# Attachment of Disilanylene–Oligothienylene Polymers on $TiO_2$ Surface by Photochemical Cleavage of the Si–Si Bonds

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When $TiO_2$ electrodes were dipped in chloroform solutions containing disilanylene–oligothienylene polymers and the solutions were irradiated ($\lambda_{max} > 400$ nm), the polymer-bound electrodes were obtained, which could be used for dye-sensitized solar cells.

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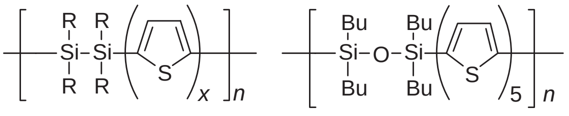
Polymers whose backbone is composed of an alternate arrangement of a $\pi$-conjugated system and an oligosilanylene unit are of interest, because of their use as functional materials, such as semiconducting materials and emissive materials.[1] It has been demonstrated that these polymers are photoactive both in the solid state and in solutions, being applicable to photoresists.[2] UV irradiation of the polymers in solutions leads to the homolytic cleavage of the Si–Si bonds, producing silyl radicals, as the major process. In the presence of a large excess of an alcohol, direct reactions of photo-excited Si–Si bonds with the alcohol, producing alkoxysilanes also would be involved. In this paper, we report the photolysis of solutions of disilanylene–oligothienylene alternate polymers with $TiO_2$ electrodes.[3] This provides a novel method to prepare polymer-bound $TiO_2$ electrodes, which can be used for dye-sensitized solar cells (DSSCs).

Chart 1 represents the structures of the disilanylene– and disiloxanylene–oligothienylene polymers used for the present study.[4] Molecular weights of the polymers determined by GPC relative to polystyrene standards, were sufficiently high with $M_w = 76000$ ($M_w/M_n = 2.5$) for DS5T and $M_w = 94000$ ($M_w/M_n = 3.8$) for DSO5T, and $M_w = 9000$ ($M_w/M_n = 2.3$) for DS6T, respectively. When $TiO_2$-coated FTO electrodes were dipped in chloroform solutions containing disilanylene–oligothienylene polymers and the solutions were irradiated with a Xe lamp (100 mW/cm$^2$) for 40 min in argon, the electrodes became yellowish brown, which could not be decolorized by washing with chloroform. In this process, irradiation at longer than 400 nm was required to avoid the activation of $TiO_2$. No coloration of $TiO_2$ was observed, when irradiated with a light shorter than 400 nm or the solutions were not irradiated. After washing the colored electrodes with chloroform, DSSCs I (FTO/$TiO_2$·DS5T/$I_2$·$I^-$/Pt) and II (FTO/$TiO_2$·DS6T/$I_2$·$I^-$/Pt) were fabricated and their performance was examined.[5] Incident photon-to-current conversion efficiencies (IPCE) of the devices and current–voltage characteristics are shown in Figure 1. As can be seen in Figure 1, the IPCE characteristics of DSSCs I and II showed clear sensitizing effects of the polymers on the performance of the DSSCs with shoulders at 460 and 490 nm, respectively. These shoulders were at a little longer wavelengths than the polymer absorption bands in THF ($\lambda_{max} = 436$ nm for DS5T and 418 nm for DS6T), probably due to the $\pi$–$\pi$ interaction on the $TiO_2$ surface. It is likely that DS6T with less bulky substituents prefers the interaction, giving rise to a larger red-shift.



**DS*x*T**
$x = 5$, R = Bu
$x = 6$, R = Et

**DSO5T**

**Chart 1.** Structures of Si–oligothiopehene polymers.

Scheme 1 depicts a possible explanation for the formation of

**Table 1.** Performance of DSSCs based on Si–oligothiophene polymers[a]

| Device | Polymer | $I_{sc}$ /mA cm$^{-2}$ | $V_{oc}$ /mV | FF /% | $\eta$ /% |
|---|---|---|---|---|---|
| I | DS5T | 0.76 | 292 | 0.52 | 0.11 |
| II | DS6T | 0.86 | 296 | 0.48 | 0.12 |
| III | DSO5T | 0.57 | 234 | 0.39 | 0.05 |

[a]Polymer-bound $TiO_2$ electrodes were prepared by immersing in the polymer solutions on UV irradiation for devices I and II, and in the dark for III, respectively.

