

Attachment of poly[(ethoxyhexylsilylene)oligothienylene]s to inorganic oxide surface

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Abstract

Poly[(ethoxyhexylsilylene)quarter- and -quinqethienylene]s (EHS_xT, $x = 4$ and 5) were prepared by Stille-coupling reactions of bis(bromothieryl)ethoxyhexylsilane and bis(tributylstannyl)di- and -terthiophenes, respectively. Treatment of ITO and TiO₂ electrodes with solutions of EHS_xT in chloroform at 40°C led to the formation of the polymer-attached electrodes. An application of the EHS₅T-attached TiO₂ electrode to dye-sensitized solar cell was examined.

Key words: Oligothiophene, Organic-Inorganic Hybrid, Dye-sensitized solar cell

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1. Introduction

Organic-inorganic hybrids have been well studied, because of their potential applications as functional materials. In these studies, organosiloxane bond (RSi-O-M) is often used as stable linkage to attach an organic group (R) to metal oxide surface. For example, it was demonstrated that modification of indium tin oxide (ITO) surface by treating with trichlorosilyl- or trialkoxysilyl-substituted triarylamine derivatives led to hybrid materials, in which triarylamine units were attached to the ITO surface by siloxane linkage [1, 2]. Interestingly, the modification enhanced hole-injection from ITO to an organic layer lying on its surface, being applicable to organic light emitting diodes. Recently, we reported that UV irradiation (> 400 nm) of TiO₂ electrodes in chloroform solutions of poly(disilanyleneoligothienylene)s (DS_xTs in Chart 1) led to attachment of DS_xT on the TiO₂ surface by the formation of Si-O-Ti bond, as a new method to organic-inorganic hybrids [3]. In that work, we demonstrated also potential applications of the polymer-attached TiO₂ electrodes to dye sensitized solar cells (DSSCs). It was noteworthy that such siloxane-linked chromophores could be used for DSSCs, since sensitizing dyes are usually attached to TiO₂ surface by ester bonds in DSSCs [4].

In this paper, we report the synthesis of poly[(ethoxyhexylsilylene)oligothienylene]s (EHS_xTs, $x = 4$ and 5 in Scheme 1) and preparation of the polymer-attached ITO and TiO₂ electrodes by treatment of the electrodes with EHS_xT solutions. An application of the latter to DSSCs is also described.

[Chart 1]

2. Experimental

2.1. General Procedure

All reactions were carried out in dry nitrogen. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone and stored over activated molecular sieves until use. Ethanol and triethylamine were distilled from magnesium ethoxide and potassium hydroxide, respectively, and stored in bottles sealed tightly until use. NMR, Mass, IR, and UV spectra were recorded on JEOL model LA-400, Shimadzu model QP-5050A, Shimadzu model FTIR-8700, and Hitachi model UV-2910 spectrometers, respectively. Polymer molecular weights were measured by gel permeation chromatography (GPC) using Shodex KF-804 and KF-806 columns connected in series eluting with THF. The polymers were detected by a UV detector at 240 nm and the molecular weights were calculated relative to polystyrene standards on SIC-480 data station.

2.2. Preparation of monomers **1a** and **1b**

To a solution of 24 g (0.10 mol) of 2,5-dibromothiophene in 100 mL of diethyl ether was added dropwise 63 mL (0.10 mol) of 1.59 M *n*-butyllithium/hexane at -80°C. After stirring at room temperature for 4 h, the resulting mixture containing bromothiényllithium was slowly added to 10 g (52 mmol) of trichlorohexylsilane at 0°C. After stirring at room temperature for 10 h, the mixture was filtered and the solvent was evaporated. The residue was distilled under reduced pressure to give 15 g a pale yellow oil (bp 225°C at 1 mmHg) whose NMR and mass spectral analysis indicated that it was composed of bis(bromothiényl)chlorohexylsilane (90%) and several unidentified byproducts. The distillate was used for the following reaction without further purification. Data for bis(bromothiényl)chlorohexylsilane: MS m/z 385 (for ^{79}Br , M^+ - Hex); ^1H NMR (δ in CDCl_3) 0.86 (t, $J = 6.8$ Hz, 3H, CH_3), 1.19-1.51 (m, 10H, CH_2),

7.15 (d, $J = 3.6$ Hz, 2H, ring H), 7.19 (d, $J = 3.6$ Hz, 2H, ring H); ^{13}C NMR (δ in CDCl_3) 14.07, 18.41, 22.48, 22.64, 31.24, 32.43 (Hex), 120.42, 131.61, 135.13, 137.98 (ring HC).

