

Synthesis, characterization and FET properties of novel dithiazolylbenzothiadiazole derivatives

Md. Akhtaruzzaman,^a Naoto Kamata,^a Jun-ichi Nishida,^a Shinji Ando,^a Hirokazu Tada,^b Masaaki Tomura^b and Yoshiro Yamashita^{*a}

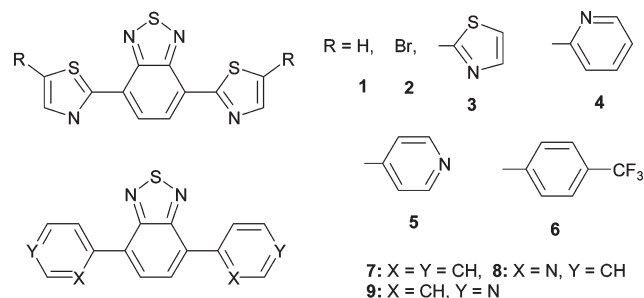
Received (in Cambridge, UK) 15th March 2005, Accepted 28th April 2005

First published as an Advance Article on the web 24th May 2005

DOI: 10.1039/b503814f

Dithiazolylbenzothiadiazoles easily obtained have high electron affinity and the FET device of a trifluoromethylphenyl derivative exhibited a good n-type performance with high electron mobility.

In recent years much attention has been paid to development of novel organic semiconductors working as active layers of organic field-effect transistors (OFETs).¹ Organic redox systems of π -conjugated molecules have been used as semiconductors.² Development of new electron acceptors with high electron affinity is particularly important since their numbers and variation are still limited and their performances are not satisfactory compared to those of electron donors.^{1,2} Although 2,1,3-benzothiadiazole is a well-known electron-accepting unit which has been used in EL devices,³ it has not been used for OFETs. This ring was linked with thiophenes for further modification since the thiophenes can be easily functionalized.^{3–5} However, introduction of electron-donating thiophene groups decreases the electron-accepting property of benzothiadiazole. On the other hand, thiazole is an electron-withdrawing heterocycle and substituents can be easily introduced at the α -position of the sulfur atom. In this context, we have now designed a 4,7-dithiazolylbenzothiadiazole unit as an electron-accepting building block. In addition to the electron-accepting property, the thiadiazole ring is expected to reduce the steric interactions between the neighbouring rings, resulting in increase of the planarity of the molecule which is favorable for intermolecular π - π interactions. We report here the synthesis and characterization of novel dithiazolylbenzothiadiazole derivatives with various aromatic groups. Their performances as n-type semiconductors in the FET devices are also presented here.



The parent compound **1** was prepared by the Stille coupling reaction of 2-(tributylstanyl)thiazole⁶ with 4,7-dibromo-2,1,3-benzothiadiazole.⁷ The dibromo compound **2** was obtained by

the reaction of **1** with NBS. Other derivatives **3–6** were synthesized from **2** by using the Suzuki, Stille or Sonogashira coupling reactions in 50–60% yields.

The single crystal structure of **1** was determined by X-ray crystallographic analysis.[†] The molecular structure of **1** is shown in Fig. 1. The molecule is almost planar with the average dihedral angle between the thiazole and benzothiadiazole rings of 6.0°. The planar structure is in contrast to the twisted structures observed in 4,7-dipyridylbenzothiadiazoles **8** and **9**.⁸ Another interesting feature is that no disorder caused by the ring rotation is observed and the S atom of the thiazole is shortly contacted with the N atom of the thiazole with a distance of 2.9 Å. This can be attributed to the electrostatic interaction between the positively charged S atom and the negatively charged N atom. This fixed geometry would be favorable for arranging molecules. The intermolecular S \cdots N contact (3.19 Å) is also observed in the crystal structure.

The physical properties of the newly prepared compounds **1–6** are summarized in Table 1. The absorption maxima of **3–6** substituted with aromatic rings are red-shifted compared to that of the parent molecule **1**. This is due to the extension of π -conjugation. All the compounds show efficient fluorescence and the higher fluorescence quantum yields are observed in the pyridyl substituted derivatives **4** and **5**. These compounds exhibit strong yellow to red fluorescence in the solid state. The emission maxima in the solid state are observed at longer wavelengths than those in solution, indicating the presence of strong intermolecular interactions in the solid state.

