Synthesis of Novel Spiro-condensed Dithienosiloles and the Application to Organic FET

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Spirobi(dithienosilole)s were prepared and their optical and FET properties were studied. They showed absorption maxima at 358–368 nm, a little red shifted from those of the corresponding non-spiro type dithienosiloles, indicating that spiro-conjugation operates in these molecules to an extent. The field-effect hole mobility of spirobi[bis(trimethylsilyl)dithienosilole] was determined to be 1.4×10^{-6} cm^2 V^{-1} s^{-1}.

A couple of years ago, we have initiated studies concerning the synthesis and properties of dithienosilole derivatives having a silole system condensed with a bithiophene system (DTS).[1] In these molecules, the silicon bridge retains the coplanarity of two thiophene rings to enhance the conjugation and, moreover, interaction between σ^* orbital of the silole silicon and π^* orbital of the inner ring butadiene unit lowers the LUMO energy level, making it possible to use these compounds as electron transporting materials for EL devices.[2] It was also found that some polymers having DTS units in the backbone would be used as hole-transports in EL devices.[3] In an effort to explore further the scope of the dithienosilole system, we prepared spiro-condensed ones as the novel σ–π conjugated compounds.

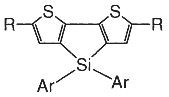
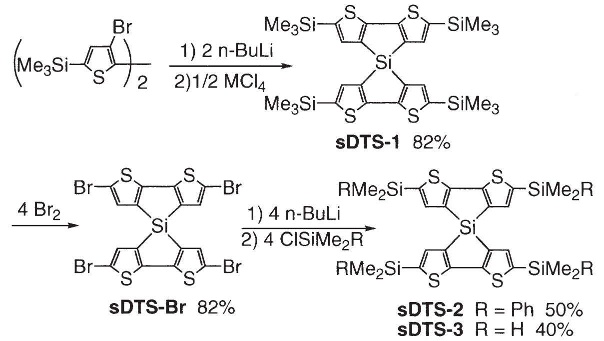


Chart 1. Dithienosilole (**DTS**)

Spiro-condensed dithienosiloles were readily obtained, as shown in Scheme 1.[4] Thus, the reaction of 3,3′-dilithio-5,5′-bis(trimethylsilyl)-2,2′-bithiophene with tetrachlorosilane gave spirobi[2,6-bis(trimethylsilyl)dithienosilole] (**sDTS-1**), as the pale yellow crystals whose melting point was observed at 308 °C by DSC higher than those of simple DTS derivatives; e.g., **DTS-1** (R = SiMe$_3$, Ar = Ph in Chart 1) melted at 158–160 °C.[2] Similar increase of morphological thermal stability of π-conjugated systems by spiro-condensation has been often observed.[5] Subsequent bromination of **sDTS-1** gave **sDTS-Br**. Lithiation of **sDTS-Br** with *n*-butyllithium, followed by treatment with chlorosilanes gave substitution products **sDTS-2** and **sDTS-3**. They melted at 204–205 °C and 223–225 °C, respectively. The present **sDTS** exhibited UV absorption and emission maxima at 366–368 nm (ε 21,000–26,000) and 434–436 nm (Φ 0.10–0.17), respectively, which were red-shifted from those of **DTS-1** by about 10 nm.[2] Cyclic voltammometric analysis of **sDTS-1** in THF/acetonitrile = 1/4 revealed an irreversible oxidation peak at 0.93 V vs Ag/Ag$^+$, at almost the same potential as that of **DTS-1**.



Scheme 1. Preparation of **sDTS**.

To know more about the electronic states of the present **sDTS**, we carried out molecular orbital (MO) calculations of the models, at the level of HF/6-31G*.[6] As shown in Figure 1, both HOMO and LUMO energy levels are affected by spiro-condensation leading to a decrease of the HOMO–LUMO energy gap, presumably by through space interaction between two orthogonal bithiophene π-orbitals, namely spiro-conjugation.[7] It is also noted that σ^*–π^* interaction takes place efficiently in the spiro-condensed system, as indicated by the LUMO orbital profile that shows mixing of Si σ^* and thiophene π^* orbitals clearly (Figure 1), similar to **DTS**.

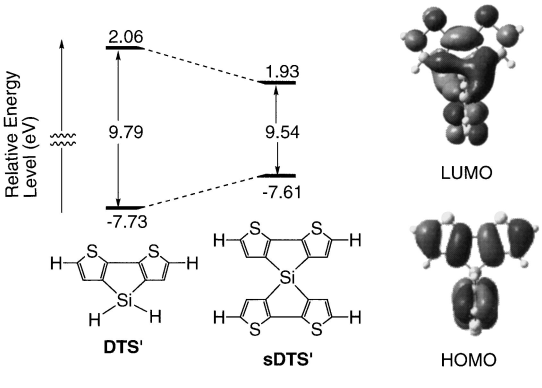


Figure 1. Relative HOMO and LUMO energy levels for model compounds, derived from MO calculations, and HOMO and LUMO orbital profiles for **sDTS**.