To a solution of 15 g of the distillate containing bis(bromothieryl)chlorohexylsilane (90% pure) and 1.5 mL (32 mmol) of ethanol in 100 mL of diethyl ether was added slowly 3.2 g (32 mmol) of triethylamine at 0°C and the mixture was stirred at room temperature for 6 h. After filtration of ammonium chloride, the solvent was evaporated and the residue was distilled under reduced pressure to give 9.8 g (38% yield from trichlorohexylsilane) of compound **1a** as a pale yellow oil: bp 229°C (2.5 mmHg); GC-MS m/z 482 (for ^{79}Br , M^+), 397 (for ^{79}Br , $\text{M}^+ - \text{Hex}$); ^1H NMR (δ in CDCl_3) 0.86 (t, $J = 6.8$ Hz, 3H, $(\text{CH}_2)_5\text{CH}_3$), 1.03-1.09 (m, 2H, $(\text{CH}_2)_5$), 1.19 (t, $J = 6.9$ Hz, 3H, OCH_2CH_3), 1.24-1.47 (m, 8H, $(\text{CH}_2)_5\text{CH}_3$), 3.77 (q, $J = 6.9$ Hz, 2H, OCH_2CH_3), 7.12 (d, $J = 3.6$ Hz, 2H, ring H), 7.14 (d, $J = 3.6$ Hz, 2H, ring H); ^{13}C NMR (δ in CDCl_3) 14.07 ($(\text{CH}_2)_5\text{CH}_3$), 15.64 (OCH_2CH_3) 18.23, 22.53, 22.67, 31.35, 32.85 ($(\text{CH}_2)_5$), 59.75 (OCH_2CH_3), 119.01, 131.39, 136.73, 137.20 (ring HC). Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{Br}_2\text{OS}_2\text{Si}$: C, 39.84; H, 4.60. Found: C, 39.57; H, 4.19.

Compound **1b** was prepared in a manner similar to that above and purified by preparative GPC eluting with chloroform: yellow oil; MS m/z 646 (for ^{79}Br , M^+), 561 (for ^{79}Br , $\text{M}^+ - \text{Hex}$); ^1H NMR (δ in CDCl_3) 0.86 (t, $J = 6.6$ Hz, 3H, $(\text{CH}_2)_5\text{CH}_3$), 1.10-1.16 (m, 2H, $(\text{CH}_2)_5$), 1.22 (t, $J = 6.9$ Hz, 3H, OCH_2CH_3), 1.25-1.53 (m, 8H, $(\text{CH}_2)_5\text{CH}_3$), 3.82 (q, $J = 6.9$ Hz, 2H, OCH_2CH_3), 6.96 (s, 4H, ring H), 7.20 (d, $J = 3.6$ Hz, 2H, ring H), 7.29 (d, $J = 3.6$ Hz, 2H, ring H); ^{13}C NMR (δ in CDCl_3) 14.09 ($(\text{CH}_2)_5\text{CH}_3$), 15.86 (OCH_2CH_3) 18.30, 22.55, 22.79, 31.37, 32.91 ($(\text{CH}_2)_5$), 59.75 (OCH_2CH_3), 111.49, 124.32, 125.22, 130.69, 133.81, 137.49, 138.47, 143.02 (ring HC). Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{Br}_2\text{OS}_4\text{Si}$: C, 44.58; H, 4.05. Found: C, 44.78; H, 3.78.