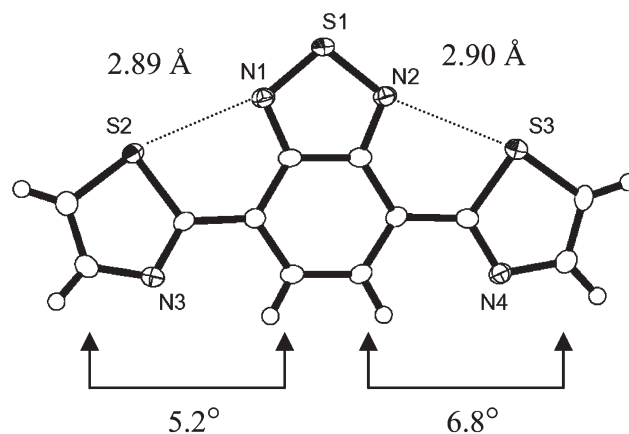


Fig. 1 Molecular structure of **1**. The short S \cdots N contact and dihedral angles are shown here.

*yoshiro@echem.titech.ac.jp

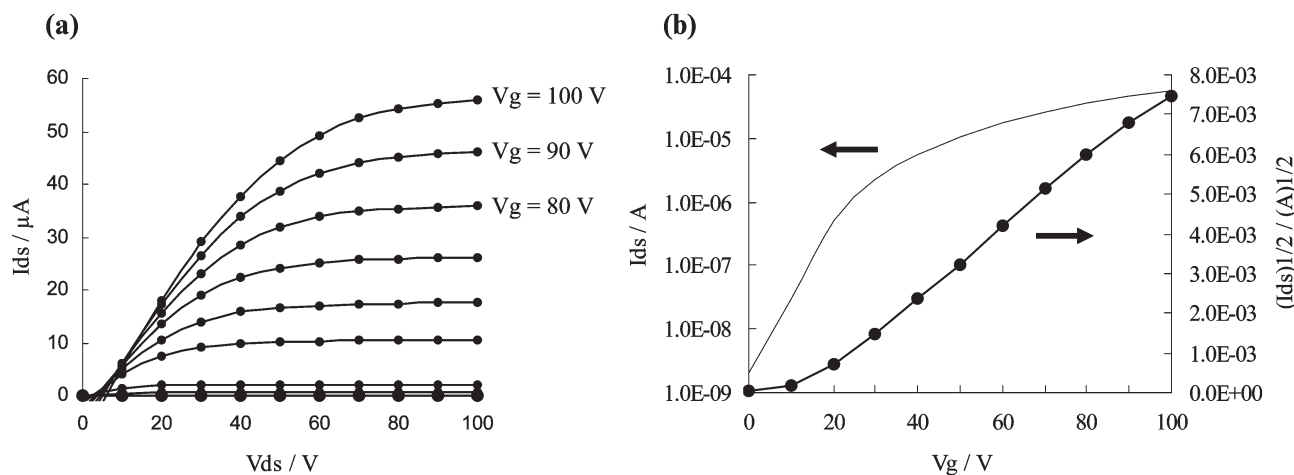


Fig. 2 a) Drain current (I_d) versus drain voltage (V_d) characteristics as a function of gate voltage (V_g) for OFET of **6** fabricated on SiO_2 at room temperature. b) I_d and $I_d^{1/2}$ versus V_g plots for the same device. The field-effect mobility calculated in the saturation regime is $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Table 1 Optical data^a and reduction potentials^b

Compound	Solution			Solid	
	λ_{max} (nm)	λ_{em} (nm)	Φ_{em}	λ_{em} (nm)	E_{red}/V^b
1	427	517	0.68	575	-1.09
2	428	537	0.60	605	-0.97
3	472	557	0.42	651	-1.15
4	465	552	0.90	643	-0.82, -1.36 ^c
5	459	546	0.84	611	-
6	465	554	0.55	607	-0.77, -1.3 ^c
7^d	380	490	0.80	-	-1.36
8^e	377	469	0.80	-	-1.25
9^e	356	448	0.68	-	-1.19

^a In CH_2Cl_2 , $\lambda_{\text{ex}} = 299 \text{ nm}$. The fluorescence quantum yields were obtained by using 2-phenylbenzoxazole ($\Phi_{\text{em}} = 0.75$) as a standard.⁷ ^b 0.1 mol dm^{-3} $n\text{-Bu}_4\text{NPF}_6$ in CH_2Cl_2 , Pt electrode, scan rate 100 mV s^{-1} , V vs SCE. ^c In DMSO. ^d Ref. 4. ^e Ref. 8. ^f Not measured due to the low solubility.

