

# Applications of Silicon-Bridged Oligothiophenes to Organic FET Materials

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Trisilanylene-bridged oligothiophenes were synthesized, and their vapor-deposited and spin-coated films were examined as p-type semiconductors in field-effect transistors (FET). Of these, the best FET performance was achieved by using tris[(ethylquinquethiophenyl)dimethylsilyl]methylsilane as the active material, whose field-effect mobility and on/off ratio were determined to be  $6.4 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $10^4$ , respectively. Interestingly, the trisilanylene-bridged oligothiophenes were found to be photoactive and the FET activity of the films was suppressed, when irradiated in air (254 nm), being potentially usable as patternable FET materials.

## Introduction

Organic field-effect transistors (FETs) have been of considerable interest, because of their utilities as, for example, flexible flat-panel displays, electronic paper, and chemical sensors.<sup>1</sup> Organic FETs of high performance have been often achieved by using expanded heteroaromatic  $\pi$ -systems including thiophene oligomers,<sup>2</sup> and acene molecules like pentacene derivatives,<sup>3</sup> as the semiconducting materials. Besides such  $\pi$ -conjugated systems, much less attention has been directed to  $\sigma$ - or  $\sigma$ - $\pi$  conjugated systems as FET materials. Recently, we have prepared monosilanylene-oligothienylene alternating polymers and examined them as p-type semiconductors for FETs, expecting that the electron-donating silicon unit and/or orbital interaction between the Si  $\sigma$ -bonds and the oligothiophene  $\pi$ -electron system would elevate the HOMO energy level of the oligothiophene unit. As expected, the polymers exhibited p-type FET activity even in the amorphous spin-coated films. However, the field-effect mobilities were rather low, ranging from  $10^{-5}$  to  $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>4</sup> In the hope of obtaining the information

for molecular designing of semiconducting materials based on the silicon-bridged oligothiophene system, we have prepared mono- and disilanylene-bridged oligothiophenes ( $n\text{T}_2\text{Si}_1$  and  $n\text{T}_2\text{Si}_2$  in Chart 1) as the models and found that the FET mobilities of their vapor-deposited films in top contact FETs were enhanced by elongation of the oligothiophene chain length.<sup>5</sup> The silicon chain length did not exert a significant influence on the FET activity of quinquethiophenes ( $n = 5$ ), but markedly affected that of quarterthiophene derivatives ( $n = 4$ ). Compound  $4\text{T}_2\text{Si}_2$  was found to be FET active in the film, while no FET activity was detected for the  $4\text{T}_2\text{Si}_1$  film. This was probably due to the difference of the film morphology between them. In fact, XRD analysis of the films indicated that the  $4\text{T}_2\text{Si}_2$  molecules stood in a perpendicular manner on the substrate to favor the carrier transport between electrodes via  $\pi$ - $\pi$  stacking, while  $4\text{T}_2\text{Si}_1$  molecules lay on the substrate.

To know more about how the silicon chain length affects the FET activity, we prepared compounds having two or three oligothiophene units bridged by a trisilanylene unit. In this study, the longer silicon bridge was anticipated to raise the HOMO energy levels by the better  $\sigma$ - $\pi$  conjugation and/or by the stronger electron donation. In addition, the more flexible trisilanylene bridge would allow the easier intermolecular  $\pi$ - $\pi$  stacking in the solid state. As expected, these oligothiophene derivatives exhibited p-type semiconducting properties in FETs. We also found that these were photoactive and irradiation of the vapor-deposited films in air decreased the hole mobility, being potentially usable as patternable semiconducting materials.

## Results and Discussion

Two types of trisilanylene-bridged oligothiophenes ( $n\text{T}_2\text{Si}_3$  and  $n\text{T}_3\text{Si}_4$ ) were synthesized as shown in Scheme 1.<sup>6</sup> Trisila-

