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Synthesis of organosilicon polymers containing donor–acceptor type π-conjugated units and their applications to dye-sensitized solar cells

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Abstract

Novel organosilicon polymers having donor–acceptor type π-conjugated units in the backbone were prepared by Stille-coupling reactions of bis(tributylstannylthienyl)silanes with diiodoquinoxialine, benzothiadiazole, and benzothiaselenazole. Dehaloganative copolymerization of di(bromothienyl)silanes and dibromoquinoxaline was also studied, which gave the corresponding random copolymer. Applications of these polymers to dye-sensitized solar cells (DSSCs) were examined and it was found that the polymer containing benzoselenadiazole units as the acceptor exhibited the best performance as the sensitizer among the present polymers.
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1. Introduction

Polymers composed of an alternating arrangement of organosilanylene and π-conjugated units are of interest [1], regarding their usefulness as functionality materials, such as for example hole-transporting materials of multi-layer EL device systems [2], active compounds for field effect transistors [3], photo- and electro-luminescent materials [3,4], and light-harvesting materials [5]. However, these studies reported so far have been restricted to the polymers having rather simple π-conjugated units. In this paper, we report the synthesis of polymers containing –SiR$_2$–D–A–D– units, where D and A are π-donating thienylene and accepting heteroaromatic units, respectively, and their applications to solar cell sensitizers. In these polymers, highly electron donating properties of the silanylene group attached to the π-donoring thienylene unit (D) would enhance the D–A interaction and its flexiblility would provide sufficient solubility of the polymers. D–A type structure is important for designing the dyes of DSSCs, since such interaction facilitates the charge separation in the photo excited states [6]. In addition, the polar heteroaromatic π-accepting unit (A) was anticipated to bind to the TiO$_2$ surface of DSSC. Applications of conjugated polymers to DSSCs as hole-transporting materials have been well examined [7]. However, to our knowledge, much less has been done for the development of polymeric sensitizing materials for DSSCs [8].

2. Results and discussion

2.1. Model reaction

First, we examined a model reaction as shown in Scheme 1 to optimize the reaction conditions for polymerization. Thus, the Stille-coupling reaction of (trimethylsilylthienyl)tributyltin (**TSn**) with diiodoquinoxaline (**QI2**) proceeded smoothly in the presence of Pd(PPh$_3$)$_4$ and CuI as the catalysts in a mixed solvent of DMF/acetonitrile (AN) = 1/1, to give the coupling product (**TQT**) almost quantitatively. As can be seen in Table 1, using CuI as

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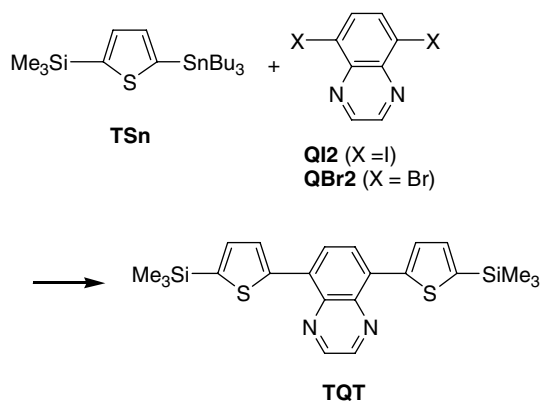
Scheme 1.

Scheme 2.

Table 1
Stille coupling reactions of **TSn** and **QX2**[a]

X	Solvent	Catalyst (5 mol%)	Yield[b] (%)
I	DMF	Pd(PPh₃)₄	49
Br	DMF	Pd(PPh₃)₄	9
I	DMF/AN[c]	Pd(PPh₃)₄/CuI	99

[a] At 80 °C for 120 h.
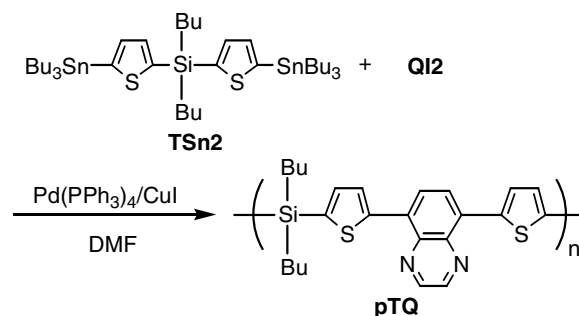[b] Isolated yield.
[c] AN = acetonitrile, DMF/AN = 1/1.

the cocatalyst was essential to obtain **TQT** in high yield. Dibromoquinoxaline (**QBr2**) was much less reactive than **QI2** under the same conditions.

