Synthesis of Tetrathiafluvalene Derivatives with Photochromic Diarylethene Moieties

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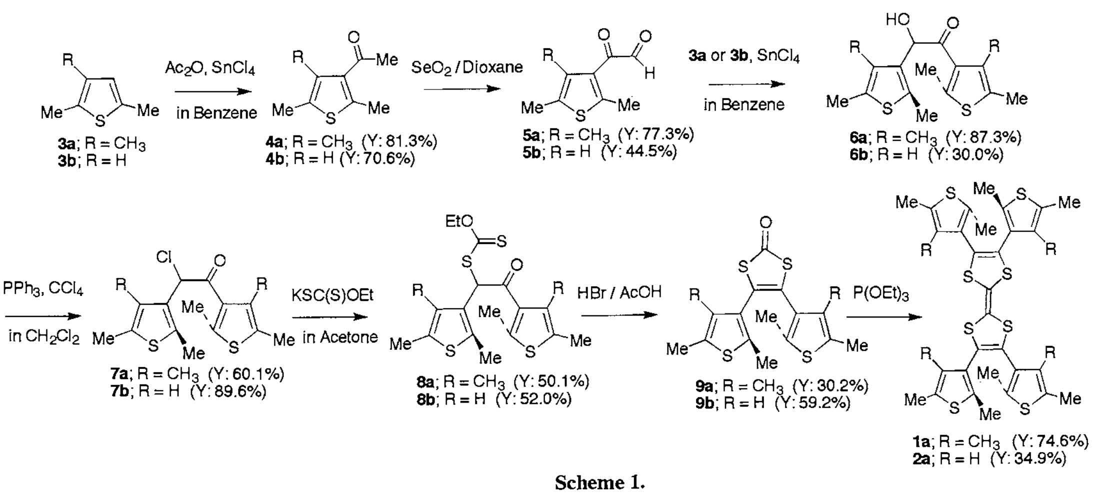
Tetrathiafulvalene (TTF) derivatives with diarylethene moieties have been synthesized. A derivative having 2,4,5-trimethylthiophene rings as the aryl groups showed photochromism, while a derivative with 2,5-dimethylthiophene rings did not show any color change by UV irradiation. The different reactivity was ascribed to the difference in the conformation of thiophene rings in the two derivatives.

Recently, various types of photochromic molecules have been developed in an attempt to apply them to organic supramolecular and photonic devices.[1] Especially, diarylethenes, one of the thermally irreversible photochromic molecules, have attracted much attention because of their fatigue resistant and thermally irreversible reactivity.[2] On the other hand, TTF molecules are important components of conductive organic solids.[3] A lot of tetrathiafulvalene derivatives have been so far synthesized to improve the conductive properties.[4,5]

Here, we report the synthesis of 4,4',5,5'-tetrakis(2,4,5-trimethyl-3-thienyl)tetrathiafulvalene (**1**)[6] and 4,4',5,5'-tetrakis(2,5-dimethyl-3-thienyl)tetrathiafulvalene (**2**)[7] that have photochromic dithienylethene units. Synthetic routes for the TTF derivatives were summarized in Scheme 1. Thiophenes **3** were acetylated by action of acetic anhydride and tin tetrachloride to give **4a** and **4b** in good yield. Obtained acetylated thiophenes were oxidized with SeO_4 to afford diketones **5a** and **5b**. The dikotones were coupled with appropriate thiophenes **3a** and **3b** to give hydroxyketo forms **6a** and **6b**. After thioesterification with potassium *o*-ethyl xanthate, the thioesters were cyclized to give diarylethenes **9a** and **9b**. The derivatives **1a** and **2a** are obtained as orange oil, after workup by column chromatography.

