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Synthesis of New Photochromic Diarylethenes Having 2,5-Bis(trimethylsilylethynyl)-3-Thienyl Unit

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New diarylethenes having a trimethylsilylethynyl substituent at the 2,5-position of the thiophene ring were synthesized. Diarylethene moiety are located in the middle of the π -conjugated chain. These molecules underwent a photochromic reaction in solution. This molecule can be used as a switching unit in the π -conjugated polymer or oligomer.

Keywords: photochemistry; photochromism; π -conjugated chain

INTRODUCTION

Various types of photochromic compounds, such as spirobenzopyrans, azobenzenes, fulgides, and diarylethenes have been reported [1]. Among the compounds, diarylethenes show very special reactivities. Both isomers are thermally stable and photoinduced coloration/discoloration cycle can be repeated many times without destruction [2].

Diarylethenes can be used for switching unit when incorporated in a π -conjugated chain. We have already reported diarylethene biradicals, which have two nitronyl nitroxide radicals at different aryl units of the diarylethene [3]. In this case, the long π -conjugated chains connected to the diarylethene decrease the cycloreversion quantum yield. To avoid this problem, we designed a new switching system, in which

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the π -conjugated chain is placed only in one of the aryl groups and the switching is controlled by the structure change of the π -conjugated chain.

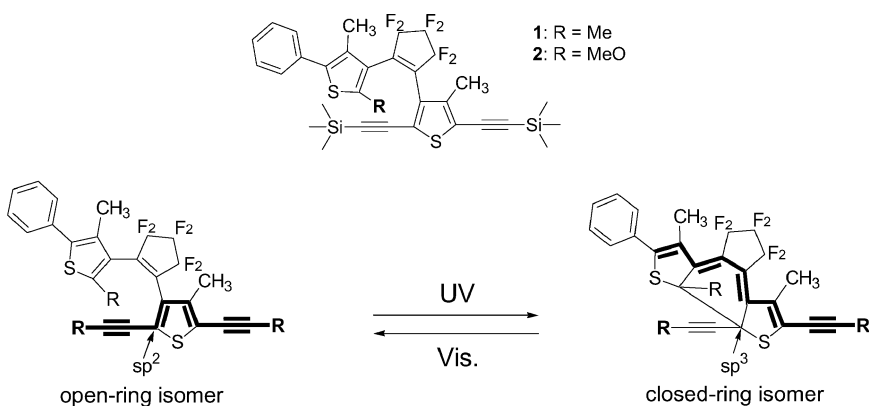
In this report, syntheses of new photochromic diarylethenes having 2,5-bis(trimethylsilylethynyl)-3-thienyl unit are reported. Utilization of the switching of the orbital hybridization will be discussed.

RESULTS AND DISCUSSIONS

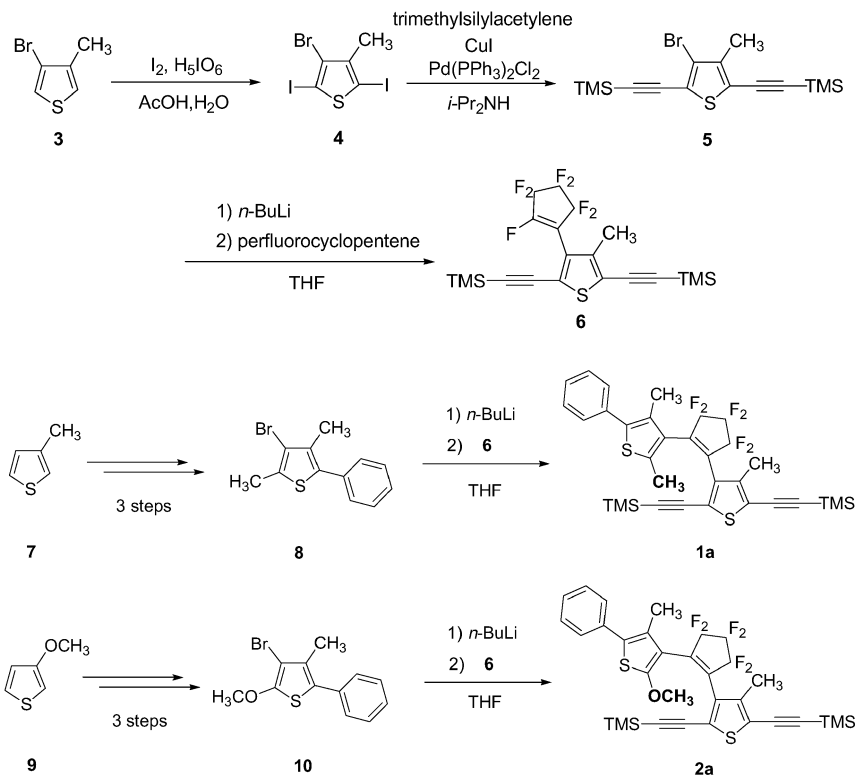
Preparation of Target Molecule

Based on the idea described above, we synthesized new unsymmetrical diarylethenes **1** and **2** which have an extended π -conjugated chains from 2,5-position of one thiophene ring. Trimethylsilylethynyl unit was introduced because this unit is a building block of the π -conjugated polymers or oligomers [4]. When these diarylethenes are in the open-ring isomer, π -conjugated system is not perturbed. On the other hand, when they are in the closed-ring isomer, π -conjugated system is disconnected at the 2-position of the thiophene ring (Scheme 1).