2.2. Polymer synthesis

Next, copolymerization of bis(tributylstannylthienyl)silanes (**TSn2**) and iodide **QI2** was carried out in DMF/acetonitrile = 1/1 under the same conditions as optimized for the model reaction (Scheme 2). Reprecipitation of the polymeric products from chloroform–methanol or hexane gave polymer **pTQ** in 26% yield. The rather low yield of the polymer would be due to the low solubility of the polymer, which probably tended to precipitate from the reaction medium to suppress the further polymerization. In fact, a large amount of insoluble polymeric substances were produced. The yield was improved to 64% by using a better solvent DMF alone (Table 2), although the reaction in DMF required about two times longer reaction period than that in DMF/AN until the monomers were consumed. The

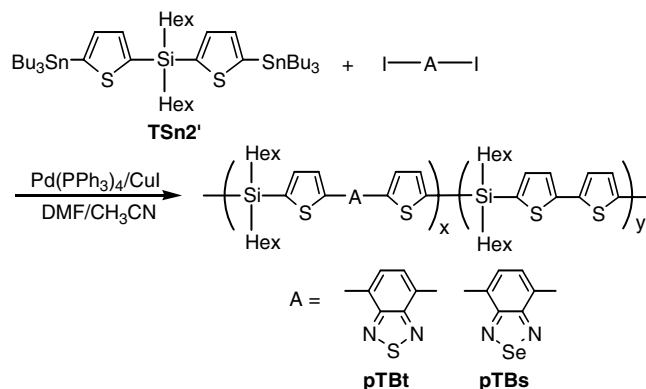NMR spectra of **pTQ** were consistent with the regular structure shown in Scheme 2 and the signal patterns of its aromatic protons and sp² carbons were quite similar to those of model compound **TQT**.

For polymers **pTBt** and **pTBs**, we used a hexyl-substituted monomer **TSn2′**, in order to improve the solubility. The polymerization was performed in DMF/AN = 3/1, since the coupling reactions no longer proceeded in DMF alone. In contrast to **pTQ**, the ¹H and ¹³C NMR spectra of **pTBt** and **pTBs** showed unidentified multiple signals in the aromatic regions, in addition to those expected from the ideal –SiHex₂-D–A–D– repeating structures. In addition, the integration ratios of benzothiadiazole and benzoselenazole sp² protons relative to those of thiophene rings were found to be much lower than expected. This seems to indicate that homo coupling reactions of **TSn2′** were involved in the polymerization, to a certain extent as shown in Scheme 3. Fig. 1 shows the ¹³C NMR spectrum of **pTBt**

Scheme 3.

Table 2
Polymer synthesis

Polymer	Yield[a] (%)	Mw[b]	Mn[b]	M.p. (°C)	UV abs λ_{max}/nm ($\varepsilon \times 10^{-3}$)[c]	Emission λ_{em}[c] (nm)
pTQ	64	6400	4100	181–185	278 (16), 320 (18), 427 (7)	546
pTBt	74	6600	4200	Oil	320 (22), 451 (9)	564
pTBs	26	6600	5100	79–105	330 (38), 482 (17)	617
r-pTQ	10	9500	6300	139–140	269 (26), 322 (36), 416 (13)	545

