Thiophene Oligomers with a Photoswitch

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Thiophene oligomers having a dithienylethene structure show large shifts in oxidation potential to the cathodic region in excess of 0.87–1.27 V by photocyclization.

Since Carter proposed the concept of 'molecular electronic devices',[1] various investigations, both theoretical and experimental, into promising devices have occurred for potential scientific and technological applications. We have reported 'multimode chemical transducers', which have integrated multiple responsive functions into a molecule.[2–4] In designing molecules for future molecular electronic devices, not only will intrinsic functions need to be improved but also highly-integrated transformation modes will need to be added to the molecules. A molecular switch connected to a conductive polymer has been proposed as a prototype for a molecular electronic device. Recently, polythiophene and thiophene oligomers have attracted much attention because of their possible use in insulating/conductive switch systems.[5,6] We report herein a new class of multimode chemical transducers, electroactive thiophene oligomers which have a photochromic dithienylethene structure in the chain. They are expected to work as an insulating/conducting photoswitch.

Recently, a diarylethene derivative having bis-pyridinium side chains was proposed as a switched molecule which converted from an unconjugated form to a conjugated form.[7] Dithienylethenes are known as thermally irreversible photochromic systems[8–13] and undergo photocyclizations to produce closed-ring forms which absorb light at longer wavelengths. The thiophene rings are in a twisted conformation in the open-ring form and are not in π-conjugated system. After photocyclization, the four double bonds in the closed-ring forms are conjugated. Consequently, the non-conjugated polythiophene chains of **1** are expected to be connected by photocyclization.

In order to understand the electrical and optical properties of polythiophene, thiophene oligomers have been widely studied.[14] For the purpose of spectroelectrochemistry, *endo*-capped thiophene oligomers with alkyl or trialkylsilyl (TMS) groups are used, because radical cations of the *endo*-capped thiophene oligomers are more stable than those without them.[15] TMS groups are suitable for the synthesis, because they are easily exchanged for bromine or hydrogen. The bromine or hydrogen forms can be polymerized through coupling by metal catalysts or electropolymerization.

We synthesized the thiophene oligomers according to Scheme 1. The thiophene oligomer **2-S** (mp 91.4 °C) was synthesized in two steps from 2,4-dibromo-5-methylthiophene **4** in 33% yield. The hydrogen form **2-H** (mp 73.6 °C) was obtained in 95% yield by hydrolysis of **2-S** with HI or in 40% yield by coupling of 3-bromo-2-methylthiophene **5** and octafluorocyclopentene. The key intermediate **2-B** for longer thiophene oligomers was obtained in 27% yield from **2-S** by substituting TMS for bromine. In a single step, we introduced the two branches on to the key intermediate **2-B**. Arylhalogen-arylboric acid coupling of **2-B** and 2-bromo-4-trimethylsilylthiophene with a palladium catalyst afforded **3-S** in 51% yield and **6**, which was coupled at one side, in 15% yield.[16] Hydrolysis of **3-S** afforded a hydrogen form **3-H** in 95% yield. In addition, **3-S** was synthesized in 23% yield by coupling of **7** and octafluorocyclopentene. The oligomers were identified by their ^{1}H, ^{13}C, ^{19}F NMR and mass spectra. Oligomers having longer branches can be synthesized according to a similar method, because longer oligothiophene-boric acids have already been reported.[17] After the introduction of branches, the oligomers can be extended by a similar procedure, hydrolysis or bromination followed by coupling.

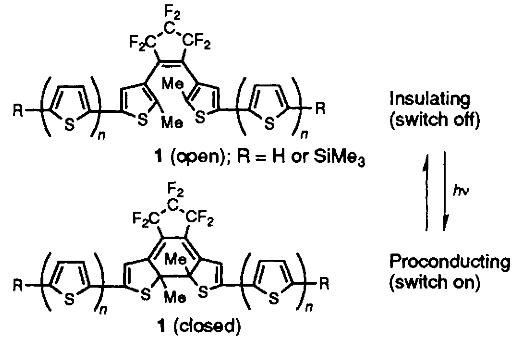
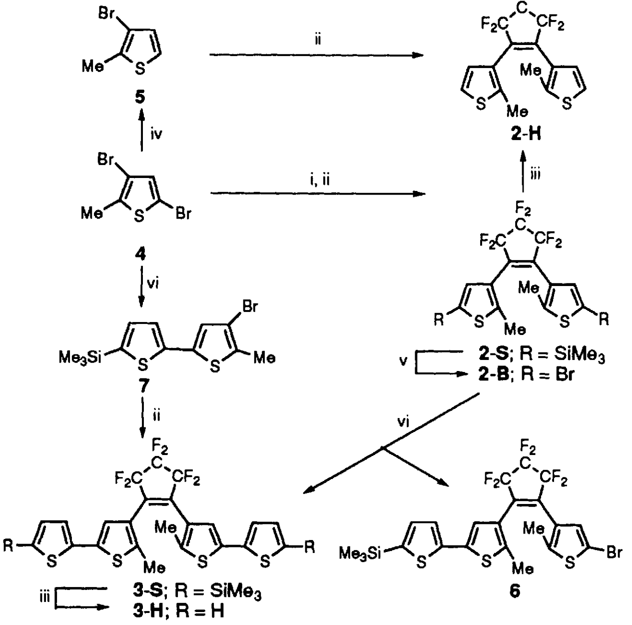