The crystal structure of **sDTS-1** was determined by a single crystal X-ray diffraction study and the ORTEP drawing is depicted in Figure 2.[8] Two dithienosilole rings of **sDTS-1** retain high coplanarity and are located in a perpendicular fashion to each other. The bond distances and angles in DTS systems closely resemble those of **DTS-2** (R = H, Ar = Ph in Chart 1),[1] indicating configuration strain arising from the spiro-condensation is negligible if at all present.

We examined a vapor-deposited film of **sDTS-1** as an FET semiconductor.[9] Figure 3 shows typical plots of the i_d versus V_d

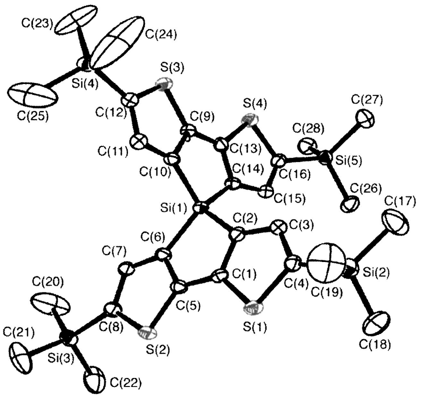


Figure 2. ORTEP drawing of **sDTS-1**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

at various V_g for the FET based on **sDTS-1**. The channel conductance increases as V_g becomes more negative, implying that the **sDTS-1** film behaves as a p-channel semiconductor. The field-effect hole mobility μ_{FET} estimated for the **sDTS-1** film was $1.4 \times 10^{-6}\,cm^2\,V^{-1}\,s^{-1}$. Although the mobility was still low, this may be improved by optimization of the deposition conditions that are known as important factors for the FET performance. **sDTS-1** is the first example of FET active oligothiophene derivatives having π-conjugated units shorter than quauterthiophene.[10] Moreover, **DTS-1** did not show any FET activities, indicating that the spiro-condensation is responsible for the FET properties of **sDTS-1**. Spiro-condensed compounds with orthogonal chromophores have been extensively studied as organic electronic materials.[5] However, no FET properties of these compounds have not yet been reported.

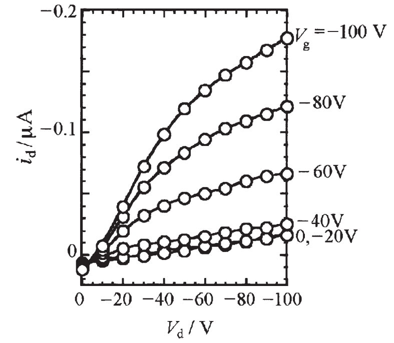


Figure 3. i_d vs V_d curves at different gate biases for the OFET device using a thin film of **sDTS-1** as the active layer.

In conclusion, we prepared novel spiro-condensed dithienosiloles by a readily accessible process. The elevated melting points by spiro-condensation seem to suggest the improved morphological stability in films. In addition, the preparation and reactions of **sDTS-Br** may allow further transformation of the spiro-compounds, leading to such as polymers and dendrimers. We also demonstrated the potential utilities of these types of the compounds as the FET materials, which may provide a new strategy for the molecular designing.

References and Notes

1 J. Ohshita, M. Nodono, T. Watanabe, Y. Ueno, A. Kunai, Y. Harima, K. Yamashita, and M. Ishikawa, *J. Organomet. Chem.*, **553**, 487 (1998).

2 J. Ohshita, M. Nodono, H. Kai, T. Watanabe, A. Kunai, K. Komaguchi, M. Shiotani, A. Adachi, K. Okita, Y. Harima, K. Yamashita, and M. Ishikawa, *Organometallics*, **18**, 1453 (1999).

3 J. Ohshita, M. Nodono, A. Takata, H. Kai, A. Adachi, K. Sakamaki, K. Okita, and A. Kunai, *Macromol. Chem. Phys.*, **201**, 851 (2000); J. Ohshita, T. Sumida, A. Kunai, A. Adachi, K. Sakamaki, and K. Okita, *Macromolecules*, **33**, 8890 (2000).

