Photoswitching of Solvatochromism Using Diarylethenes with 2,5-Disubstituted 3-Thienyl Unit

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Novel photochromic bis(3-thienyl)ethene with a 2,5-disubstituted thienyl unit, which shows photoswitching of solvatochromic property, was synthesized. The open-ring isomer showed solvatochromic behavior, while the closed-ring isomer did not. It was suggested that the alteration of the π-conjugated bond structure is the main cause of the switching of the solvatochromic property.

Photochromic compounds have been developed not only for the photoinduced color changes but also for the photoswitching of the physical properties originating from the molecular structural changes.[1] Recently, several examples are reported on the application of diarylethenes, which is one of the most robust photochromic units, to the photoswitching of physical properties, including intramolecular magnetic interaction,[2] organogel characteristics,[3] morphology of single crystals,[4] fluorescence,[5] and electric conductivity.[6] Beside these applications, photochromic compounds are also suitable for "molecular electronics" because "molecular electronics" deals with the molecular structure for the control of the flow of information signals through them.[7] In this study, we report the use of the photochromic compounds for the photoswitching of the solvatochromism, which also originates from the electronic interaction through a π-conjugated chain.

Photochromism of diarylethenes changes the molecular structure from hexatriene to cyclohexadiene at the photoreactive moiety.[1a] We have already reported the photoswitching of the electronic interaction using the change of hybrid orbital at the reactive carbon of bis(3-thienyl)ethenes with a 2,5-bis(arylethynyl)-3-thienyl group.[2k,8] The photoswitching mechanism is explained by the model compound having a 2,5-disubstituted thienyl unit (Figure 1). In the open-ring isomer, the two functional substituents are linked by a π-conjugated chain. Therefore, the intramolecular electronic interaction occurs between the two substituents. In the closed-ring isomer, the hybrid orbital of the carbon atom at the 2-position of the thiophene ring changes from sp^2 to sp^3. Accordingly, the π-conjugated chain between the two substituents is disconnected and the intramolecular interaction gets weaker. Therefore, this molecular system can alter the electronic interaction via the π-conjugated chain between substituents.

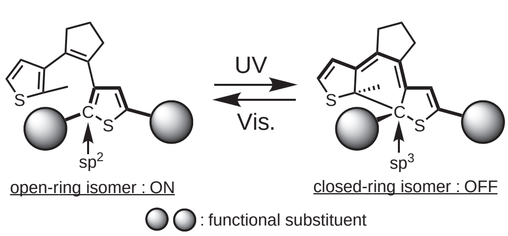


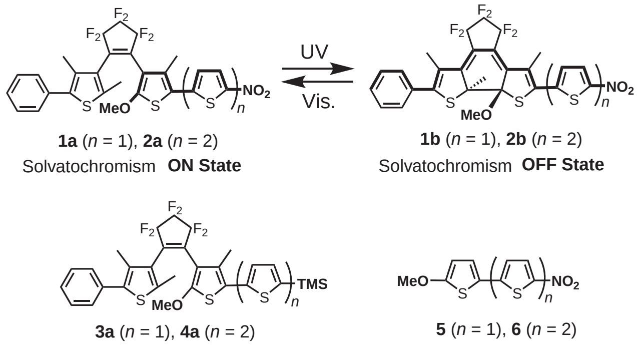
Figure 1. Photoswitching mechanism of bis(3-thienyl)ethene using 2-position carbon atom of the thiophene ring.

Solvatochromism is mostly attributed to the donor–acceptor interaction through the π-conjugated chain.[9] Therefore, by introducing the donor and the acceptor moiety into one of the thienyl groups of bis(3-thienyl)ethene, solvatochromic property can be integrated into the photochromic diarylethene. Practically, a methoxy group was chosen for the donor moiety and a nitro group was chosen for the acceptor group.

According to this strategy, we synthesized new compounds **1** and **2** which have both a bis(3-thienyl)ethene structure as a photochromic unit and a donor–spacer–acceptor structure as a solvatochromic unit (Figure 2).[10] Trimethylsilyl-protected compounds **3** and **4** were deprotected to give desilylated compounds. Target molecules **1** and **2** were prepared by mild nitration using nitric acid in acetic anhydride solution as nitration reagent into α-position of thiophene ring of the desilylated compounds.[11]

Bis(3-thienyl)ethene derivatives **1**–**4** underwent reversible isomerization by irradiation with UV and visible light. The absorption spectra of the open- and the closed-ring isomers are shown in Figure 3. Upon irradiation with 365 nm light, the open-ring isomer **1**–**4a** underwent photocyclization reaction in *n*-hexane and methanol solution. All the closed-ring isomer **1**–**4b** underwent cycloreversion reaction to the open-ring isomers **1**–**4a** completely by photoirradiation with 578 nm light.

