M^+).

9 The following oxidation potentials (V vs SCE) are reported.[7a,b] **2a**: 0.36, 0.53 V, **2b**: 0.54, 0.70 V, **3a**: 0.63 V, **3b**: 0.80 V.

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