[a] After reprecipitation.
[b] Determined by GPC, relative to polystyrene standards.
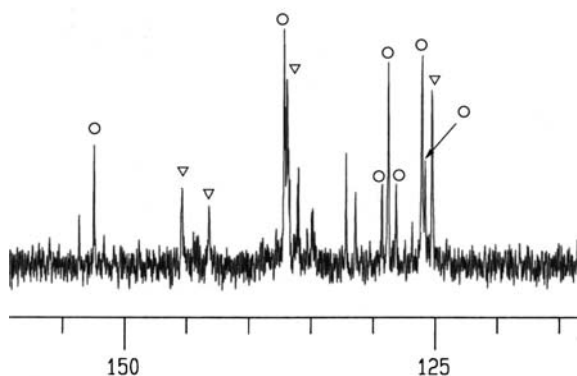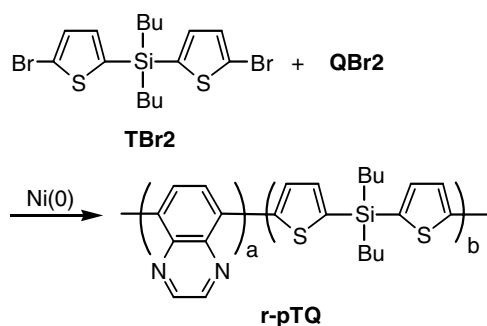[c] Excited at the absorption maximum in THF.

Fig. 1. ^{13}C NMR spectrum of **pTBt** in CDCl$_3$ (sp^2 region) with tentative assignment of dithienylenebenzothiadiazole ($\bigcirc$) and bithienylene ($\bigtriangledown$) carbons.
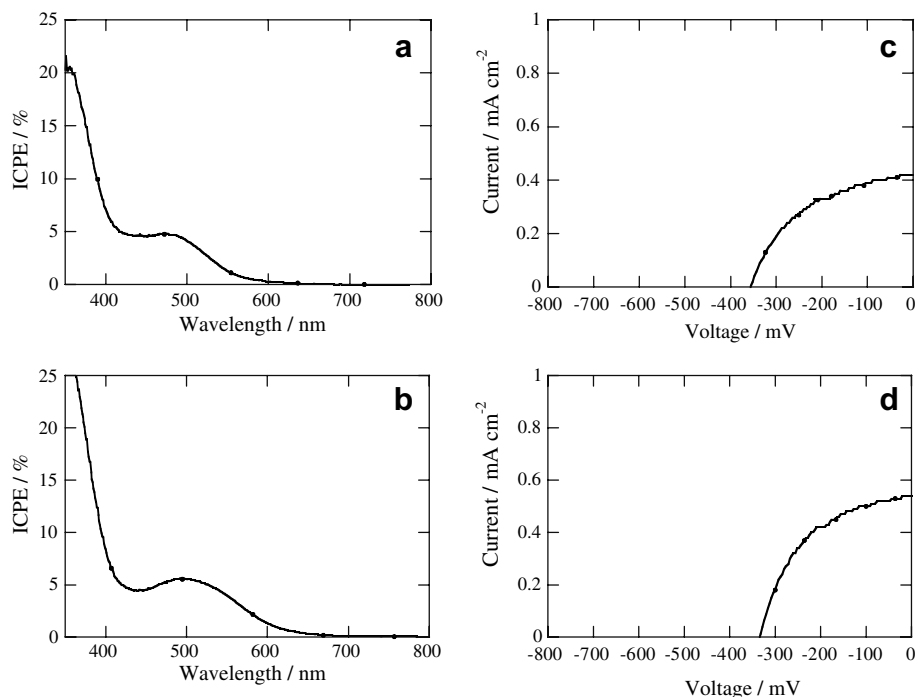

Scheme 4.

Table 3
Performance of DSSCs based on **pTBt** and **pTBs**

Polymer	IPCE$_{max}$ (%)	I_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
pTBt	4.7	0.42	358	0.40	0.06
pTBs	5.6	0.54	336	0.49	0.09

with tentative assignment made by comparison with the literature data for poly(organosilanylenebithienylene)s [9] and 2,7-di(4-hexylthienyl)benzothiadiazole [10]. However, we could not determine the exact x/y ratios, since unidentified signals with low intensities were still observed in the spectra, some of which were presumably due to the end groups. The x/y values were thus only roughly estimated by proton integration ratios to be 1.0 and 0.8 for **pTBt** and **pTBs**, respectively.