The absorption spectra of open-ring isomer **1a** depended on the solvents. The color of the methanol solution of **1a** was orange and the hexane solution of **1a** was yellow. The absorption maximum was observed at 403 nm and the absorption edge was located at 460 nm in hexane. The methanol solution of **1a** was orange and the absorption maximum was observed at 421 nm. The absorption maximum in methanol was red-shifted about 20 nm in comparison with the hexane solution. In addition, the absorption edge in methanol is 530 nm, which is also 70 nm



1a (*n* = 1), **2a** (*n* = 2)
1b (*n* = 1), **2b** (*n* = 2)
3a (*n* = 1), **4a** (*n* = 2)
5 (*n* = 1), **6** (*n* = 2)

Figure 2. Photochromic reaction of diarylethenes having solvatochromic unit **1** and **2** and reference compounds **3**–**6**.

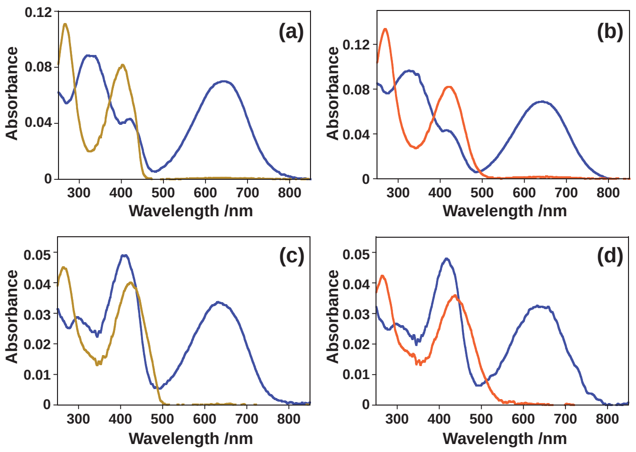


Figure 3. Absorption spectral changes of bis(3-thienyl)ethene isomers. Yellow lines and orange lines: the open-ring isomers. Blue lines: the closed-ring isomers. (a) *n*-Hexane solution of bithiophene derivative **1**. (b) Methanol solution of **1**. (c) *n*-Hexane solution of terthiophene derivative **2**. (d) Methanol solution of **2**.

longer than that in hexane. The absorption wavenumbers of the $\lambda_{\max}$ and the π^* scales according to Kamlet and Taft showed good correlation,[12] which was reported for the reference compound **5**.[10b] On the other hand, the solution of **1b** is blue and showed the similar absorption band in the visible region in both hexane and methanol. The absorption maxima in both solvents were observed at 644 nm. The absorption spectrum of closed-ring isomer **1b** was not affected by solvent polarity.[13]

Diarylethene **2** having a terthiophene unit also showed similar switching behavior. Open-ring isomer **2a** also showed the positive solvatochromic property like reference compound **6**.[10b] But closed-ring isomer **2b** showed blue-green color in both hexane and methanol and has absorption maxima at 633 nm in both solutions. The spectrum was not affected by the solvent polarity.

The necessity of donor and acceptor substituents was exemplified by the fact that the closed-ring isomer, in which the methoxy group is out of the π-conjugated unit, did not show any solvatochromism and that both isomers of non-nitrated precursors **3** and **4** did not show any solvent-dependence of the absorption spectra. Nitro and methoxy groups should be directly connected by the π-conjugated chain to show solvatochromism. By incorporating the oligothiophene unit having donor and acceptor substituents, the solvatochromic property was endowed only to the diarylethene open-ring isomer, which retains the donor–spacer–acceptor structure.

The positive solvatochromism is the outcome of the stabilization of the excited state in the polar solvent. The absorption band of **1b** and **2b** was irrespective of the solvent polarity, suggesting that solvation of the exited state is not affected by changing the solvents. On the other hand, the longest absorption bands of **1a** and **2a** changed by the solvent polarity. The solvation energy is different between the open- and closed-ring isomers. The calculation results (AM1) of LUMO orbitals support that the bond structure is altered by photochromism.[14] The orbital shape of the closed-ring isomer showed the connection between the donor and the acceptor, though the π-conjugation circumvents the methoxy group in the closed-ring isomer.

In conclusion, we developed photochromic compounds which show photoswitching of the solvatochromic property. It was clarified that alteration of the π-conjugated bond structure is the main cause of the switching of the solvatochromic property.

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11 For the detail of the synthesis, see Supporting Information which is available electronically on the CSJ-Journal web site; http://www.csj.jp/journals/chem-lett/.
12 M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **1983**, *48*, 2877. See Supporting Information for the plot.
13 The absorption maxima is listed in Supporting Information.
14 For the calculation results, see Supporting Information.

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