Dithienylbenzobis(thiadiazole) based organic semiconductors with low LUMO levels and narrow energy gaps[†]

Takahiro Kono,^a Daisuke Kumaki,^b Jun-ichi Nishida,^a Shizuo Tokito^{ab} and Yoshiro Yamashita^{*a}

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Novel OFET materials showing high mobility $(0.77 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ and good air-stability were developed using a benzobis(thiadiazole) (BBT) unit and the high FET performance was attributed to the low LUMO level and the film morphology.

Control of energy levels and band gaps is very important since they determine the optical and electrochemical properties of organic compounds, and the characteristics of their electronic devices.¹ Especially, semiconductors for organic field-effect transistors (OFETs) are required to have suitable energy levels for efficient carrier-injection from electrodes.² Organic redox systems of π -conjugated molecules have been used as semiconductors since their HOMO and LUMO levels can be tuned by suitable design of electron-donating and -accepting moieties. Although some superior air-stable p-channel OFETs are known, high-performance air-stable n-channel OFETs are still rare and their development is crucial for low-voltage and high-gain CMOS inverters.³ For development of n-channel OFET materials, high electron affinity is important to match the LUMO levels with the work function of the electrodes as well as to enhance the air stability.

Recently, BBT derivatives have been used for electronic applications.⁴ However, to our best knowledge, high performance and air-stable n-channel OFET materials using the BBT skeleton have not been reported yet. In this context, we expect benzobis(thiadiazole) (BBT) derivatives to be viable n-channel organic semiconductors for the following reasons. First, BBT is a stronger electron acceptor than benzothiadiazole $(BTD)^5$ because of an additional thiadiazole ring attached to BTD with a hypervalent sulfur atom. Second, intermolecular interactions are expected by intermolecular S···N contacts between the thiadiazole rings.^{5,6} Third, small HOMO–LUMO energy gaps are expected in the BBT derivatives, which would be useful to induce ambipolar behavior. Fourth, the BBT derivatives with thiophene units are planar molecules with some quinoidal characteristics.⁶ We report here the synthesis

and physical properties of BBT derivatives, and their semiconducting characteristics by FET measurements.

BThBBT 2 and FPTBBT 3 (Fig. 1) were obtained by the Stille coupling reaction of 4,10-dibromobenzobis(thiadiazole) (5) with the corresponding stannyl reagents.^{6,7} Trifluoromethyl groups were introduced in 3 since they are effective to enhance n-type FET behaviors by improving the crystallinity of films and lowering the LUMO energy level.⁵ For comparison, dithienyl derivative ThBBT 1 was synthesized according to a reported method.^{5a} Black block crystals of BThBBT 2 were obtained by slow sublimation. The ORTEP structure shows that 2 has a planar structure and the benzothiophene rings are disordered (Fig. 2). Intermolecular S···N contacts of *ca*. 3.21 Å are observed between the columns. This is due to the electrostatic interaction between the positively polarized S atom and the negatively polarized N atom.^{5,6}

The HOMO and LUMO energies are summarized in Table 1. The redox potentials of these compounds were measured by cyclic voltammetry (CV) at 100 °C due to the low solubility. The LUMOs of 1–3 are lower than that of 4, suggesting that 1–3 would be able to work as n-channel semiconductors. This is attributed to the bisthiadiazole unit of BBT containing a hypervalent sulfur atom leading to a stronger electron-accepting property. The LUMO levels estimated from the CV of 2 and 3 satisfy the proposed air-stable LUMO level (4.0–4.1 eV).^{3e} The end-absorption of the thin film of 3 is red-shifted from that of 1 and is further red-shifted from that of 4 (Table 1).

Besides the CVs, the ionization potentials (IP) were measured with ultraviolet photoelectron spectroscopy (UPS) in air to investigate the energy levels in the thin films. The HOMO and LUMO levels are summarized in Table 1. These IP data are different from the CV data in solution. The difference can be attributed to the difference in measurement methods (UPS or CV)



Fig. 1 BBT derivatives 1–3 and FPTBTD 4.

^a Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8502, Japan. E-mail: yoshiro@echem.titech.ac.jp; Fax: (+81)45-924-5489; Tel: (+81)45-924-5571

^b NHK Science and Technical Research Laboratory, Kinuta, Setagaya-ku, Tokyo 157-851, Japan

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Fig. 2 ORTEP drawing (a) and packing view (b) of 2.

as well as the difference in the state (solution or film). In the thin film, the LUMO level of 3 is much lower than those of 1 and 2. The large difference in 3 may be attributed to the fact that the crystallinity of film 3 is better than those of 1 and 2, resulting in stronger intermolecular interactions in the thin film of 3.

The thin films of **1–3** deposited on HMDS-treated substrates were investigated by X-ray diffraction (XRD) (Fig. S4, ESI†). The film of **3** showed five diffraction peaks. In contrast, the films of **1** and **2** only showed very small peaks. This result indicates that the film **3** has higher crystallinity than **1** and **2**. The primary reflection peaks were observed at $2\theta = 4.62^{\circ}$ (*d*-spacing = 19.11 Å) for **3**, $2\theta = 8.12^{\circ}$ (*d*-spacing = 10.88 Å) for **2**, and $2\theta = 10.88^{\circ}$ (*d*-spacing = 8.12 Å) for **1**. The film of **3** at 130 °C showed seven peaks in the XRD (Fig. 3), indicating that the crystallinity was enhanced with an increase of substrate temperature at 130 °C.