Fig. 1 Thiophene oligomer with an insulating/proconducting photoswitch



Scheme 1 *Reagents and conditions*: i, Bu^{n}Li, Et$_2$O, −78 °C, trimethylsilyl bromide: ii, Bu^s–Li, Et$_2$O, −78 °C, octafluorocyclopentene; iii, HI; iv, Bu^{n}Li, H$_2$O; v, Br$_2$; vi, 2-bromo-4-trimethylsilylthiophene, Pd^0(PPh$_3$)$_4$

Table 1 Absorption maxima and oxidation potentials of the open-ring and closed-ring forms

	Open-ring form		Closed-ring form	
Oligomer	λ_{max}/nm[a]	P_{ox}/V[b]	λ_{max}/nm[a]	P_{ox}/V[b]
2-H	—[c]	1.98	505	0.71
2-S	—[c]	1.90	540	0.69
3-H	320	1.55	605	0.63
3-S	322	1.57	602	0.63

[a] In *n*-hexane. [b] In MeCN containing tetrabutylammonium tetrafluoroborate *vs.* Ag/AgClO$_4$. [c] End-absorption below 350 nm.

n-Hexane solutions of the oligomers showed photochromisms owing to photocyclizations from the open-ring forms to closed-ring forms by irradiation with 350 nm light for several minutes.† The absorption maxima of the closed-ring forms appeared in the VIS region (Table 1). The closed-ring forms were fairly stable at room temperature and were converted back to open-ring forms by irradiation with VIS light. The absorption maxima of **2-H** (504 nm) and **2-S** (540 nm) were similar to those of 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (525 nm) and 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (565 nm).[10] The absorption maxima of **3-H** (605 nm) and **3-S** (603 nm) were shifted to longer wavelengths in comparison with the above compounds. The asymmetric oligomer **6** (560 nm) showed an absorption maximum between those of **2-S** and **3-S**. The oligomer having the longer side chain showed an absorption maximum in the longer wavelength region. The absorption maximum, which shifts with increasing conjugation length, indicates that the closed-ring form has conjugated side chains.

Fig. 2 shows cyclic voltammograms of **3-S** in MeCN containing tetrabutylammonium tetrafluoroborate (0.1 mol dm^{-3}) at 100 mV s^{-1}. The open-ring form showed an oxidation wave, (*a*), due to oxidation of a bithiophene group at P_{ox} 1.58 V (Ag/AgClO$_4$). Owing to the strong electron-drawing ability of perfluorocyclopentene ring, the oxidation potential of the open-ring form was in the more anodic region than that of bithiophene. Upon irradiation with light (350 nm) for 1 h, a new oxidation wave, (*b*) P_{ox} 0.63 V, appeared at a lower potential than that of the open-ring form. The 0.8 V shift of oxidation potential indicates that the closed-ring form had a conjugated side chain. Upon subsequent irradiation with light (550 nm) for 1 h,† the cyclic voltammogram changed to (*c*) showing that **3-S** was converted back to the open-ring form. These results indicated that the open-ring form was unconjugated and the closed-ring form was conjugated. The large shifts of oxidation potentials of the other thiophene oligomers are summarized in Table 1. The oxidation potentials of **2-S**, P_{ox} 1.98 V (open-ring form) and P_{ox} 0.71 V (closed ring form) were at a more anodic potential than those of **3-S**. The potential shifts in the order of chain length are similar to the observations in the absorption spectrum.

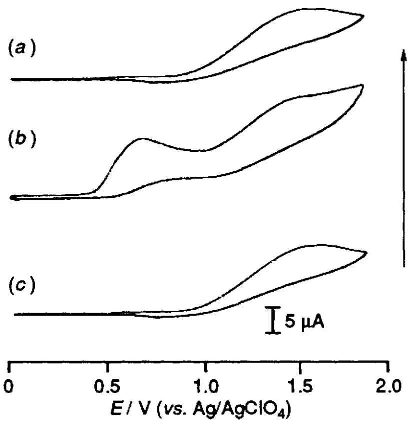


Fig. 2 Cyclic voltammograms of **3-S** (*a*) before irradiation at 350 nm, (*b*) after irradiation at 350 nm, and (*c*) after irradiation at 550 nm

It is expected that the *endo*-hydrogen forms are polymerized by an electrooxidation as with thiophene. In the case of **2-H**, neither the open-ring form (P_{ox} 1.98 V) nor the closed-ring form (P_{ox} 0.71 V) afford a polymer with electrooxidation. On the other hand, **3-H** was oxidized at P_{ox} 1.55 V for the open-ring form and P_{ox} 0.63 V for the closed-ring form and an insoluble film was deposited on the electrode by the oxidation at 1.55 V. This film was both photochemically and electrochemically inactive.

Received, 8th June 1994; Com. 4/03470H

Footnote

† The light source was a 500 W Xenon lamp (Ushio UXL-500). Light at *ca.* 350 nm was selected by passing the light through a UV-transmitting, VIS-absorbing filter (Toshiba UV-D35) and light (550 nm) was obtained by using an interference filter with 15 nm halfwidth (Toshiba KL-55).

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