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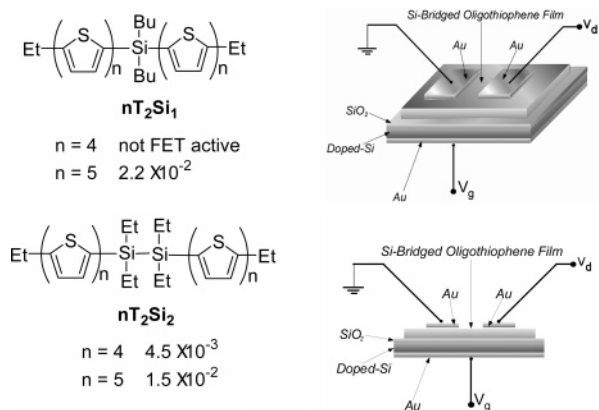
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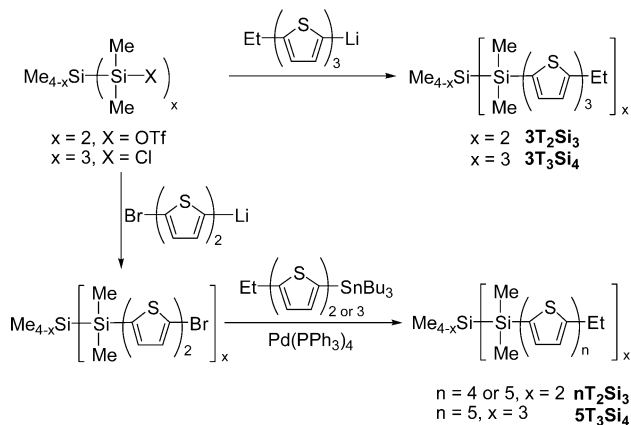
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**Chart 1. Mono- and Disilanylene-Bridged Oligothiophenes and the FET Mobilities of the Vapor-Deposited Films [ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ], and the Structure of the Top Contact FET Device System**



**Scheme 1. Synthesis of Trisilanylene-Bridged Oligothiophenes**



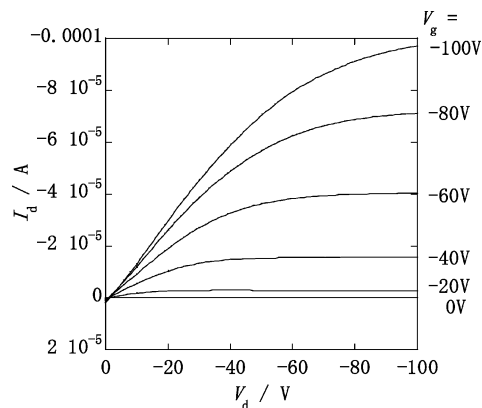
**Chart 2. UV  $\lambda_{\text{max}}$  of  $\alpha,\omega$ -Dihexyloligothiophenes and Field-Effect Mobilities of Their Films, As Reported by Marks et al. (Refs 7, 8)**

	$\lambda_{\text{max}}/\text{nm}$	$\mu_{\text{FET}}/\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$
$n = 3$	374	$2 \times 10^{-4}$
$n = 4$	402	$6.1 \times 10^{-2}$
$n = 5$	426	$5.1 \times 10^{-2}$

**Chart 3**

	$\mu_{\text{FET}}/\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ on/off ratio
$3\text{T}_2\text{Si}_4'$	not active
$4\text{T}_2\text{Si}_2\text{O}$	$1.1 \times 10^{-3}$ $10^4$
$4\text{T}_2\text{Si}_3'$	$5.9 \times 10^{-5}$ 90

nylene-bridged terthiophenes  $3\text{T}_2\text{Si}_3$  and  $3\text{T}_3\text{Si}_4$  were obtained by the reactions of terthiophenyllithium with 1,3-bis(trifluoromethanesulfonyl)hexamethyltrisilane and tris(chlorodimethylsilyl)methylsilane, respectively, while quarter- and quinquethiophene derivatives  $4\text{T}_2\text{Si}_3$ ,  $5\text{T}_2\text{Si}_3$ , and  $5\text{T}_3\text{Si}_4$  were obtained by Stille-coupling reactions of (ethylbi- and terthiophenyl)-tributyltin with 1,3-bis(bromobithiophenyl)hexamethyltrisilane and tris[(bromobithiophenyl)dimethylsilyl]methylsilane, respectively. Contrary to our expectation, UV absorption maxima of these compounds appeared at almost the same wavelength as



**Figure 1. Drain-current ( $I_d$ ) versus drain voltage ( $V_d$ ) as a function of gate voltage ( $V_g$ ) for an FET device with a vapor-deposited film of  $5\text{T}_3\text{Si}_4$ .**