Table 2 summarizes the yields, molecular weights, and λ_{max} values of absorption and emission spectra of the polymers in THF. The absorption and emission maxima of **pTQ** appeared at almost the same energies as those of the model compound (**TQT**: $\lambda_{max} = 277, 306, 426$ nm; $\lambda_{em} = 545$ nm). These polymers showed strong fluorescence in THF, whose quantum yields were determined to be $\Phi = 0.22$ (**pTQ**), 0.31 (**pTBt**), and 0.07 (**pTBs**), relative to a solution of 9,10-diphenylanthracene as the standard ($\Phi = 0.90$). Both the absorption and emission maxima moved to longer wavelength in the order of **pTQ** < **pTBt** < **pTBs**.

We also prepared random copolymer **r-pTQ** by reductive coupling of dibromides **TBr2** and **QBr2** with a nickel (0) complex, as shown in Scheme 4. The incorporation ratio of a/b in the polymer backbone was determined approximately to be 55/45 by its ^{1}H NMR spectrum. The

Fig. 2. Performance of DSSCs with using polymers **pTBt** (a), (b) and **pTBs** (c), (d).

UV absorption and emission maxima of **r-pTQ** appeared at slightly shorter wavelength than those of **pTQ**.

2.3. Application of polymers *pTBt* and *pTBs* to sensitizers of DSSCs

We fabricated DSSCs using the present polymers as the sensitizer (FTO/TiO$_2$ · polymer/I$_2$ · I$^-$/Pt). As expected, polymers **pTBt** and **pTBs** exhibited clear sensitizing effects on the DSSC performance (Table 3). As shown in Fig. 2, the maximum photocurrents (I_{sc}) of 0.42 and 0.54 mA/cm^2 were obtained from the DSSCs, at 490 and 500 nm for the devices with **pTBt** and **pTBs**, respectively. Incident photon-to-current conversion efficiencies (IPCE) at these wavelengths were determined to be around 5% each. Other polymers were also examined as the sensitizer in DSSCs. However, they showed only ambiguous sensitizing effects.

3. Conclusion

In conclusion, we prepared novel silicon-containing polymers containing donor-acceptor type π-conjugated units. They exhibited high PL quantum yields in THF solutions. Their potential utilities as the sensitizers for DSSCs also were demonstrated. Rather low IPCEs of the present polymers may be due to their low affinity to TiO$_2$ surface. Presumably, the thiadiazole and selenadiazole units are not adequately polarized, and thus introduction of better binding sites, such as carboxylic acid groups, into the polymer structures seems be necessary to improve the DSSC performance. However, this is the first synthesis of Si-π alternating polymers that may be used as DSSC sensitizer. Further studies to develop solar cell sensitizer base on Si-π system with better properties are under way.

4. Experimental

4.1. General procedure

All reactions were carried out in dry nitrogen. DMF was dried over CaH$_2$ and distilled just before use. AN was distilled from KOH and stored over activated molecular sieves. Bromothienyltrimethylsilane [11], bis(bromothienyl)dibutylsilane [12], and monomers **QI2**, **QBr2**, diiodobenzothiadiazole, and diiodobenzoselenadiazole were prepared as described in the literature [13].

4.2. Preparation of bis(bromothienyl)dihexylsilane

To a mixture of lithiobromothiophene, prepared from 8.32 g (34.4 mmol) of dibromothiophene and 24.0 mL of a 1.6 M hexane solution of *n*-butyllithium in 40 mL of ether, was added 4.39 g (16.3 mmol) of dichlorodihexylsilane in 40 mL of ether at −80 °C. After stirring the mixture at room temperature for 20 h, the mixture was hydrolyzed with water. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was evaporated