The syntheses of **1** and **2** were carried out according to Scheme 2. Syntheses of thiophene unit **8** and **10** were performed according to the general synthetic procedure. Another thiophene unit with extended π -conjugated chain **6** was prepared from 3-bromo-4-methylthiophene by three steps. Unsymmetrical diarylethene 2'-methyl derivative **1a** and 2'-methoxy derivative **2a** were synthesized by the coupling of **6** and lithiated **8** and **10** in 79% and 90%. These



SCHEME 1 Photochromic reaction of diarylethene **1** and **2** which have extended π -conjugated chain at the 2,5-position of the thiophene unit.



SCHEME 2 Syntheses of unsymmetrical diarylethenes **1a** and **2a**.

compounds can be readily desilylated by KOH aq. in THF/MeOH so that the π -conjugated chain can be extended. These compounds were characterized by NMR, Mass spectroscopy and elemental analysis.

PHOTOCHROMIC REACTION

Upon irradiation with 366 nm light, **1a** and **2a** underwent photochromic reactions in solution. Figures 1 and 2 show the absorption spectral changes of compound **1a** and **2a** in ethyl acetate. Upon irradiation to the solution of **1a** with 366 nm light, **1a** converted to **1b** and a new 595 nm band appeared. An isosbestic point was observed at 360 nm. Upon irradiation with 578 nm light for 2 min, the spectrum converted back to the original one. In the case of **2a**, upon irradiation with 366 nm light, the 610 nm band increased and reached the photostationary state, and an isosbestic point was observed at 360 nm.

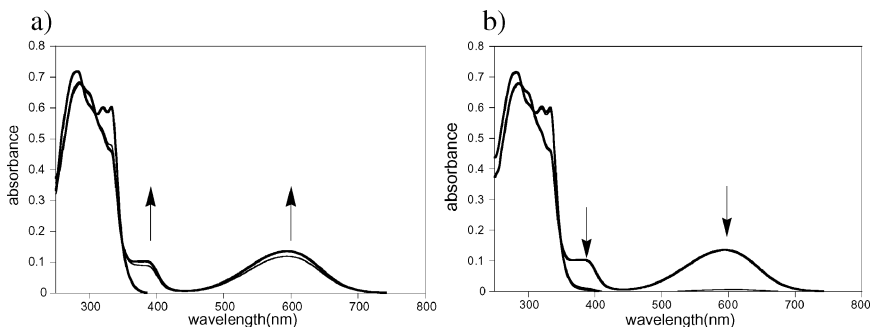


FIGURE 1 a) Absorption spectral change of **1a** in ethyl acetate starting from the open-ring isomer to the photostationary state upon irradiation with 366 nm light. Initial, 1 min, 2 min (in the photostationary state) irradiation. b) Absorption spectral change of cycloreversion reaction starting from the photostationary state to the open-ring isomer upon irradiation with 578 nm light. Initial, 1 min, 2 min (= the open-ring isomer) irradiation.

Although any difference was not observed in the cyclization reactions between **1** and **2**, the cycloreversion reaction of **2b** was strongly suppressed in comparison with the reaction of **1b**. This difference is attributed to the decrease in the quantum yield of the cycloreversion reaction by introducing of the methoxy group.

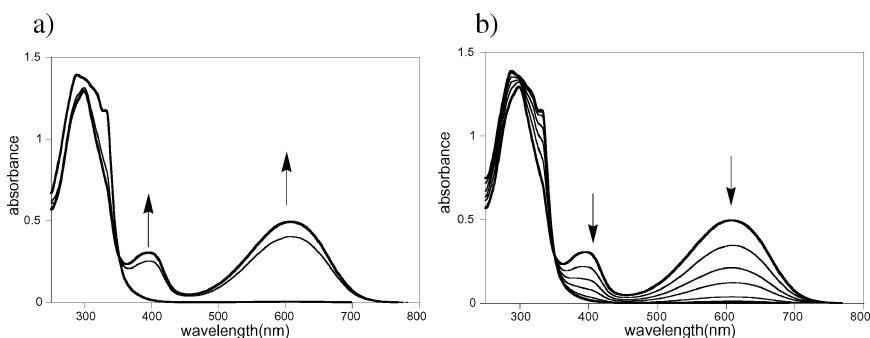


FIGURE 2 a) Absorption spectral change of **2a** in ethyl acetate starting from the open-ring isomer to the photostationary state upon irradiation with 366 nm light. Initial, 1 min, 2 min (in the photostationary state) irradiation. b) Absorption spectral change of cycloreversion reaction starting from the photostationary state to the open-ring isomer upon irradiation with 578 nm light. Initial, 1 min, 2 min, 3 min, 5 min, 7 min, 10 min (= the open-ring isomer) irradiation.

CONCLUSION

Diarylethenes having a 2,5-bis(trimethylsilylethynyl)-3-thienyl unit were synthesized. Upon alternate irradiation with UV and visible light, diarylethene **1** and **2** underwent normal photochromic reactions. These diarylethenes can be used to switch the π -conjugated chain length upon photoirradiation.

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