**Table 1. UV Absorption Maxima, FET Performance, and XRD  $d$ -Space Values for Trisilanylene-Bridged Oligothiophenes**

oligothiophene	UV in THF $\lambda_{\text{max}}/\text{nm}$	FET performance $\mu_{\text{FET}}/\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	on/off ratio	film XRD $d$ -space/ $\text{\AA}$
$3\text{T}_2\text{Si}_3$	371	$1.9 \times 10^{-5}$	102	20.4
$4\text{T}_2\text{Si}_3$	403	$2.3 \times 10^{-4}$	103	25.3
$5\text{T}_2\text{Si}_3$	426	$5.1 \times 10^{-2}$	104	30.2, 27.4 <sup>a</sup>
$3\text{T}_3\text{Si}_4$	372	$4.4 \times 10^{-5}$	102	21.4
$5\text{T}_3\text{Si}_4$	423	$6.4 \times 10^{-2}$	104	31.1

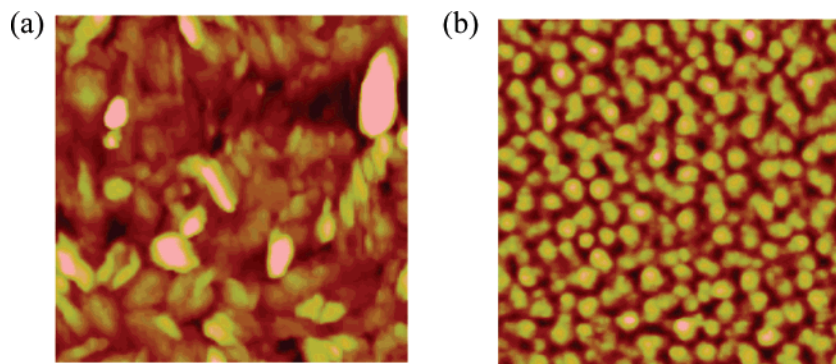
<sup>a</sup> Minor phase.

those of mono- and disilanylene-bridged analogues<sup>5</sup> and  $\alpha,\omega$ -dihexyloligothiophenes, reported previously (Chart 2).<sup>7</sup>

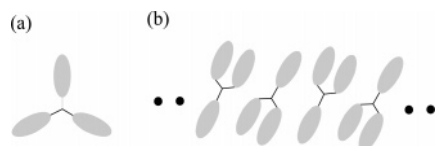
To evaluate the FET activity of the present trisilanylene-bridged oligothiophenes, we fabricated top contact type FETs having their thin solid films prepared by vapor deposition at ambient temperature as the active layers. As expected, these devices showed p-type FET activity. Figure 1 represents the FET characteristics of  $5\text{T}_3\text{Si}_4$  as a typical example, and Table 1 summarizes the FET mobilities and on/off ratios of the FETs. Interestingly, even terthiophenes  $3\text{T}_2\text{Si}_3$  and  $3\text{T}_3\text{Si}_4$  exhibited FET activity, although the mobilities were only about  $10^{-5} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ . Because monosilanylene-bridged terthiophene  $3\text{T}_2\text{Si}_1$  (Chart 1) did not show FET activity, this is indicative of the effects of the trisilanylene-linkage enhancing the semiconducting properties. These results inspired us to examine a tetrasilanylene-bridged terthiophene as an FET material. However,  $3\text{T}_2\text{Si}_4'$  (Chart 3) was not FET active in the vapor-deposited film. This is not only due to the electronic state and/or the molecular structure of  $3\text{T}_2\text{Si}_4'$ , but also to the morphology of the film. As can be seen in Figure 2a, the film of  $3\text{T}_2\text{Si}_4'$  consists of large grains, in contrast to those of trisilanylene-bridged oligothiophenes whose AFM images show more homogeneous surface with much smaller grains (for example, see Figure 2b), providing better adhesion between the grains to enhance the hole mobility.

XRD analysis of the films of all of the present trisilanylene-bridged oligothiophenes indicated that the molecules stood on the  $\text{SiO}_2$  substrate in a perpendicular fashion, similar to the case of  $4\text{T}_2\text{Si}_2$ . Quinquethiophene  $5\text{T}_2\text{Si}_3$  exhibited a rather complex XRD pattern in its film with a minor phase, which however seems to affect little the FET activity. Recently, we obtained two stable structures of  $3\text{T}_3\text{Si}_4$  by MO calculations, as shown in Figure 3, of which the folk-shaped molecule was predicted to be less stable than the fan-shaped molecule by 11.2 kcal

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**Figure 2.** AFM images of vapor-deposited films of (a)  $3T_2Si_4$  ( $4 \times 4 \mu\text{m}$ ) and (b)  $5T_3Si_4$  ( $2 \times 2 \mu\text{m}$ ).