To investigate the morphologies of 2 and 3 films in more detail, scanning electron microscopy (SEM) measurements were carried out. The SEM images of 3 are shown in Fig. 4 and ESI[†], revealing the formation of large grains at r.t., 80 and 130 °C.

An interesting finding is that the number of grains on the film surface decreases and the flat region is increased at $T_{sub} = 130$ °C. The film at 130 °C was further investigated by AFM, where a terrace-like structure with steps was observed (Fig. 4(d)).

The semiconductor characteristics were investigated with top-contact (TC) and bottom-contact (BC) FETs fabricated



Fig. 3 X-Ray diffraction pattern of film 3 deposited at 130 °C.



Fig. 4 SEM images of films of FPTBBT **3** at (a) $T_{sub} = r.t.$, (b), r.t. on electrode and (c) 130 °C. (d) AFM image of T_{sub} 130 °C film.

onto hexamethyldisilazane (HMDS) treated Si/SiO₂ substrates. The FET measurements were carried out in vacuum at room temperature. The films of **1** and **2** with BC showed ambipolar FET characteristics when deposited at r.t. ($\mu_e = 1.6 \times 10^{-4}$ and $\mu_h = 3.4 \times 10^{-7}$ cm² V⁻¹ s⁻¹ for **1** and $\mu_e = 2.0 \times 10^{-5}$ and $\mu_h = 1.5 \times 10^{-5}$ cm² V⁻¹ s⁻¹ for **2**). This is due to their narrow HOMO–LUMO gaps and the HOMO and LUMO levels being close to the work function of gold and chromium which were used as the source and drain electrodes (Au: *ca*, 5.1 eV and Cr: 4.5 eV).

The film **3** with BC exhibited only n-channel behavior because the HOMO level of **3** (6.25 eV from the IP) is different from the work function of Au and Cr, resulting in a large injection barrier of hole-carriers between the organic layer and electrode interface. High electron mobility of $\mu_e =$ 0.17–0.40 cm² V⁻¹ s⁻¹ was observed when deposited at r.t, which is much higher than those of **1** and **4**.^{5b} This is attributed

 Table 1
 HOMO and LUMO levels of 1–3 and FPTBTD 4

Compd.	λ_{\max}^{a}/nm	HOMO ^a (IP)/eV	$E_{\rm g}{}^b/{\rm eV}$	LUMO ^c /eV	HOMO ^d (CV)/eV	LUMO ^d (CV)/eV	$E_{\rm g}~({\rm CV})/{\rm eV}$
1	806 720	5.60	1.30	4.30	5.32	3.96	1.36
23	810	6.25	1.35	4.30 5.05	5.29	4.03	1.32
4	475	e	2.00	e	5.50	3.30	2.20

^{*a*} 100 nm thin films on quartz plates. ^{*b*} Measured with thin film and estimated from the end-absorption. ^{*c*} HOMO (IP) + E_{g} . ^{*d*} CV measured in PhCN containing 0.1 M Bu₄NPF₆. HOMO and LUMO were estimated from onset of CV peaks. ^{*e*} Not observed.



Fig. 5 Transfer curves (a), and V_{th} (red) and mobility (blue) plots (b) of **3** in vacuum and air.

to the BBT skeleton with trifluoromethylphenyl groups which are helpful to create suitable films for carrier accumulation and transportation. The FET mobility of **3** was improved when deposited at 130 °C (up to 0.77 cm² V⁻¹ s⁻¹). This improvement can be related to the crystallinity of the film. As observed in the SEM images, the film morphologies changed with increasing the substrate temperatures. The terrace-step structure observed in the AFM image (Fig. 4(d)) seems to be suitable for the high carrier mobility.

The film **3** with TC showed a mobility of 0.28 cm² V⁻¹ s⁻¹. The air-stability of the device was investigated by using the TC devices as shown in Fig. 5, where the transfer curves and the change of mobility and V_{th} in air are depicted. It is noteworthy that V_{th} showed a small positive shift (10 to 19 V) upon standing in air and the mobility was constant at 0.16 cm² V⁻¹ s⁻¹ after 50 days (Table S2, ESI[†]). In contrast, the film of FPTBTD **4** showed a very large V_{th} shift in air.⁸ This fact indicates that the high air-stability of film **3** is attributed to its low LUMO energy level (4.04 eV from the CV, and lower level in the thin film, as estimated from UPS and end-absorption measurements).

On the other hand, the BC based device of **3** showed lower air stability. Although the reason is still uncertain, this may be related to the difference in crystallinity on the HMDS treated surface from that on the Au surface because the grains on the HMDS surface were a little larger than those on the Au surface (Fig. 4(b)) The film **2** (BC device) did not show FET performance in air. This is attributed to the poor crystallinity, as revealed from XRD, as well as to the higher LUMO level in the film.

In conclusion, we have developed oligomer-based BBT derivatives and their semiconductor characteristics were investigated by FET measurements. The LUMO levels are lower than that of the BTD analogue **4** owing to the electron-withdrawing BBT skeleton with a hypervalent sulfur atom. The film of **3** is highly ordered, as revealed from the XRD, SEM and AFM measurements. The FET mobility of **3** was found to be very high even when deposited at room temperature. The topcontact FET device showed high air-stability due to the low LUMO levels and/or the film morphology. The mobility reached levels up to $0.77 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with the bottom-contact FET. This result shows that BBT is a promising unit for airstable high-performance n-channel FETs.

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