The reduction potentials listed in Table 1 were measured by cyclic voltammetry. The values of the dithiazole derivatives **1–6** are higher than that of the derivatives **7–9**^{4,8} owing to the electron-withdrawing property of the thiazole ring. Introduction of the pyridyl and trifluoromethylphenyl group further increases the reduction potentials. The value of the dipyrindyl derivative **4** is higher than those of dipyrindylbenzothiadiazoles **8** and **9**. This can be attributed to the extended π -conjugation in the former in addition to the electron-withdrawing effect of the thiazole. These dithiazolobenzothiadiazoles would be of interest as EL emitters due to their highly fluorescent and electron-accepting properties.

Next, the n-type semiconducting behavior of **3–6** has been investigated by using them as active layers of FETs. The FET devices were fabricated on SiO_2/Si substrate by high-vacuum evaporation (10^{-5} Torr) using bottom and top contact geometry. The n-doped silicon substrate was used as gate. For the bottom contact geometry, gold electrodes forming channels of $25 \mu\text{m}$ length (L) and 6 mm width (W) were photolithographically defined. The semiconductor layer was then evaporated on the entire electrode/dielectrode surface. The SiO_2 gate dielectric was 600 nm thick. For the alternate top contact geometry, gold electrodes were defined after semiconductor deposition by using shadow masks with W/L of $1.0 \text{ mm}/100 \mu\text{m}$ and $1.0 \text{ mm}/50 \mu\text{m}$.

The SiO_2 gate dielectric was 200 nm thick. The electrical characteristics were obtained at room temperature in high vacuum conditions using a semiconductor parameter analyzer. The FET devices based on **3** and **4** showed no FET performance. The pyridyl derivative **5** afforded an n-type FET device although the mobility was poor ($1.1 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). On the other hand, the FET devices using trifluoromethylphenyl derivative **6** exhibited a good n-type performance. The output characteristics of the top contact device are shown in Fig. 2. The channel conductance increases as the gate voltage becomes more positive, indicating the n-type semiconducting behavior. The mobility was $4.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a high on/off ratio of 10^5 in the bottom-contact device. The mobility was increased in the top-contact device ($5.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, on/off ratio: 10^4) and the threshold voltage was 20 V . The FET performance was further improved by raising the substrate temperature. Thus, at $50 \text{ }^\circ\text{C}$ the mobility was $6.8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (on/off ratio: 3×10^4 , threshold voltage: 15 V). The high performance can be attributed to the effect of the trifluoromethylphenyl group which is favorable for electron-injection and molecular alignment⁹ as well as the high electron affinity of **6**. The thin film of **6** deposited on SiO_2/Si substrate was investigated by X-ray diffraction (XRD) in reflection mode. The sharp and strong reflections up to the second order were observed (Fig. 3), indicating the formation of lamellar

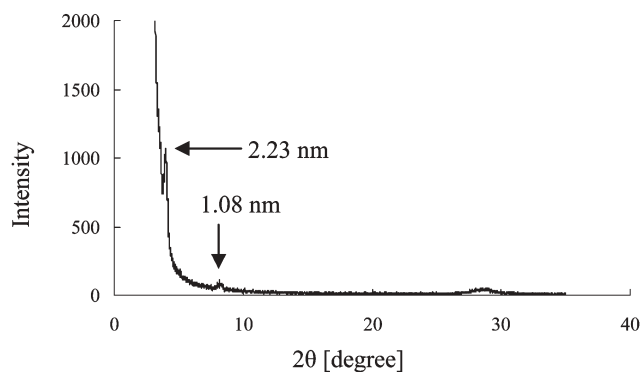


Fig. 3 X-ray diffraction of film (50 nm thickness) deposited at room temperature for **6**.

ordering and crystallinity to the substrate. The d -spacing obtained from the first reflection peak ($2\theta = 3.96$) is 2.23 nm, indicating that the molecule is almost perpendicular to the substrate since the molecular length is 2.29 nm. This is an ideal molecular arrangement on the substrate for charge transport.¹⁰ It is considered that other molecules **3–5** were not arranged in such a manner on the substrate since no peaks were observed in the XRD measurements.