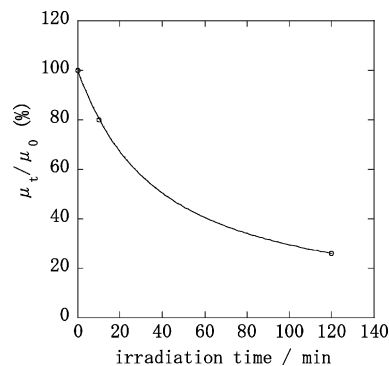


**Figure 3.** Two possible structures, (a) fan- and (b) folk-shaped types of tri(oligothiophenyl)-substituted compounds with assumed molecular alignment in the solid state.

$\text{mol}^{-1}$ .<sup>6a</sup> Similar results were obtained for analogous tri(oligothiophenyl)tetrasilanes.<sup>6b</sup> In contrast, however, the solid-state structure of tris(bromobithiophenyl)heptamethyltetrasilane was determined as possessing the folk-shaped structure by X-ray crystallographic analysis.<sup>6b</sup> Presumably, the folk-shaped structure is preferred in the solid state, because of its more dense packing and the stabilization arising from the  $\pi$ - $\pi$  stacking. This folk-shaped structure may be responsible for the XRD pattern of tri(oligothiophenyl)-substituted compounds being similar to that of di(oligothiophenyl)-substituted ones, as shown in Figure 3b.

The FET activity was found to be enhanced significantly by elongating the oligothiophene chain length from  $n = 3$  to 5. Although elongation of the silicon chain length also tends to enhance the activity, the effects of silicon chain length are not as clear as that of the oligothiophene chain. However, it must be pointed out that  $5T_2Si_3$  showed 2–3 times higher mobility than the mono- and disilanylene analogues ( $5T_2Si_1$  and  $5T_2Si_2$ ).<sup>5</sup> To know more about the effects of the oligosilanylene chain,  $4T_2Si_2O$  (Chart 3) was prepared, and the FET activity was compared to that of di- and trisilanylene derivatives. The FET activity of the films was improved in the order of  $4T_2Si_3 < 4T_2Si_2O < 4T_2Si_2$ . This may indicate that the  $\sigma$ - $\pi$  conjugation between the oligothiophene units and the silanylene bridge is not so important as we expected, although there must be some factors operative other than the molecular structure, such as film morphology and molecular alignment in the solid film, as mentioned above.

The best FET performance was achieved with tris(quinquethiophenyl) compound  $5T_3Si_4$ . Both  $3T_2Si_4$  and  $5T_3Si_4$  showed slightly higher mobilities than those of  $3T_2Si_3$  and  $5T_2Si_3$ , respectively. This may be due to the increased number of the oligothiophene units in the molecule, which enhances the intermolecular  $\pi$ - $\pi$  interaction in the solid states. Intramolecular  $\pi$ - $\pi$  stacking as represented in Figure 3b also may be a reason for the improved FET activity. The mobilities of the present trisilanylene-bridged ter- and quinquethiophenes were comparable to those of  $\alpha,\omega$ -dihexyloligothiophenes with the same oligothiophene chain length reported by Marks et al. (Chart 2),<sup>8</sup> except for  $4T_2Si_3$  whose mobility was determined to be



**Figure 4.** Trace of field-effect mobility ( $\mu_{\text{FET}}$ ) of the  $5T_3Si_4$ -based FET on irradiation with a low-pressure mercury lamp in air.

**Table 2.** FET Performance of Devices Having Spin-Coated  $4T_2Si_3$  Films

annealing temp/°C	$\mu_{\text{FET}}/\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	on/off ratio
not annealed	$1.1 \times 10^{-3}$	$10^3$
60	$4.1 \times 10^{-3}$	$10^4$
100	$2.9 \times 10^{-3}$	$10^2$

much smaller than that of dihexylquarterthiophene. We also prepared 1,3-bis(hexylquarterthiophenyl)hexamethyltrisilane ( $4T_2Si_3'$ , see Chart 3), but the FET mobility was only  $5.9 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ .

It is known that deposition temperature of organic compounds sometimes affects considerably the FET properties of the films. However, in the present case, no evident influence of the deposition temperature was observed. The film of  $5T_3Si_4$  prepared on the substrate heated at  $60^\circ\text{C}$  showed the mobility of  $5.4 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , comparable to that prepared at ambient temperature. Annealing the  $5T_3Si_4$  film again affected little the FET activity. The mobilities of the films of  $5T_3Si_4$  annealed at 60 and  $100^\circ\text{C}$  were determined to be  $4.9 \times 10^{-2}$  and  $3.3 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , respectively.

FET activity of a spin-coated film of  $4T_2Si_3$  was also examined, and the results are shown in Table 2. Interestingly, the spin-coated film showed better FET activity than that of the vapor-deposited one. Annealing the spin-coated film led to even better activity. In contrast to this, a spin-coated film of hexyl derivative  $4T_2Si_3'$  did not show detectable FET activity. Annealing the film did not affect the results. The trisilanylene-bridged quinquethiophenes were hardly soluble in organic solvents, and therefore they could not be processed to films by spin-coating.

These compounds were found to be photoactive in the films in air. Figure 4 shows the changes of the FET activity of  $5T_3Si_4$  on irradiation of the film with a low-pressure mercury lamp (254 nm) in air. The mobility decreased along the irradiation

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time, reaching ca. 1/5 of the initial value. Such photodegradation of silicon-based materials in air is not unexpected and would be due to the photooxidation of the compounds.<sup>9</sup>

In conclusion, we prepared several trisilanyl-bridged oligothiophenes and found that they were FET active in their vapor-deposited films. One of them showed high mobilities also in the spin-coated films. On the basis of the results described above, we conclude that star-shaped molecules with oligothiophene units linked by an organosilanyl core are hopeful as FET materials. In addition, these compounds were found to be photoactive, and irradiation of the film led to a decrease of the FET activity, indicating that the present oligothiophenes are potentially usable as novel patternable semiconducting materials. Patterning of semiconducting materials is an important process to fabricate FETs, locating the active materials at appropriate positions with complete isolation from each others.<sup>10</sup> The present method would provide a novel method to pattern FET materials, without a development process. Studies to increase the contrast of mobilities between the irradiated and nonirradiated areas are underway.

## Experimental Section

**General.** All reactions were carried out in dry nitrogen. Toluene and ether, used as the reaction solvents, were dried over sodium and distilled just before use. EI-MS was measured on a Shimadzu QP5050A spectrometer. NMR spectra were measured on a JEOL model LA-400 spectrometer (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C). FAB-MS was measured at the Natural Science Center for Basic Research and Development, Hiroshima University. Synthesis of **3T<sub>2</sub>Si<sub>3</sub>**, **3T<sub>3</sub>Si<sub>4</sub>**, and **5T<sub>3</sub>Si<sub>4</sub>** was reported previously.<sup>6a</sup> Hydrolytic workup mentioned below involves hydrolysis of the reaction mixture with water, separation of the organic layer, extraction of the aqueous layer with ether, drying the combined organic layer and extracts over anhydrous magnesium sulfate, and evaporation of the solvent, in this order.

**Preparation of 1,3-Bis(5'-bromo-2,2'-bithiophenyl)hexamethyltrisilane.** To a solution of 5-bromo-5'-lithio-2,2'-bithiophene prepared from 5.0 g (15 mmol) of dibromobithiophene and an equimolar amount of a *n*-butyllithium hexane solution in 50 mL of ether was added 2.8 g (6.0 mmol) of 1,3-bis(trifluoromethanesulfonyl)hexamethyltrisilane at -80 °C, and the resulting mixture was stirred for 24 h at room temperature. After hydrolytic workup, the residue was subjected to silica gel column chromatography with hexane as eluent to give 2.3 g (3.4 mmol, 57% yield) of the title compound as a light yellow solid: mp 49–51 °C; EI-MS *m/z* 662 (*M*<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 0.17 (s, 6H, CH<sub>3</sub>Si), 0.35 (s, 12H, CH<sub>3</sub>Si), 6.85 (d, 2H, *J* = 3.8 Hz, ring H), 6.93 (d, 2H, *J* = 3.8 Hz, ring H), 6.96 (d, 2H, *J* = 3.4 Hz, ring H), 7.10 (d, 2H, *J* = 3.4 Hz, ring H); <sup>13</sup>C NMR ( $\delta$  in CDCl<sub>3</sub>) -6.74 (CH<sub>3</sub>Si), -2.06 (CH<sub>3</sub>Si), 110.84, 123.65, 125.23, 130.57, 134.83, 138.92, 139.10, 141.47 (ring carbons). Anal. Calcd for C<sub>22</sub>H<sub>26</sub>Br<sub>2</sub>S<sub>4</sub>Si<sub>3</sub>: C, 39.87; H, 3.95. Found: C, 39.96; H, 3.98.