4 Data for **sDTS-1**: MS m/z 644 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.32 (s, 36H), 7.07 (s, 4H); ^{13}C NMR (δ in $CDCl_3$) 0.05, 136.91, 137.16, 142.14, 157.24; ^{29}Si NMR (δ in $CDCl_3$) −6.65, −39.51. Anal. Calcd for $C_{28}H_{40}S_4Si_5$: C, 52.11; H, 6.25. Found: C, 52.14; H, 6.26%; **sDTS-2**: TOF-MS m/z 893.18; ^{1}H NMR (δ in $CDCl_3$), 0.56 (s, 24H), 7.04 (s, 4H, thiophene); 7.33–7.38 (m, 12H, *m*- and *p*-Ph), 7.56 (dd, 8H, $J =$ 7.5 and 1.9 Hz, *o*-Ph); ^{13}C NMR (δ in $CDCl_3$) −1.31, 127.90, 129.43, 133.90, 136.96, 137.54, 138.37, 140.04, 157.76; ^{29}Si NMR (δ in $CDCl_3$) −11.73, −39.37. Anal. Calcd for $C_{48}H_{48}S_4Si_5$: C, 64.52; H, 5.41. Found: C, 64.33; H, 5.46%; **sDTS-3**: MS m/z 588 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.37 (d, 24H, $J = 3.6$ Hz), 4.53 (septet, 4H, $J = 3.6$ Hz, -SiH), 7.09 (s, 4H, thiophene); ^{13}C NMR (δ in $CDCl_3$) −2.82, 136.96, 138.17, 138.58, 157.69. Anal. Calcd for $C_{24}H_{32}S_4Si_5$: C, 48.92; H, 5.47. Found: C, 49.01; H, 5.49%.

5 U. Mitschke and P. Bäuerle, *J. Chem. Soc., Perkin Trans. 1*, **2001**, 740; R. L. Wu, J. S. Schumm, D. L. Person, and J. M. Tour, *J. Org. Chem.*, **61**, 6906 (1996).

6 "Gaussian 98, revision A.9," Gaussian, Inc., Pittsburgh, PA.

7 T. Katoh, Y. Ogawa, Y. Inagaki, and R. Okazaki, *Bull. Chem. Soc. Jpn*, **70**, 1109 (1997).

8 Crystal data for **sDTS-1**: space group $I4_1/a$ (#88) with $a = 24.5701(3)$ Å, $c = 24.7008(3)$ Å, $V = 14911.6(3)$ Å^3, $Z = 16$, $D_{calcd} = 1.150\,g/cm^3$, $F(000) = 5471.00$, μ(Mo $K\alpha$) $= 4.32\,cm^{-1}$. 8507 Intensity data were collected at 108 K on a Rigaku RAXIS-RAPID imaging plate diffractometer using a $0.5 \times 0.3 \times 0.2\,mm^3$ sized crystal. 5776 unique reflections; with $I > 3°(I)$ (reflns/para = 15.44) were used in refinement; $R = 5.4$, $Rw = 8.7$%. Selected bond distances (Å) and angles (deg): Si(1)–C(2) = 1.875(6), Si(1)–C(6) = 1.869(9), Si(1)–C(10) = 1.876(6), Si(1)–C(14) = 1.865(6), S(1)–C(1) = 1.717(6), S(1)–C(4) = 1.741(6), C(1)–C(2) = 1.378(8), C(1)–C(5) = 1.462(8), C(2)–C(3) = 1.419(8), C(5)–C(6) = 1.385(8), C(2)–Si(1)–C(6) = 92.2(3), C(2)–Si(1)–C(10) = 119.6(3), C(6)–Si(1)–C(10) = 119.3(3), C(2)–Si(1)–C(14) = 116.8(3), C(6)–Si(1)–C(14) = 119.1(3), C(10)–Si(1)–C(14) = 92.3(3). Four thiophene and two silole rings in the molecule show essentially the same structural parameters, respectively. Crystallographic data for **sDTS-1** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-239560.

9 An FET based on **sDTS-1** was fabricated on doped Si wafers with a 230 nm thermally grown SiO_2 as a bottom contact type. The drain-source channel length and width are 5 µm and 20 mm, respectively. Field-effect characteristics of the device were measured under vacuum at room temperature. The field-effect mobility was calculated in the saturation regime of the i_d as shown in a previous paper. See, Y. Kunugi, K. Takimiya, K. Yamane, K. Yamashita, Y. Aso, and T. Otsubo, *Chem. Mater.*, **15**, 6 (2003). XRD measurement of the vapor-deposited film showed no signals, indicating that the film is amorphous.

10 For FET properties of oligothiophenes, see M. Melucci, M. Gazzano, G. Barbarella, M. Cavallini, F. Biscarini, P. Maccagnani, and P. Ostoja, *J. Am. Chem. Soc.*, **125**, 10266 (2003); S. Ponomarenko and S. Kirchmeyer, *J. Mater. Chem.*, **13**, 197 (2003).