Photochromic Oligothiophenes

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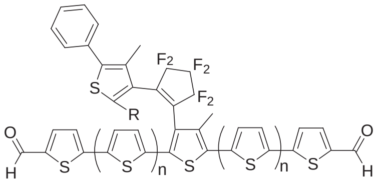
New oligothiophenes having a photochromic switching unit were synthesized. Upon irradiation with UV and visible light the oligomers underwent photochromic reactions in solution. The chain length dependence on the photoreactivity was examined to reveal that the reactivity decreased as the chain length gets longer. These molecules can be used as new photoswitching units.

Oligothiophene, which is constructed by 2,5-thienylene unit, is of great interest as a candidate for a potential molecular wire and thereby various types of oligothiophenes have been reported so far.[1] The unique redox,[2] photophysical,[3] and conductive[4] properties have been utilized for novel optoelectronic materials. The π-conjugated olefinic electronic structure is the key feature of this material. In this paper, we propose a new oligothiophene, in which a photochromic diarylethene[5] unit is incorporated. The π-conjugated chain length of the oligothiophene can be altered by the irradiation with appropriate wavelength of light due to the change of the hybrid orbital at the 2-position of the thiophene ring from sp^2 to sp^3.[6] The photochromic reactivity of the new diarylethene derivatives will be discussed.

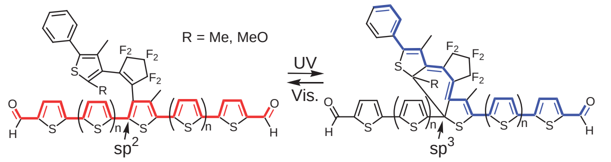
The pentathiophenes **1a**, **2a**, heptathiophenes **3a**, **4a**, and nonathiophenes **5a**, **6a** are listed in Chart 1. The switching unit is located in the middle of the π-conjugated chain. When oligothiophene chromophores are placed at both sides of a diarylethene, the photocyclization quantum yield is strongly suppressed.[7] To avoid the decrease of the quantum yield, the switching unit was introduced in the middle of the oligothiophene. Formyl substituent was introduced at each end of the π-conjugated chain for the further modification. The photochromic reaction is shown in Scheme 1. Upon irradiation with UV light, the photocyclization reaction of the diarylethene unit would break the π-conjugation of the oligothiophene.

The syntheses of **1a**–**6a** were performed according to Scheme 2. Diarylethenes having TMS-substituted terthiophene unit **7a** and **8a** were synthesized by two successive nucleophilic substitutions into perfluorocyclopentene. Bromo-substituted **9a** and **10a** were prepared by *N*-bromosuccimide in THF. Suzuki coupling with appropriate thienyl boronic acid derivatives gave oligothiophenes **1a**–**6a**. The structures of the compounds were confirmed by the NMR, UV–vis, and high-resolution mass spectroscopy.[8]

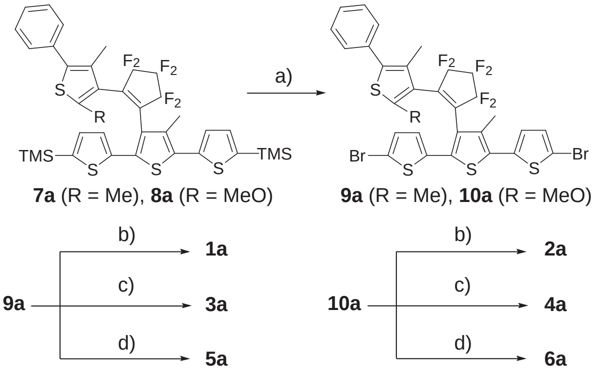


1a R = Me , n = 1 **4a** R = MeO, n = 2
2a R = MeO, n = 1 **5a** R = Me , n = 3
3a R = Me , n = 2 **6a** R = MeO, n = 3

Chart 1. Oligothiophenes having a diarylethene.



Scheme 1. Photochromism of thiophenes oligomer having a diarylethene.



Scheme 2. a) NBS, THF, 74–90%; b) 5-Formylthiophene-2-boronic acid, Na_2CO_3, $Pd(PPh_3)_4$, THF, and H_2O, 51–88%; c) 5-(1,3-Dioxolane-2-yl)-[2,2′-bithiophene]-5′-boronic acid, $Pd(PPh_3)_4$, Na_2CO_3, THF, H_2O, and then H^+, 45–50%; d) 5-(1,3-Dioxolan-2-yl)-[2,2′:5′,2″-terthiophene]-5″-boronic acid, $Pd(PPh_3)_4$, Na_2CO_3, THF, H_2O, and then H^+, 23–40%.

