Synthesis of Silicon-bridged Oligothiophenes and Applications to Thin Film Transistors

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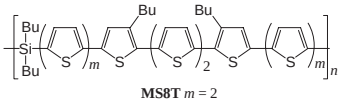
Mono- and disilanylene-bridged oligothiophenes were synthesized and their TFT properties were investigated as p-type semiconductors. Among them, the best TFT performance was achieved by using bis(ethylquinquethienyl)dibutylsilane as the active compound whose mobility and on/off ratio were determined to be 2.2×10^{-2} cm^2 V^{-1} s^{-1} and 10^5, respectively.

Over the past few years, organic thin film transistors (OTFTs) have attracted a great deal of interest due to the viewpoint of low-cost, large-area, and flexible substrates such as for flat-panel display, electronic paper, and chemical sensors.[1] It was previously reported that OTFTs with good performance have been achieved based on thiophene oligomers[2] and acene molecules like pentacene.[3]

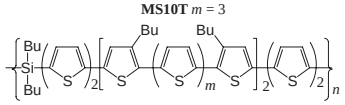
Recently, we prepared monosilanylene–oligothienylene alternating polymers (**MS8T**–**MS14T** shown in Chart 1) and examined them as p-type semiconductors for OTFTs, expecting that the silicon unit would provide the elevated HOMO energy level of the oligothiophene unit by its electron-donating properties. As expected, the polymers exhibited TFT activities even in the amorphous spin-coated films, e.g., field effect mobility (μ FET) $= 6.9 \times 10^{-5}$ cm^2 V^{-1} s^{-1} for **MS12T**.[4] To obtain superior materials based on the silicon-bridged oligothiophene system, we prepared mono- and disilanylene-bridged quarter and quinquethiophenes.

Mono- and disilanylene-bridged oligothiophenes **D*n*T-MS** and **DS** were readily prepared by the Stille cross-coupling reactions of the corresponding bis(bromothienyl)- and bis(bromobithienyl)silane and disilane[5] with 5″-ethyl-5-(tributylstannyl)terthiophene using tetrakis(triphenylphosphine)-palladium as the catalyst in moderate yield as yellow or orange solids (Scheme 1).[6] The compounds with $n = 4$ (**D4T-MS** and **DS**) were slightly soluble in chloroform and could be purified by HPLC. Whereas, **D5T-MS** and **DS** were only sparingly soluble in boiling aromatic solvents. Accordingly, the compounds with $n = 5$ were purified by sublimation or continuous washing with hot hexane in a Soxlet apparatus. Their purities were confirmed by elemental analysis.

The field effect characteristics were measured on a top-con-

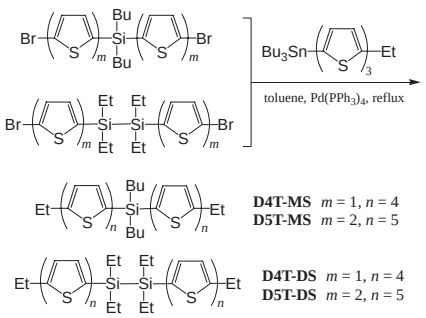


MS8T $m = 2$
MS10T $m = 3$



MS12T $m = 2$
MS14T $m = 3$

Chart 1. Monosilanylene–oligothiophene polymers (**MS*x*T**).



Scheme 1. Preparation of **D*n*T-MS** and **D*n*T-DS**.