**Preparation of Stannyloligothiophenes.** To a solution of 0.81 g (3.0 mmol) of 5-bromo-5'-ethyl-2,2'-bithiophene in 10 mL of ether was added an equimolar amount of a *n*-butyllithium hexane solution at -80 °C, and the mixture was stirred for 1 h at room temperature. To this was added 1.0 g (3.1 mmol) of tributyltin chloride, and the resulting mixture was stirred for 2 h at room temperature. After hydrolytic workup, the residue was distilled under reduced pressure to give 1.3 g (2.7 mmol, 92% yield) of 5'-ethyl-5-(tributylstannyl)-

2,2'-bithiophene as a light yellow oil. This sample contained a trace amount of tetrabutyltin, but was used for the following reactions without further purification: bp 230–250 °C (1 mmHg); <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 0.89 (t, *J* = 7.2 Hz, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.07–1.12 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.26–1.39 (m, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> and CH<sub>3</sub>-CH<sub>2</sub>), 1.53–1.65 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.82 (q, 2H, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>), 6.67 (d, 1H, *J* = 3.6 Hz, ring H), 6.97 (d, 1H, *J* = 3.6 Hz, ring H), 7.02 (d, 1H, *J* = 3.4 Hz, ring H), 7.20 (d, 1H, *J* = 3.4 Hz, ring H).

Other stannyloligothiophenes, 5'-hexyl-5-(tributylstannyl)-2,2'-bithiophene and 5'-ethyl-5-(tributylstannyl)-2,2':5',2''-terthiophene, were prepared in a fashion similar to that above. They were less volatile than 5'-ethyl-5-(tributylstannyl)-2,2'-bithiophene and could not be purified by distillation. They were used for the following reactions after removal of volatile substances under reduced pressure.

**Preparation of 4T<sub>2</sub>Si<sub>3</sub>.** A mixture of 0.10 g (0.15 mmol) of 1,3-bis(5'-bromo-2,2'-bithiophenyl)hexamethyltrisilane, 0.15 g (0.32 mmol) of 5'-ethyl-5-(tributylstannyl)-2,2'-bithiophene, 8.8 mg (5 mmol%) of Pd(PPh<sub>3</sub>)<sub>4</sub>, and 1.4 mg (5 mmol%) of CuI in 5 mL of toluene was heated at 110 °C for 48 h. After filtration, the solvent was evaporated and the residue was subjected to preparative GPC using benzene as eluent to give the crude compound. Recrystallization of the crude compound from chloroform gave 0.024 g (0.026 mmol, 17% yield) of **4T<sub>2</sub>Si<sub>3</sub>** as a yellow powder: mp 205–207 °C; FAB-MS 888 (*M*<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 0.19 (s, 6H, CH<sub>3</sub>Si), 0.37 (s, 12H, CH<sub>3</sub>Si), 1.32 (t, 6H, *J* = 7.5 Hz, CH<sub>3</sub>CH<sub>2</sub>), 2.83 (q, 4H, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>), 6.67 (d, 2H, *J* = 3.6 Hz, ring H), 6.94–7.01 (m, 12H, ring H), 7.15 (d, 2H, *J* = 3.4 Hz, ring H); <sup>13</sup>C NMR ( $\delta$  in CDCl<sub>3</sub>) -6.68 (CH<sub>3</sub>Si), -1.99 (CH<sub>3</sub>Si), 15.78 (CH<sub>3</sub>-CH<sub>2</sub>), 23.56 (CH<sub>2</sub>CH<sub>3</sub>), other carbon signals could not be observed due to the low solubility. Anal. Calcd for C<sub>42</sub>H<sub>44</sub>S<sub>8</sub>Si<sub>3</sub>: C, 56.71; H, 4.99. Found: C, 56.42; H, 4.89.