2.3. Preparation of EHSxT

A mixture of 49 mg (0.10 mmol) of **1a**, 76 mg (0.10 mmol) of 5,5'-bis(tributylstannyl)bithiophene, 5.8 mg (5 mol%) of tetrakis(triphenylphosphine)-palladium, 1.0 mg (5 mol%) of copper iodide, and 1.1 mL of THF was heated at 150°C for 24 h in a degassed sealed glass tube. The mixture was evaporated and the residue was reprecipitated from chloroform-hexane to give 32 mg of EHS4T (65% yield) as a dark yellow solid: GPC M_w (M_w/M_n) = 18,500 (2.3); $^1\text{H NMR}$ (δ in CDCl_3) 0.76-0.88 (m, $(\text{CH}_2)_5\text{CH}_3$), 1.10-1.65 (m, $(\text{CH}_2)_5$), 3.68-3.84 (m, OCH_2CH_3), 6.86-7.39 (m, ring H); IR 1078 cm^{-1} (Si-O); UV (in CHCl_3) λ_{max} 411 nm.

Polymer EHS5T was prepared in a manner similar to that above, using 5,5''-bis(tributylstannyl)terthiophene instead of 5,5'-bis(tributylstannyl)bithiophene: dark yellow solid; GPC M_w (M_w/M_n) = 9,700 (1.8); $^1\text{H NMR}$ (δ in CDCl_3) 0.78-0.93 (m, $(\text{CH}_2)_5\text{CH}_3$), 1.10-1.54 (m, $(\text{CH}_2)_5$), 3.74-3.88 (m, OCH_2CH_3), 6.85-7.34 (m, ring H); IR 1074 cm^{-1} (Si-O); UV (in CHCl_3) λ_{max} 434 nm.

2.4. Fabrication of DSSC using EHS5T as the sensitizing dye

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 TiO_2 slurry. The TiO_2 ($5 \times 5\text{ mm}^2$) layer was prepared on an 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 EHS5T at 40°C for 3h in an argon atmosphere and the plate was washed with chloroform and air-dried at room temperature. Finally, a DSSC was fabricated with a thin liquid layer of an acetonitrile solution containing LiI

(0.5 M)/I₂ (0.05M), which was sandwiched between the TiO₂/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).

3. Results and discussion

3.1. Polymer synthesis

Previously, we reported the synthesis of poly[(ethoxypropylsilylene)oligothienylene]s (EPS_xTs, $x = 3-5$ in Chart 1) [5], while for the present study, we introduced a hexyl group to the silicon atom to increase the polymer solubility. Poly[(ethoxyhexylsilylene)oligothienylene]s (EHS_xT, $x = 4$ and 5) were prepared by Stille-coupling reactions of bis(bromothienyl)ethoxyhexylsilane (**1a**) and bis(tributylstannyl)di-, and -terthiophenes (**2a** and **2b**) in THF, as shown in Scheme 1. First, we examined polymerization of **1a** and **2a** at 70°C under the same conditions as those for the synthesis of EPS_xT, reported previously [5]. However, the reaction gave only hexane-soluble oligomers (Table 1, runs 1). We next carried out similar reactions in the presence of copper iodide as the co catalyst at the same temperature. Reprecipitation of the resulting organic products from chloroform-hexane gave polymers EHS_xT with rather low molecular weights (runs 2 and 4). Finally, EHS_xT with higher molecular weights were obtained at 150°C (runs 3 and 5) that were used for the following experiments. Less reactive properties of **1a** towards Stille coupling reaction than the propyl analog seems to be due to higher degree of electron-donation from the hexyl group, which would suppress oxidative addition of the C-Br bond to palladium (0).