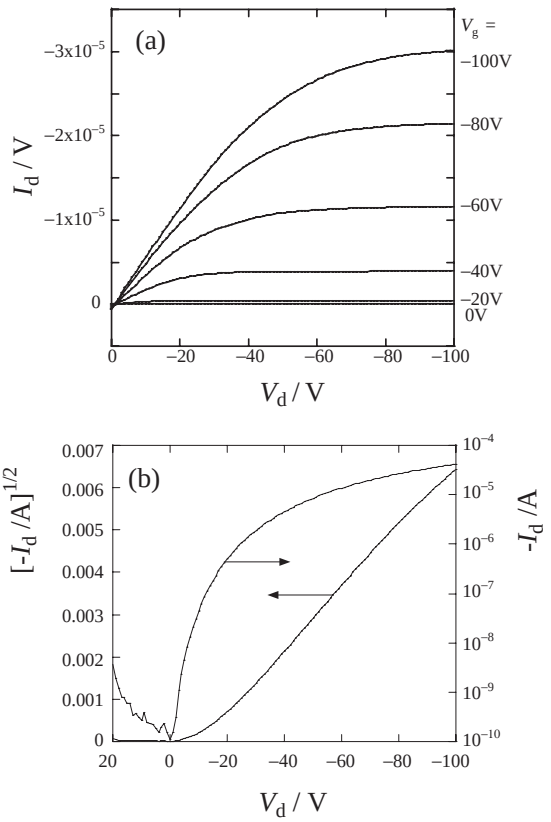


Figure 1. TFT characteristics of an exemplary OTFT with a vacuum-deposited film of **D5T-MS**, grown on a room temperature SiO_2 substrate. (a) Drain-current I_d versus drain voltage as a function of gate voltage. (b) A transfer curve in the saturated regime at a constant source–drain voltage of −100 V and square root of the absolute value of the current as a function of the gate voltage.

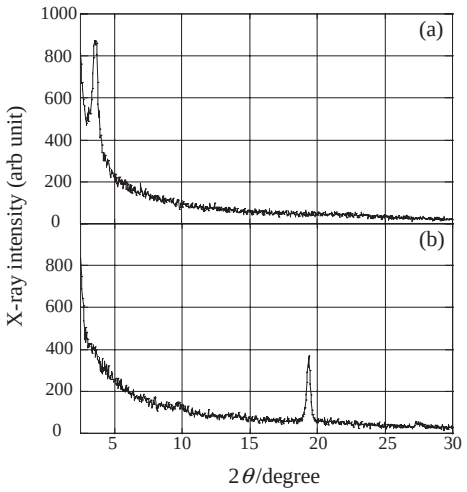


Figure 2. X-ray diffraction patterns of a vacuum-deposited film of **D4T-DS** (a) and **D4T-MS** (b) on a SiO_2 substrate.

tact type TFT on a SiO_2 substrate using gold as source and drain electrodes. The channel length (L) and width (W) were 50 μm and 1.5 mm, respectively. The organic films were prepared by vapor deposition (10^{-3} Pa) with a thickness of 40–50 nm on a substrate at ambient temperature. Although **D4T-MS** was not FET active, the OTFTs of **D4T-DS**, **D5T-MS**, and **D5T-DS** showed clear p-type semiconducting behaviors, as illustrated in Figure 1 for **D5T-MS**. The field effect hole mobilities were determined to be μ FET $= 4.5 \times 10^{-3}$ for **D4T-DS**, 2.2×10^{-2} for **D5T-MS**, and 1.5×10^{-2} $cm^2 V^{-1} s^{-1}$ for **D5T-DS**, respectively.[7] The resulting on/off ratios were 10^4 for **D4T-DS**, and 10^5 for **D5T-MS** and **DS**, respectively (on/off ratio of the I_d between $V_g = 0$ and -100 V). The mobilities of **D5T-MS** and **DS** were comparable to those of a α,ω-dihexyl-substituted quarter-, quinque-, and sexithiophenes' thin films, prepared under the conditions similar to the present experiments without controlling the substrate temperature (μ FET $= 4.4$–6.1×10^{-2} $cm^2 V^{-1} s^{-1}$),[8] and much higher than that of **MS12T**.[4]