and the residue was distilled under reduced pressure (9×10^{-6} torr) and the fraction of the boiling range of 180–220 °C was corrected to give 3.86 g of the title compound (45% yield): pale brown oil; MS *m/z* 435 (M$^+$-Hex); ^{1}H NMR (δ in CDCl$_3$) 0.86 (6H, t, CH$_3$, $J = 5.4$ Hz), 1.00 (4H, m, CH$_2$Si), 1.26 (16H, m, CH$_2$), 7.04 (2H, d, ring H, $J = 3.6$ Hz), 7.11 (2H, d, ring H, $J = 3.6$ Hz); ^{13}C NMR (δ in CDCl$_3$) 14.1 14.3, 22.6, 23.5, 31.3, 33.1, 118.1, 131.3, 136.5, 137.8. Anal. Calc. for C$_{20}$H$_{30}$Br$_2$S$_2$Si: C, 45.98; H, 5.79. Found: C, 45.79; H, 5.79%.

4.3. Preparation of *TSn*, *TSn2*, and *TSn2'*

For the preparation of compounds **TSn**, **TSn2**, and **TSn2'**, the corresponding bromides were lithiated with *n*-butyllithium in ether and the lithiated thineylsilanes were treated with tributyltin chloride. After filtration of the lithium slats and evaporation of the solvent, the residue was heated at 250 °C for 4 h under reduced pressure (ca. 1 mmHg) to remove volatile substances. The resulting viscous oil was used for the following coupling reactions without further purification.

4.4. Model reaction

A mixture containing 0.115 g (0.300 mmol) of **QI2**, 0.267 g (0.600 mmol) of **TSn**, 17 mg (5.0 mol %) of Pd(PPh$_3$)$_4$, 2.9 mg (5.0 mol%) of CuI in 6 mL of DMF/AN = 1/1 was heated at 80 °C for 5 days. The resulting mixture was poured into 100 mL of water and extracted with chloroform. After drying over anhydrous magnesium sulfate, the solvent was evaporated and the residue was subjected to chromatrapy on a silica gel column eluting with hexane/ethyl acetate = 50/1 to give 0.130 g (99% yield) of **TQT** as the yellow solids: m.p. 191°C; ^{1}H NMR (δ in CDCl$_3$) 0.38 (s, 18 H, TMS), 7.32 (d, 2H, thienylene, $J = 3.6$ Hz), 7.87 (d, 2H, thienyenel, $J = 3.6$ Hz), 8.10 (s, 2H, quinoxaline H on C2 and C3), 8.98 (s, 2H, quinoxaline H on C6 and C7); ^{13}C NMR (δ in CDCl$_3$) −0.0, 128.1, 128.7, 132.3, 134.0, 140.0, 143.3, 143.6, 143.9; UV (λ_{max} in THF) 276.8 nm ($\varepsilon = 6300$), 305.6 nm (9600), 426.0 nm (8000). Anal. Calc. for C$_{22}$H$_{26}$N$_2$S$_2$Si$_2$: C, 60.22; H, 5.97; N, 6.38. Found: C, 60.22; H, 5.98; N, 6.38%.

4.5. Polymer synthesis by Stille-coupling

A mixture containing 0.115 g (0.300 mmol) of **QI2**, 0.265 g (0.300 mmol) of **TSn2**, 17 mg (5.0 mol %) of Pd(PPh$_3$)$_4$, 2.9 mg (5.0 mol%) of CuI in 6 mL of DMF was heated at 80 °C for 2 days. The resulting mixture was poured into 100 mL of water and extracted with chloroform. The organic layer was separated and washed several times with 10% hydrochloric acid. After drying over anhydrous magnesium sulfate, the solvent was evaporated and the residue was subjected to reprecipitation from chloroform–methanol then from chrloroform–hexane to give

0.083 g (64% yield) of **pTQ** as the brown solids: ^{1}H NMR (δ in CDCl$_3$) 0.90–1.41 (m, 18H, Bu), 7.45 (br s, 2H, thienylene), 7.95 (br s, 2H, thienylene), 8.12 (br s, 2H, quinoxaline H on C2 and C3), 8.96 (br s, 2H, quinoxaline H on C6 and C7); ^{13}C NMR (δ in CDCl$_3$) 13.71, 14.54, 25.95, 26.54 (Bu), 128.1, 128.8, 132.1, 136.2, 138.6, 139.9, 143.6, 144.9.