¹H NMR spectra of the polymers revealed broad peaks ascribed to those of ethoxyhexylsilylene and oligoethienylene units, together with unidentified multiple

signals at 7.6-7.8 ppm with low intensities. The ^1H integration ratios of CH_2 (at ca. 3.8 ppm)/ CH_3 (at ca. 0.8 ppm) are approximately 2.8 ($x = 4$) and 2.6 ($x = 5$), higher than the theoretical value of 1.5 for OCH_2/CH_3 of hexyl, probably indicating the existence of terminal tributylstannyl groups and decomposition of Si-OEt units to produce siloxane units. Rather high polydispersities are also indicative of the formation of siloxane cross-linking units to an extent. The UV spectra of EHS x T showed the maxima at 417 nm and 436 nm for $x = 4$ and 5, respectively, at almost the same energies as those for EPS x T (411 nm for $x = 4$ and 434 nm for $x = 5$) [5]. Polymers EHS x T are dark yellow solids and soluble in chloroform, THF, toluene, and ethyl acetate, but hardly soluble in saturated hydrocarbons and alcohols. They are stable in the solid state and can be stored in air. We examined polymerization of **1b** and **2a** expecting EHS 6 T. However, only a polymer whose absorption maximum appears at 434 nm, similar to that of EHS 5 T was obtained.

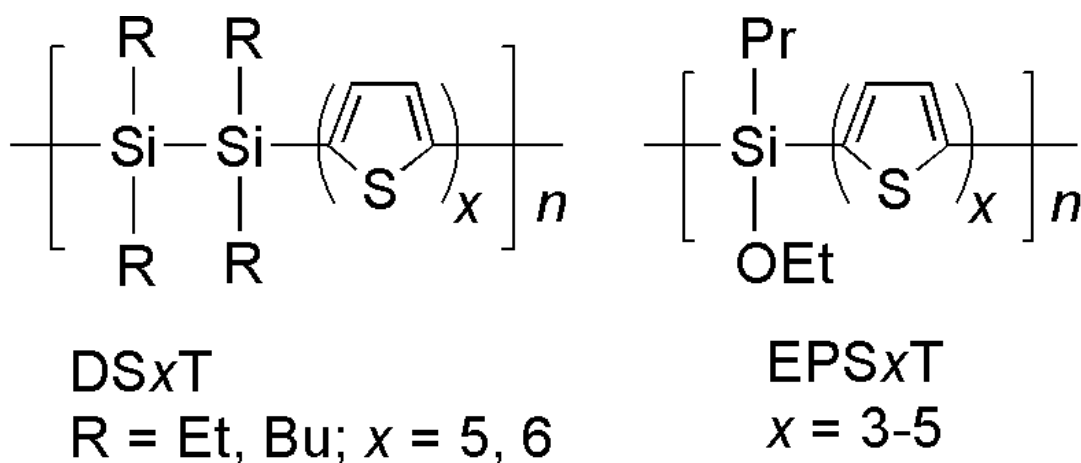
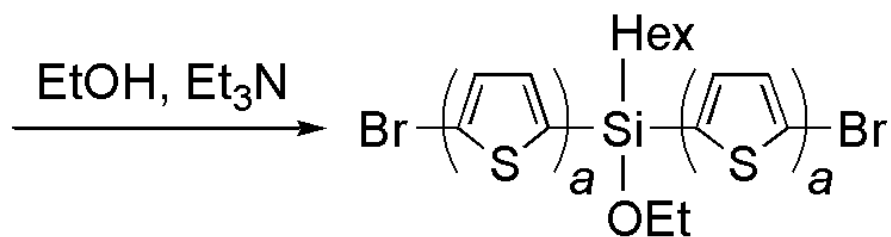
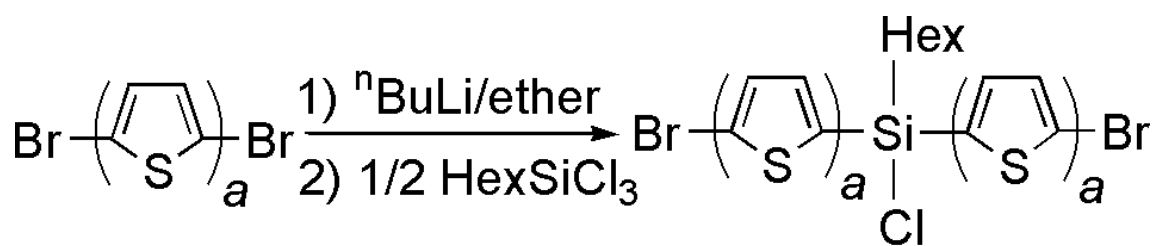
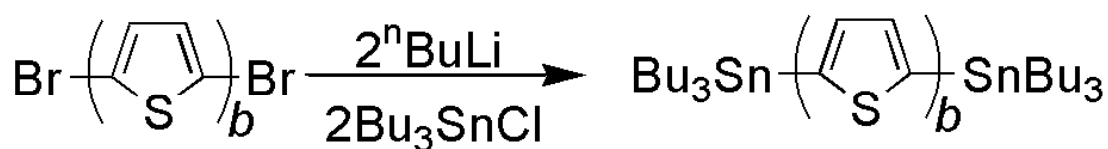