UV absorption maxima of **D4T-MS** and **DS** appeared at 409 and 406 nm in THF, respectively, indicating similar electronic states for these compounds, in marked contrast to that they exhibited quite different TFT behaviors in films; i.e., **D4T-DS** was FET active but **D4T-MS** was not. Figure 2 shows X-ray diffraction (XRD) patterns of vacuum-deposited films of **D4T-MS** and **DS** on SiO_2 (50 nm). Clear XRD peaks corresponding to the *d*-spacing were observed at 4.6 Å for **D4T-MS** and 23.7 Å for **D4T-DS**, respectively. Interestingly, to the *d*-spacing, the **D4T-DS** molecules containing disilanylene unit stand almost perpendicular to the substrate, while **D4T-MS** molecules containing monosilanylene unit lie on the SiO_2 substrate. The different crystal packing depending on the length of the silicon bridge would be responsible for the different TFT properties of the films. The **D5T-DS** film exhibited a rather complex XRD pattern with multiple peaks.

In conclusion, we prepared silicon-bridged oligothiophene derivatives as p-type organic semiconductors with high mobilities. The X-ray diffraction studies of vacuum–deposited films indicated different crystal packing for the mono- and disilane-based compounds, which significantly affected the TFT properties of the films. These results seem to provide a new strategy of the molecular designing for TFT materials. Studies to optimize the conditions for device fabrication by changing the parameters, such as for example the substrate temperature for vapor deposition are underway.[9]

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References and Notes

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6 Data for **D4T-MS**: mp. 178–180 °C; TOF-MS *m/z* 856; ^{1}H NMR (δ in $CDCl_3$) 0.91 (t, 6H, $J = 7.1$ Hz, CH_3 of Bu), 1.08–1.12 (m, 4H, CH_2 of Bu), 1.32 (t, 6H, $J = 7.6$ Hz, CH_3 of Et), 1.36–1.48 (m, 8H, CH_2 of Bu), 2.83 (q, 4H, $J = 7.6$ Hz, CH_2 of Et), 6.69 (d, 2H, $J = 3.5$ Hz), 6.97–6.99 (m, 4H), 7.04–7.05 (m, 4H), 7.10 (d, 2H, $J = 3.9$ Hz), 7.22–7.23 (m, 4H); ^{13}C NMR (δ in $CDCl_3$) 13.68, 14.36, 15.83, 23.53, 25.84, 26.48, 123.49, 123.62, 124.11, 124.19, 124.22, 124.71, 124.92, 134.33, 134.87, 135.21, 135.87, 136.31, 136.90, 136.96, 143.11, 147. Anal. Calcd for $C_{44}H_{44}S_8Si$: C, 61.63; H, 5.17%. Found: C, 61.48; H, 5.01%; Data for **D4T-DS**: mp. 179–181 °C; TOF-MS *m/z* 886 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.99–1.07 (m, 20H, $SiCH_2CH_3$), 1.32 (t, 6H, $J = 7.6$ Hz, CH_3), 2.83 (q, 4H, $J = 7.6$ Hz, CH_2), 6.69 (d, 2H, $J = 3.4$ Hz), 7.02–7.07 (m, 8H), 7.08 (d, 4H, $J = 3.9$ Hz), 7.21 (d, 2H, $J = 3.4$ Hz); ^{13}C NMR (δ in $CDCl_3$) 5.13, 8.15, 15.73, 23.50, 123.50, 123.69, 123.95, 124.01, 124.15, 124.21, 124.40, 124.87, 134.37, 135.32, 135.79, 136.00, 136.20, 136.84, 142.39, 147.15. Anal. Calcd for $C_{44}H_{46}S_8Si_2$: C, 59.54; H, 5.22%. Found: C, 59.49; H, 5.22%; Data for **D5T-MS**: mp. 240–242 °C; Anal. Calcd for $C_{52}H_{48}S_{10}Si$: C, 61.13; H, 4.74%. Found: C, 60.89; H, 4.53%; Data for **D5T-DS**: mp. 256–258 °C; Anal. Calcd for $C_{52}H_{50}S_{10}Si_2$: C, 59.38; H, 4.79%. Found: C, 59.24; H, 4.69%.

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9 The mobility of oligothiophene was reported to be enhanced to about twice by vapor deposition of the film on the substrate at 70 °C (see Ref. 8).

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