Polymers **pTBt** and **pTBs** were obtained in a similar fashion to above. Data for **pTBt** (prepared in DMF/AN = 3/1, purified by reprecipitation from chloroform–methanol): dark brown oil; ^{1}H NMR (δ in CDCl$_3$) 0.87–1.38 (m, 26H, Hex), 7.24–7.50 (m, 2.8H, thienylene presumably including the homo coupled bithiophene protons), 7.63–7.77 (m, 0.5H, thienylene, and terminal thiophene and iodobenzothiadiazole protons), 7.88 (br s, 0.8H, thienylene), 8.22 (br s, 1.0H, benzothiadiazole protons); ^{13}C NMR (δ in CDCl$_3$) 14.13, 14.60, 22.59, 23.61, 31.39, 33.20 (Hex), 125.3, 126.1, 128.8, 132.2, 136.9, 137.1, 152.5, several minor sp^2 signals were also observed. Data for **pTBs** (prepared in DMF/AN = 3/1, purified by reprecipitation from chloroform–methanol): dark brown solid; ^{1}H NMR (δ in CDCl$_3$) 0.85–1.50 (m, 26H, Hex), 7.38–7.77 (m, 6.0H, thienylene presumably including the homo coupled bithiophene protons, and terminal thiophene and iodobenzoselenadiazole protons), 8.11 (br s, 1.3H, benzothiadiazole protons); ^{13}C NMR (δ in CDCl$_3$) 14.1, 14.6, 22.6, 23.7, 31.4, 33.2, 126.3, 128.4, 128.7, 134.5, 136.8, 145.7, several minor sp^2 signals were also observed.

4.6. Preparation of r-pTQ

A mixture of 0.050 g (0.18 mmol) of **QBr2**, 0.081 g (0.18 mmol) of **TBr2**, 0.660 g (0.42 mmol) of 2,2′-bipyridyl, 0.116 g (0.42 mmol) of Ni(cod)$_2$, and 6 mL of DMF was stirred at 60 °C for 60 h. The resulting precipitates were filtered and the filtrate was washed with water, an aqueous solution of EDTA, and then with 28% NH$_3$ (aq). After the solvents were evaporated, the residue was reprecipitated from chloroform–methanol, then from chloroform–hexane to give 0.015 g (10% yield) of **r-pTQ** as the red-brown solids: m.p. 139–140 °C; ^{1}H NMR (δ in CDCl$_3$) 0.88–1.42 (m, Bu), 7.21–7.46 (m, thienylene), 7.65 (br s, thienylene), 7.93 (br s, thienylene), 8.13 (br s, quinoxaline H on C2 and C3), 8.97 (br s, quinoxaline H on C6 and C7).

4.7. Fabrication of DSSCs

In a ball-milling apparatus was placed 1.3 g of TiO$_2$ (Degussa P-25, 80% anatase + 20% rutile). To this was added deionized water (1.86 mL) in 6 portions and the mixture was ground and mixed at ambient temperature at 300 rpm for 10 min every after the addition. Then the mixture was further mixed with 80 mg of PEG and 3–5 drops of nitric acid by ball-milling at 300 rpm for 2–3 h to give a TiO$_2$ slurry. The TiO$_2$ (5 × 5 mm^2) layer was prepared on a FTO glass plate by casting the slurry, and the plate was sintered at 500 °C for 30 min. The TiO$_2$-coated FTO glass plate was immersed in a chloroform solution of a polymer for 30 min and the plate was air-dried at room temperature. Finally, a DSSC was fabricated with a thin liquid layer of an acetonitrile solution containing LiI (0.5 M)/I$_2$ (0.05 M), which was sandwiched between the TiO$_2$/FTO and Pt counter electrodes. The DSSC thus prepared was irradiated with a monochromatic light from the FTO side and the photocurrent was monitored as a function of wavelength by a digital electrometer (Advantest TR-8652).

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