Figure 1 shows UV-vis absorption spectral changes of **1** in hexane. Upon irradiation with UV-light, the colorless solution changed to yellow. The yellow color was bleached by visible light (λ >450 nm) irradiation. The ^{1}H NMR spectral changes upon UV and visible light irradiation were carefully examined. In the ^{1}H NMR spectrum of **1a**, five methyl signals (1.92, 1.96, 2.00, 2.06, and 2.24 ($CH_3 \times 2$) ppm) attributable to methyl protons of the thiophene rings in parallel and anti-parallel conformations, were observed. Upon UV irradiation, additional five methyl signals (1.82, 1.93, 1.97, 1.99 ($CH_3 \times 2$), and 2.02 ppm) appeared (Figure 2). The new signals were attributable to the closed-ring form **1b**. In the NMR spectrum of the closed-ring form of bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene **10**, only two methyl signals were observed. The appearance of 5 methyl signals for **1b** indicates that one of the diarylethene units converted to the closed-ring form. The photo-generated signals disappeared by visible light irradiation.

Although the TTF derivative **1** underwent reversible photochromic reactions, **2** did not show any color change by UV irradiation. In order to clearify the different reactivity, ^{1}H NMR spectra of both derivatives were compared with that of **10**.[8] The methyl protons of the methyl groups attached to the reacting carbons of **2** and **10** were observed at 2.01and 2.04 (for **2**), and 1.81 ppm (for **10**), respectively. The aryl protons at 3-positions of the thiophene rings were observed at 6.46 and 6.42 (for **2**), and 6.71 ppm (for **10**), respectively. As described in previous papers,[9] methyl signals attached to the reacting carbons of anti-parallel conformation were always observed in higher fields in comparison with the methyl signals of parallel conformers. Based on the NMR chemical shifts, the conformation of TTF **2** is considered to be the same as that of **2r** in Scheme 2, in which both reaction sites are kept in opposite sites. Therefore, **2r** is photochemically inactive. In **2r**, methyl groups attached to the reacting carbons are free from



Scheme 1.

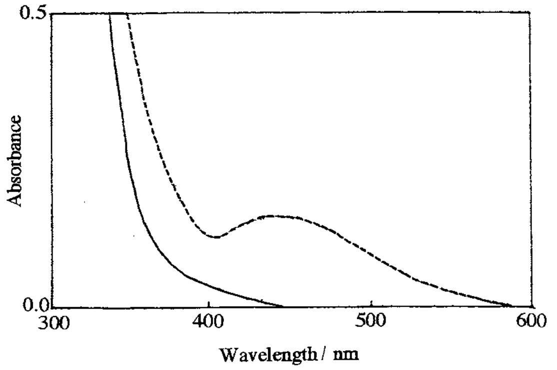


Figure 1. Absorption spectral change of **1a** (———) upon irradiation with 254 nm light in hexane. The line (·········) is due to the closed-ring form.

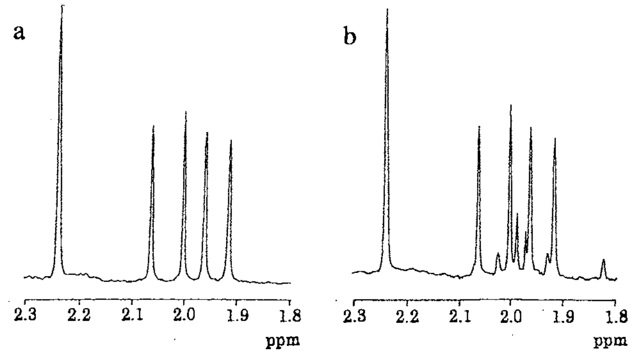
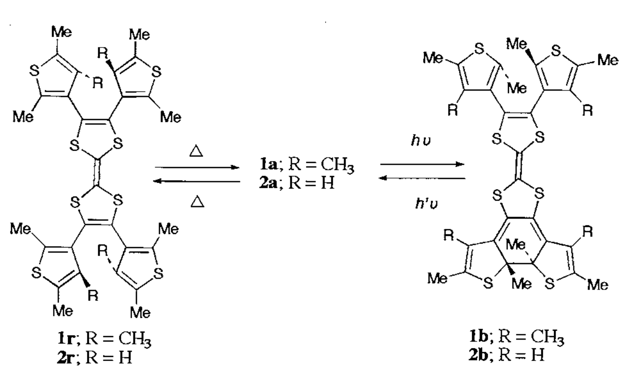


Figure 2. The ^{1}H NMR spectra of **1a** before UV irradiation (a) and after UV irradiation (b) in CDCl$_3$.

ring-current effect of the thiophene rings in the face. Repulsion between the methyl groups is avoided. This is the reason why **2a** did not show any photochromic reactivity. Photo-reactive **1** showed the methyl protons of the methyl groups attached to the reacting carbons at 1.92 and 1.96 ppm. They are close to the chemical shift of that of **10**. That indicates conformation of **1** is similar to that of **10**, which is photochemically active.