**Preparation of 5T<sub>2</sub>Si<sub>3</sub>.** A mixture of 0.10 g (0.15 mmol) of 1,3-bis(5'-bromo-2,2'-bithiophenyl)hexamethyltrisilane, 0.23 g (0.41 mmol) of 5'-ethyl-5-(tributylstannyl)-2,2':5',2''-terthiophene, 3.8 mg (2 mol %) of Pd(PPh<sub>3</sub>)<sub>4</sub>, and 0.8 mg (3 mmol%) of CuI in 5 mL of toluene was heated at 110 °C for 48 h. The resulting precipitate was collected by filtration and washed with ether in a Soxhlet extraction apparatus to give 0.12 g (0.12 mmol, 80% yield) of **5T<sub>2</sub>Si<sub>3</sub>** as an orange solid. Anal. Calcd for C<sub>50</sub>H<sub>48</sub>S<sub>10</sub>Si<sub>3</sub>: C, 56.99; H, 4.59. Found: C, 56.93; H, 4.53. Because of the low solubility, spectrometric analysis could not be carried out.

**Preparation of 4T<sub>2</sub>Si<sub>2</sub>O.** To a solution of 0.15 g (0.17 mmol) of **4T<sub>2</sub>Si<sub>2</sub>** in 10 mL of THF was added 0.03 g (0.25 mmol) of trimethylamine oxide at room temperature, and the mixture was heated to reflux for 12 h. After evaporation of the solvent, the residue was sublimed under reduced pressure to give 0.13 g (82% yield) of **4T<sub>2</sub>Si<sub>2</sub>O** as a yellow solid: mp 193–195 °C; TOF-MS *m/z* 902; <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 0.85 (q, 8H, *J* = 7.6 Hz, CH<sub>2</sub> of SiEt), 1.02 (t, 12H, *J* = 7.6 Hz, CH<sub>3</sub> of SiEt), 1.32 (t, 6H, *J* = 7.56 Hz, CH<sub>3</sub> of ethyl), 2.83 (q, 4H, *J* = 7.56 Hz, CH<sub>2</sub>), 6.68 (d, 2H, *J* = 3.4 Hz), 6.96 (d, 4H, *J* = 3.68 Hz), 7.01 (d, 2H, *J* = 3.64 Hz), 7.02 (d, 2H, *J* = 3.68 Hz), 7.07 (d, 2H, *J* = 3.68 Hz), 7.15 (d, 2H, *J* = 3.16 Hz), 7.20 (d, 2H, *J* = 3.4 Hz); <sup>13</sup>C NMR ( $\delta$  in CDCl<sub>3</sub>) 6.74, 7.76, 15.84, 23.53, 123.42, 123.60, 124.06, 124.16, 124.53, 124.70, 134.37, 135.22, 135.52, 136.02, 136.12, 136.61, 136.82, 140.93, 142.39, 147.12. Anal. Calcd for C<sub>44</sub>H<sub>46</sub>OS<sub>8</sub>Si<sub>2</sub>: C, 58.49; H, 5.13. Found: C, 58.73; H, 5.18.

**Preparation of 4T<sub>2</sub>Si<sub>3</sub>'.** A mixture of 0.051 g (0.077 mmol) of 1,3-bis(5'-bromo-2,2'-bithiophenyl)hexamethyltrisilane, 0.11 g (0.17 mmol) of 5'-hexyl-5-(tributylstannyl)-2,2'-bithiophene, 0.9 mg (1 mol %) of Pd(PPh<sub>3</sub>)<sub>4</sub>, and 0.2 mg (1 mmol%) of CuI in 5 mL of toluene was heated at 110 °C for 48 h. After filtration, the solvent was evaporated, and the residue was subjected to preparative GPC using benzene as eluent to give 0.054 g (0.054 mmol, 70% yield) of **4T<sub>2</sub>Si<sub>3</sub>'** as a yellow solid: mp 158–160 °C; FAB-MS *m/z* 1000