The photochromic reactivity of **1a**–**6a** was studied in ethyl acetate solution. Before irradiation, the solution showed yellow, yellow, pale orange, orange, reddish orange, and reddish orange for **1a**, **2a**, **3a**, **4a**, **5a**, and **6a**, respectively. As the π-conjugation chain gets longer, the absorption maximum of the open-ring isomer shifts to longer wavelengths. These oligothiophenes underwent photochromic reactions upon irradiation with UV light. The solutions of **1a** and **2a** turned blue green by irradiation with 365 nm light. The blue green color is due to the formation of the closed-ring isomer **1b** and **2b**. The formation of the closed-ring isomer was supported by the ca. 0.1 ppm downfield shift of methyl or methoxy proton on the reactive carbon. These colors were bleached by the irradiation with visible light. The solution of **4a** turned dark brown. The color changes of solutions of **3a**, **5a**, and **6a** were much less than the solutions of **1a**, **2a**, and **4a** (Figure 1). The conversion from the open- to the closed-ring isomer decreased as the π-conjugation chain becomes longer. The low conversion is ascribed to the low cyclization quantum

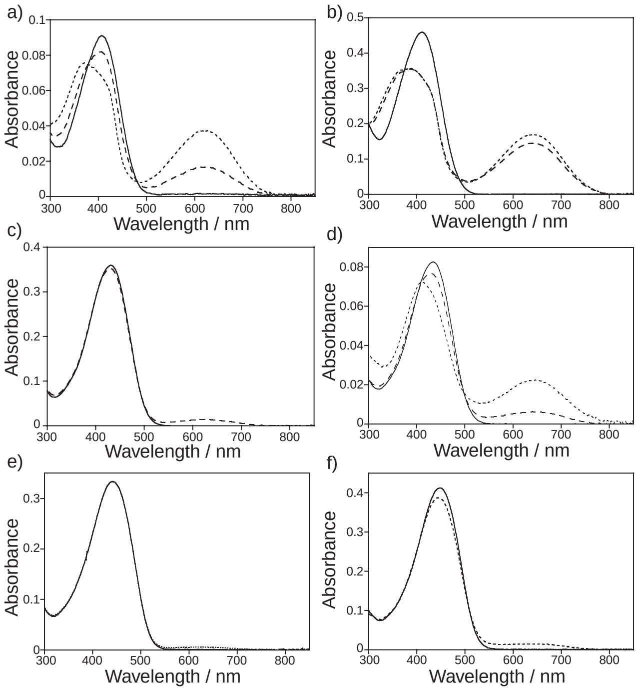


Figure 1. Absorption spectra of photochromic oligothiophenes. Solid line: the open-ring isomer; dotted line: the closed-ring isomer; dashed line: in the photostationary state. a) **1a**, b) **2a**, c) **3a**, d) **4a**, e) **5a**, and f) **6a**.

yields and relatively high cycloreversion quantum yield. The color of the closed-ring isomer was also dependent on the π-conjugated chain length. Bathochromic shift was observed for the longer oligothiophene derivatives. The methoxy-substituted oligothiophenes also showed significant bathochromic shift.

Cyclization and cycloreversion quantum yields were measured in ethyl acetate using 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene as a reference.[9] The quantum yields and the absorption maxima were summarized in Table 1. The cyclization quantum yields of photochromic oligothiophenes were smaller than those of regular diarylethenes. Compound **2a** has methoxy substituent at reactive carbon, which is known to suppress the cycloreversion reaction.[10] The cycloreversion reaction of **2b** is much smaller than that of **1b** and cyclization quantum yield of **1a** and **2a** were almost the same. Therefore, the conversion of **2a** (87%) is higher than the value of **1a** (49%). Heptathiophene **4a** has very small cyclization and cycloreversion quantum yield. But, cyclization quantum yield is larger than cycloreversion reaction by the effect of methoxy substituent. Therefore, the closed-ring isomer was accumulated by the irradiation with UV light. Cyclization quantum yield depended on π-conjugated chain length. As the π-conjugated chain of oligothiophene elongates, cyclization quantum yield is suppressed. Energy dissipation can be the main cause of the suppression of cyclization reaction.

Table 1. Absorption maxima and quantum yields of **1**–**6** in ethyl acetate

	$\lambda_{\max}$/nm		Quantum yield		Conversion/%
	a	**b**	**a** → **b** (365 nm)	**b** → **a** (575 nm)	
1	408	619	0.019	0.010	49
2	411	640	0.016	0.00060	87
3	432	625	N/A	N/A	≈5
4	434	645	0.00079	0.00069	35
5	445	629	N/A	N/A	≈1
6	447	650	N/A	N/A	≈10

As indicated in Scheme 1, the photochromic reaction can switch the pathway of the conjugation. In the open-ring isomer the conjugation extends along red line while the conjugation extends through blue line in the closed-ring isomer. The molecules can be used as new photoswitching units.

In conclusion, new oligothiophenes having a photochromic diarylethene unit were synthesized and their photoreactivity was studied to reveal that the reactivity decreased as the chain length gets longer.

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