Chart 1. Si-oligothiophene alternate polymers.



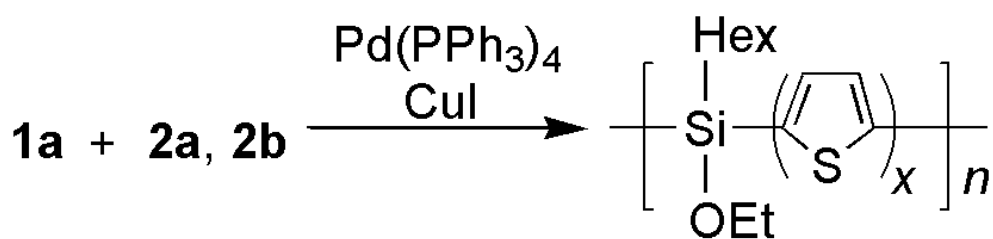
1a $a = 1$

1b $a = 2$



2a $b = 2$

2b $b = 3$

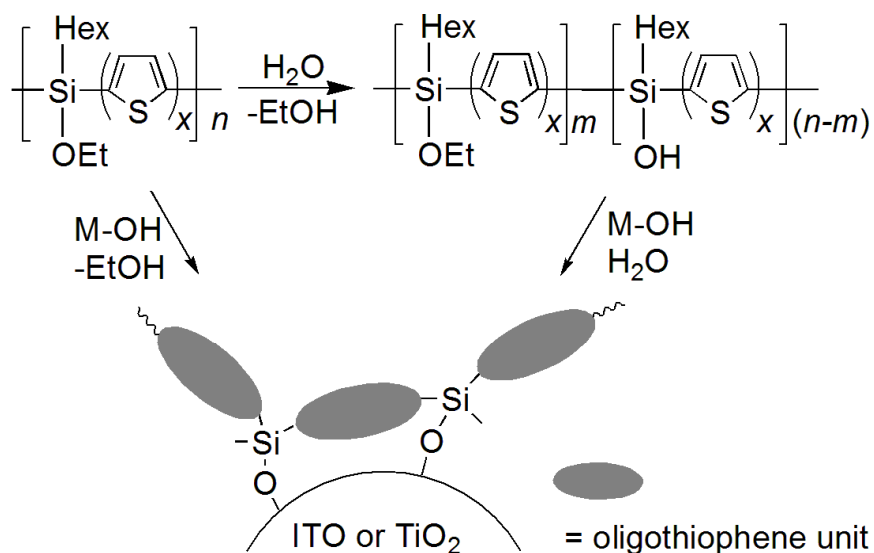


EHS_xT
 $x = 4, 5$

Scheme 1. Synthesis of EHS_xT.

3.2. Attachment of polymers EHSxT on indium tin oxide (ITO) and TiO₂

When ITO-coated glass plates were dipped in chloroform solutions containing polymers EHSxT and the solutions were heated at 40°C for 3 h in argon, the plate became brownish yellow. After washing with chloroform, the colored plate was analyzed by UV spectroscopy, which revealed an absorption band at 456 nm, indicating attachment of the polymer on the ITO surface. No reactions occurred at room temperature. TiO₂-coated FTO electrodes were also treated with the polymer solutions under the same conditions to give polymer-attached TiO₂ electrodes. Scheme 2 depicts a possible explanation for the formation of the polymer-attached inorganic oxides, including direct reactions of Si–OEt bonds with M–OH groups of the surface. It is also likely that a trace of water absorbed on the surface reacts with Si–OEt bonds to give Si–OH units, which would further interact with M–OH bonds to form M–O–Si linkage.