In conclusion, we have explored novel dithiazolylbenzothiadiazole derivatives which show efficient fluorescence with high electron affinity. The trifluoromethylphenyl derivative could be used as an active layer for a high performance n-type FET. Since substituents can be easily introduced to the α -position of thiazole, the dithiazolylbenzothiadiazole unit would be useful as a core for unique electron-accepting π -conjugated molecules.

This work was supported by the The 21st Century COE program and a Grant-in-Aid for Scientific Research on Priority Areas (No. 15073212) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Md. Akhtaruzzaman,^a Naoto Kamata,^a Jun-ichi Nishida,^a Shinji Ando,^a Hirokazu Tada,^b Masaaki Tomura^b and Yoshiro Yamashita^{*a}

^aTokyo Institute of Technology, 4259-Nagatsuta, Midori-ku, Yokohama, 226-8502, Japan. E-mail: yoshiro@echem.titech.ac.jp; Fax: +81-45-924-5489; Tel: +81-45-924-5571

^bInstitute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

Notes and references

† Crystal data of **1**. The measurement of **1** was made on a RAXIS-RAPID Imaging Plate diffractometer with Mo-K α radiation ($\lambda = 0.71075$ 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 the calculated positions. Absorption correction was applied using an empirical procedure. C₁₂H₆N₄S₃, $M = 302.39$, crystal dimension $0.30 \times 0.15 \times 0.07$ mm, monoclinic, space group $P2_1/c$, $a = 4.941(6)$, $b = 17.81(2)$, $c = 13.56(2)$ Å, $\beta = 90.62(5)$, $V = 1193.0(9)$ Å³, $Z = 4$, $D_C = 1.683$ g cm⁻³, $F(000) = 616$, 10939 reflection collected, 2667 independent ($R_{int} = 0.037$), G.O.F = 0.81, 172 parameters, $R_I = 0.035$, $wR_2 = 0.057$ for all reflections. CCDC reference number 265881. See <http://www.rsc.org/suppdata/cc/b5/b503814f/> for crystallographic data in CIF or other electronic format.

- 1 C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.*, 2002, **14**, 99; Y. Sun, Y. Liu and D. Zhu, *J. Mater. Chem.*, 2005, **15**, 53.
- 2 B. Xu, X. Xiao, X. Yang, L. Zang and N. Tao, *J. Am. Chem. Soc.*, 2005, **127**, 2386; C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J.-L. Brédas, P. C. Ewbank and K. R. Mann, *Chem. Mater.*, 2004, **16**, 4436.
- 3 M. T. S. Ritonga, H. Sakurai and T. Hirao, *Tetrahedron Lett.*, 2002, **43**, 9009; Y. Yamashita, K. Suzuki and M. Tomura, *Synth. Met.*, 2003, **133**, 341; S.-I. Kato, T. Matsumoto, T. Ishi-i, T. Thiemann, M. Shigeiwa, H. Goroamaru, S. Maeda, Y. Yamashita and S. Mataka, *Chem. Commun.*, 2004, 2342.
- 4 J.-M. Raimundo, P. Blanchard, H. Brisset, S. Akoudad and J. Roncali, *Chem. Commun.*, 2000, 939.
- 5 M. Jayakannan, P. A. Van Hal and R. A. J. Janssen, *J. Polym. Sci. Part A: Polym. Chem.*, 2002, **40**, 2360; Y. Yamashita, K. Suzuki and M. Tomura, *Synth. Met.*, 2003, **133**, 341; C. J. Tonzola, M. M. Alam, W. Kaminsky and S. A. Jenekhe, *J. Am. Chem. Soc.*, 2003, **125**, 13548.
- 6 D. Peters, A.-B. Hörmfeldt and S. Gronowitz, *J. Heterocycl. Chem.*, 1990, **27**, 2165.
- 7 K. Pilgram, M. Zupan and R. Skiles, *J. Heterocycl. Chem.*, 1970, **7**, 629.
- 8 Md. Akhtaruzzaman, M. Tomura, J. Nishida and Y. Yamashita, *J. Org. Chem.*, 2004, **69**, 2953.
- 9 S. Ando, J.-I. Nishida, H. Tada, Y. Inoue, S. Tokito and Y. Yamashita, *J. Am. Chem. Soc.*, 2005, **127**, 5336.
- 10 A. J. Lovinger, D. D. Davis, A. Dodabalapur and H. E. Katz, *Chem. Mater.*, 1996, **8**, 2836; T. Yamamoto, H. Kokubo, M. Kobashi and Y. Sakai, *Chem. Mater.*, 2004, **16**, 4616.