Light triggered electrochemistry of **1** was examined by cyclic voltammetry (Potentiostats HABF501, Hokuto Denko). Cyclic voltammograms for **1** in acetonitrile were shown in Figure 3, which indicates that **1** can undergo direct electron transfer reaction with the electrode under UV-light irradiation, whereas visible light irradiation decreased the Faradaic current.



Scheme 2.

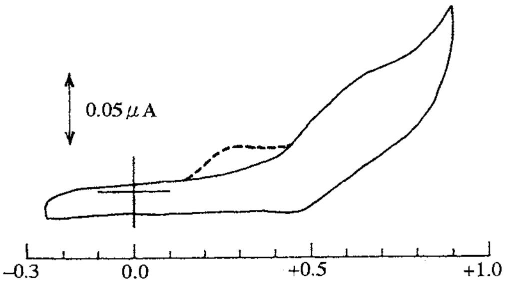


Figure 3. Cyclic voltammograms for the **1** in acetonitrile solution at 25 ℃. (Supporting electrolyte, 0.1 mol dm^{-3} Bu$_4$N$^+$ClO$_4^-$) ; Sweep rate, 100 mV / s). (———) Visible light irradiation (λ >450 nm, 5 min), (·········) UV light irradiation (λ = 254 nm, 5 min).

In conclusion, we have synthesized TTF derivatives that have photochromic diarylethene moieties. Derivative **1** that has 2,4,5-trimethylthiophene rings showed photochromic performance. On the other hand, a derivative **2** that has 2,5-dimethylthiophene rings did not show any coloration by UV irradiation. This is due to the inactive conformation of the derivative. The electrochemical switching function was also observed accompanied with the photochromism.

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References and Notes

1 H. Duerr and H. Bouas-Laurent, "Photochromism Molecules and Systems,"Elsevir, Amsterdam (1990).

2 M. Irie and M. Mohri, *J. Org. Chem.*, **53**, 803 (1988); M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, **73**, 985 (1998); S. H. Kawai, S. L. Gilat, and J-M. Lehn, *Chem. Eur. J.*, **1**, 285 (1995); G. M. Tsivgoulis and J-M. Lehn, *Chem. Eur. J.*, **2**, 1399 (1996); C. Denekamp and B. L. Feringa, *Adv. Mater.*, **10**, 1082 (1998).

3 J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1974).

4 M. B. Nielsen, N. Thorup, and J. Becher, *J. Chem. Soc., Perkin Trans. 1*, **1998**, 1305.

5 A. Charlton, A. E. Underhill, G. Williams, M. Kalaji, P. J. Murphy, K. M. A. Malik, and M. B. Hursthouse, *J. Org. Chem.*, **62**, 3098 (1997).

6 **1**: Orange oil; ^{1}H NMR (CDCl$_3$, 400 MHz) δ =1.92 (s, 6H), 1.96 (s, 6H), 2.00 (s, 6H), 2.06 (s, 6H), 2.24 (s, 12H)., MS (m / z) 700 (M$^+$).

7 **2**: Orange oil; ^{1}H NMR (CDCl$_3$, 400 MHz) δ =2.01 (s, 12H), 2.31 (s, 12H), 6.46 (s, 4H). ; MS (m / z) 644 (M$^+$).

8 S. Kobatake, T. Yamada, K. Uchida, N. Kato, and M. Irie, *J. Am. Chem. Soc.*, **121**, 2380 (1999).

9 K. Uchida, Y. Nakayama, and M. Irie, *Bull. Chem. Soc. Jpn.*, **63**, 1311 (1990); K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura, and M. Irie, *Chem. Lett.*, **1999**, 63; M. Irie, O. Miyatake, K. Uchida, and T. Eriguchi, *J. Am. Chem. Soc.*, **116**, 9894 (1994).