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(M<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 0.19 (s, 6H, CH<sub>3</sub>Si), 0.37 (s, 12H, CH<sub>3</sub>Si), 0.89 (br t, 6H,  $J = 6.5$  Hz, CH<sub>3</sub>CH<sub>2</sub>), 1.30–1.39 (m, 12H, CH<sub>2</sub>), 1.68 (qui, 4H,  $J = 7.2$  Hz, CH<sub>2</sub>), 2.78 (t, 4H,  $J = 7.4$  Hz, CH<sub>2</sub>), 6.66 (d, 2H,  $J = 3.4$  Hz, ring H), 6.94–7.01 (m, 12H, ring H), 7.15 (d, 2H,  $J = 3.4$  Hz, ring H); <sup>13</sup>C NMR ( $\delta$  in CDCl<sub>3</sub>) –6.71 (CH<sub>3</sub>Si), –2.07 (CH<sub>3</sub>Si), 14.09, 22.58, 28.76, 30.19, 31.56 (Hex, one carbon may be overlapped), 123.35, 123.55, 124.02, 124.07, 124.26, 124.82, 124.90, 134.43, 134.87, 135.23, 135.89, 136.09, 136.77, 138.69, 142.22, 145.59 (thiophene ring carbons). Anal. Calcd for C<sub>50</sub>H<sub>60</sub>S<sub>8</sub>Si<sub>3</sub>: C, 59.95; H, 6.04. Found: C, 59.75; H, 6.03.

**Preparation of 3T<sub>2</sub>Si<sub>4</sub>'.** To a solution of 5''-ethyl-5-lithio-2,2':5',2''-terthiophene prepared from 0.10 g (0.28 mmol) of the corresponding bromide and an equimolar amount of a *n*-butyllithium hexane solution in 10 mL of ether was added 0.074 g (0.14 mmol) of 1,4-bis(trifluoromethanesulfonyl)octamethyltetrasilane at –80 °C, and the resulting mixture was stirred at room temperature for 24 h. After hydrolytic workup, the residue was subjected to preparative GPC using benzene as eluent to give 0.026 g (0.033 mmol, 24% yield) of 3T<sub>2</sub>Si<sub>4</sub>' as a yellow solid: mp 109–111 °C; FAB-MS 782 (M<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 0.12 (s, 12H, CH<sub>3</sub>Si), 0.39 (s, 12H, CH<sub>3</sub>Si), 1.31 (t, 6H,  $J = 7.5$  Hz, CH<sub>3</sub>CH<sub>2</sub>), 2.83 (q, 4H,  $J = 7.5$  Hz, CH<sub>2</sub>CH<sub>3</sub>), 6.68 (d, 2H,  $J = 3.6$  Hz, ring H), 6.96 (d, 2H,  $J = 3.4$  Hz, ring H), 6.97 (d, 2H,  $J = 3.6$  Hz, ring H), 7.02 (d, 2H,  $J = 3.6$  Hz, ring H), 7.04 (d, 2H,  $J = 3.6$  Hz, ring H), 7.18 (d, 2H,  $J = 3.6$  Hz, ring H); <sup>13</sup>C NMR ( $\delta$  in CDCl<sub>3</sub>) –5.75 (CH<sub>3</sub>Si), –1.76 (CH<sub>3</sub>Si), 15.84 (CH<sub>3</sub>CH<sub>2</sub>), 23.52 (CH<sub>2</sub>CH<sub>3</sub>), 123.29, 123.57, 124.13, 124.19, 124.83, 134.48, 134.85, 135.58, 136.65, 138.87, 142.25,

146.99 (thiophene ring carbons). Anal. Calcd for C<sub>36</sub>H<sub>46</sub>S<sub>6</sub>Si<sub>4</sub>: C, 55.19; H, 5.92. Found: C, 55.19; H, 6.23.

**Fabrication of FET Devices.** An organic film (50 nm thick) was prepared by vapor deposition (base pressure:  $1.0 \times 10^{-3}$  Pa) of trisilanylene-bridged oligothiophene on doped Si wafers with a 210 nm thermally grown SiO<sub>2</sub> as the top contact type. The 4T<sub>2</sub>Si<sub>3</sub> film was also prepared on the Si/SiO<sub>2</sub> substrate by spin-coating using a 0.4 wt % solution in CHCl<sub>3</sub> at 2000 rpm for 1 min. The drain-source channel length and width were 50  $\mu$ m and 1.5 mm, respectively. FET characteristics of the device were analyzed under vacuum at room temperature. The mobility was determined in the saturation regime of  $i_d$  as reported in the literature.<sup>11,12</sup>

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(12) A reviewer pointed out the possibility of thermal decomposition of the present trisilanylene-bridged oligothiophenes in the vapor deposition process. However, the  $d$ -space values derived from the XRD analysis agree with the molecular packing model with tilted molecules standing on the substrate. This clearly indicates that decomposition with bond scission did not occur in this process.