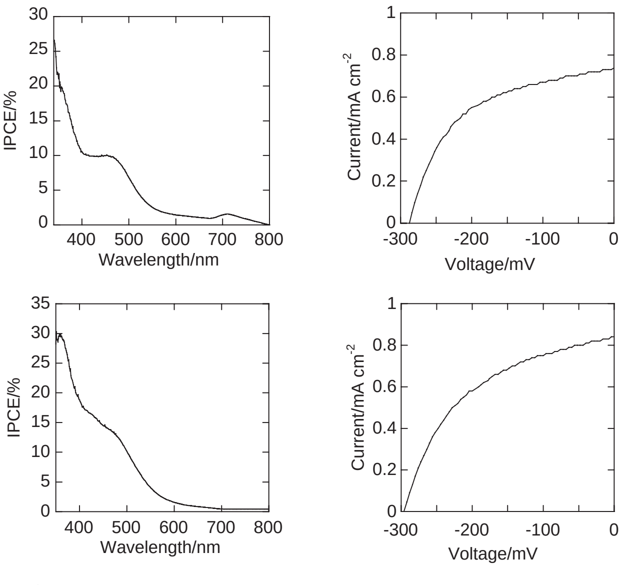
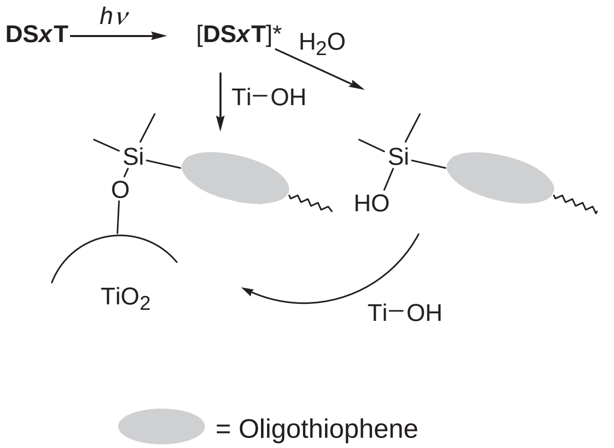


**Figure 1.** Performance of DSSCs I (top) and II (bottom).



**Scheme 1.** A mechanistic interpretation for the formation of polymer-bound $TiO_2$.

polymer-bound $TiO_2$ electrodes.[6] Direct reactions of photo-excited Si–Si bonds with OH groups on the $TiO_2$ surface would be involved. It is also likely that a trace of water absorbed on the $TiO_2$ surface reacts with the photo-excited Si–Si bonds to give Si–OH units. The Si–OH units would interact with the Ti–OH surface to afford Ti–O–Si linkages as the binding sites. Similar photo oxidation of poly(phenylsilane) has been previously reported by Hayase et al. They have demonstrated that poly(phenylhydroxysiloxane) produced by photo-oxidation of the polysilane interacts with $TiO_2$ nanoparticles as a chemical binder of the particles.[7]

The IR spectra of the polymer-bound $TiO_2$ used for the devices I and II were essentially the same as those of polymers DS5T and DS6T, respectively, indicating that only a trace of the Si–Si bonds reacted to form the binding sites. The degree of polymer introduction on the $TiO_2$ surface was determined to be approximately $S/Ti = 1/50$ by SEM–EDS analysis of the DS5T-bound $TiO_2$. The formation of siloxane units from DS*x*T, which may interact with the $TiO_2$ surface, would be also involved. However, this does not seem primarily responsible for the attachment of oligothiophene chromophores on the $TiO_2$ surface, in the present system. In fact, the device with a $TiO_2$ electrode pretreated with polymer DSO5T in dark (DSSC III) showed inferior performance to those of DSSCs I and II, as shown in Table 1.

Although the energy conversion efficiencies of the present devices I and II were not high, the results demonstrated by the present study clearly indicate that treatment of $TiO_2$ with disilanylene–oligothienylene alternate polymers under UV irradiation led the attachment of the polymers on the $TiO_2$ surface. This is a convenient method without any thermal treatment and special reagents, and can be performed under neutral conditions in non-polar solvents without any by-products librating. This method seems to be applicable to surface modification of a variety of inorganic oxides with organic chromophores.

This work was supported by a Grant-in-Aid for Scientific Research in a Priority Area "Super-Hierarchical Structures" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

### References and Notes

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3 For the photochemical properties of disilanylene–oligothienylene polymers, see: J. Ohshita, D. Kanaya, M. Ishiakwa, *Appl. Organomet. Chem.* **1993**, *7*, 269; J. Ohshita, D. Kanaya, M. Ishikawa, *J. Organomet. Chem.* **1994**, *468*, 55; A. Kunai, T. Ueda, K. Horata, E. Toyoda, I. Nagamoto, J. Ohshita, M. Ishikawa, K. Tanaka, *Organometallics* **1996**, *15*, 2000.

4 Applications of DS5T and DSO5T to hole-transporting materials in multi-layered electroluminescence devices have been reported, previously. See: J. Ohshita, K. Yoshimoto, M. Hashimoto, D. Hamamoto, A. Kunai, Y. Harima, Y. Kunugi, K. Yamashita, M. Kakimoto, M. Ishikawa, *J. Organomet. Chem.* **2003**, *665*, 29.

5 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 $TiO_2$ ($5 \times 5\,mm^2$) 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 with or without irradiation in an argon atmosphere. After being washed with chloroform several times until the chloroform became colorless, 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).

6 Similar direct addition of alcohol to photo-excited disilanylene–oligothienylene polymers, giving alkoxy–Si bonds has been reported. See Ref. 3.

7 K. Soeda, D. Kosugi, T. Kado, S. Hayase, *Chem. Lett.* **2005**, *34*, 650.