Scheme 2. A mechanistic interpretation for the formation of polymer-attached ITO and TiO₂.

A DSSC (FTO/TiO₂·EHS5T/I₂·I/Pt) was fabricated and its performance was examined. Incident photon-to-current conversion efficiencies (IPCE) and current-voltage (*I-V*) characteristics of the DSSC are shown in Figure 1. The IPCE characteristics showed clear sensitizing effects of the polymer with the maximum IPCE of 11% at about 450 nm, corresponding to the λ_{max} of EHS5T. Parameters of $I_{\text{sc}} = 0.44 \text{ mA/cm}^2$, $V_{\text{oc}} = -338 \text{ mV}$, $\text{FF} = 0.48\%$, and $\eta = 0.13\%$ were noted for the DSSC performance. Although a DSSC with the structure of FTO/TiO₂·EHS4T/I₂·I/Pt was also prepared, EHS4T did not show any detectable sensitizing effect in this cell.

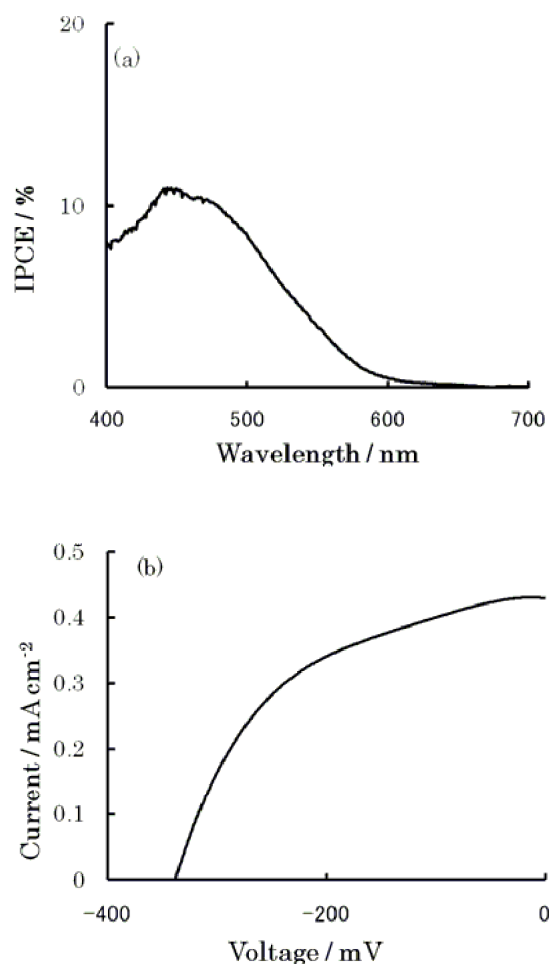


Fig. 1. Performance of DSSC with EHS5T-attached TiO₂ electrode. (a) IPCE and (b) *I-V* characteristics.

In conclusion, we demonstrated that ethoxysilylene-oligothiophene polymers EHS_xT reacted readily with ITO and TiO₂ surface at 40°C leading to the formation of the polymer-attached materials. Although the energy conversion efficiency of the present DSSC using the EHS5T-attached TiO₂ electrode is not high, the present study provides a new method to attach organic chromophores on inorganic oxide surface. This method can be readily performed under neutral conditions in non polar aprotic solvents. In conventional method, trialkoxy- or trichloro-derivative is often employed to form organic-inorganic hybrid by Si-O-M linkage [1, 2]. However, they readily undergo hydrolysis even with atmospheric moisture. In contrast, the present polymers are sufficiently stable and easy to handle.

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