

Fatigue Property of Oxidized Photochromic Dithienylethene Derivative for Permanent Optical Recording

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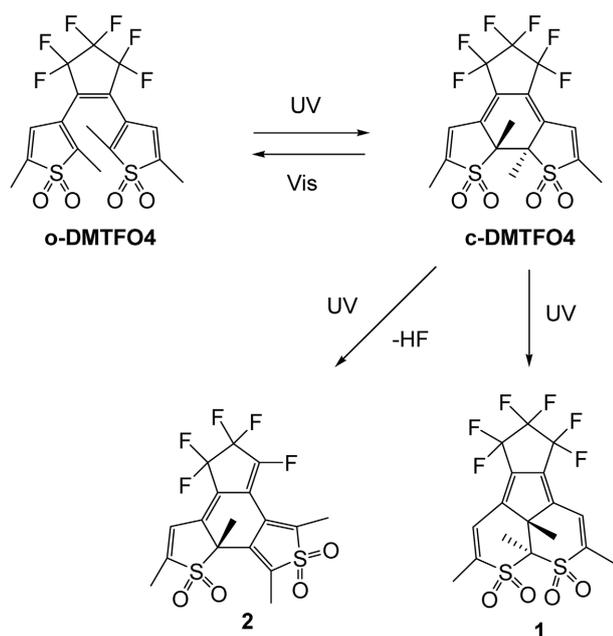
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Photochromic diarylethenes, such as 1,2-bis(2-methyl-1-benzothiophene-3-yl)perfluorocyclopentene (BTF6)¹ and 1,2-bis(2,5-dimethylthien-3-yl)perfluorocyclopentene (DMTF6),² have been extensively investigated in recent years in order to develop materials for molecular photonic devices such as optical memory and switch.^{3,4} In the design of photochromic materials, thermal stability and fatigue resistant are important features to be considered.^{3a} The thiophene analogues undergo photochromic ring closure efficiently but the fatigue property is generally low, resulting irreversible photochromism. If the photochromism is in an irreversible manner it could be applied in the permanent optical recording such as write once read many (WORM) memory. This motivates us to examine the effect of oxidation in the photophysical properties of diarylethenes with thiophene unit. As the thiophene analogues, we chose DMTF6 and its oxidized analogue, 1,2-bis(2,5-dimethylthien-1,1-dioxide-3-yl)perfluorocyclopentene (DMTFO4). Herein we report the synthesis and characterization of the photochromic properties including the fatigue property of DMTFO4.



Scheme 1. Photochromic reaction and the formation by-products of DMTFO4.

DMTF6 was prepared according to the procedures described in the literature.² DMTFO4 was prepared from the oxidation of DMTF6 using 3-chloroperbenzoic acid (*m*-CPBA) in 85% yield.^{5,6} The structure of DMTF6 and DMTFO4 was characterized using ¹H-NMR and HRMS.

Figure 1 shows the change of absorption spectra of DMTF6 (A) and DMTFO4 (B), as a function of time in ethyl acetate solution (1×10^{-5} M) at room temperature upon 312 nm irradiation using hand-held lamp. Upon UV illumination, the open-ring isomer of DMTF6 (o-DMTF6) and DMTFO4 (o-DMTFO4) undergoes photo-cyclization reaction showing new absorption bands at 480 nm and 360 nm for c-DMTF6 and c-DMTFO4, respectively. Upon visible illumination, the c-DMTF6 is completely returned back to the corresponding open-ring isomer (Figure 1C), whereas the absorption spectrum of c-DMTFO4 slightly changes and doesn't match with corresponding o-DMTFO4 as can be seen in Figure 1D. This result implies that an irreversible side reaction might be occurred from c-DMTFO4 under UV irradiation.

To elucidate the origin of the spectral changes in absorption spectra of DMTFO4 upon UV exposure, we examined ¹H-NMR change under UV light irradiation for 20 hours. Figure 2 shows ¹H-NMR of the thiophene ring protons of

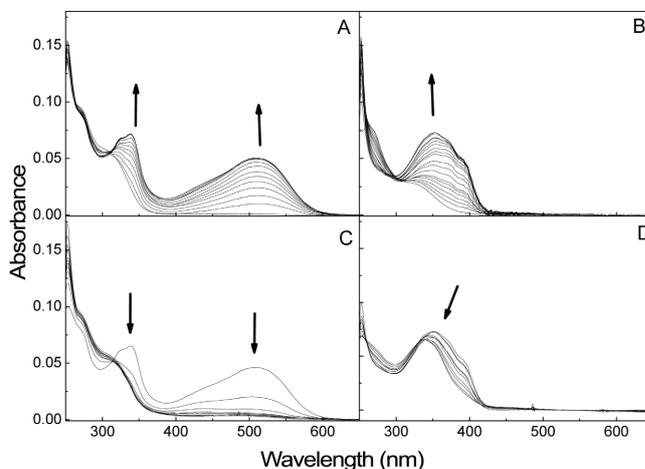


Figure 1. Changes of absorption spectra of DMTF6 and DMTFO4 as a function of time in ethyl acetate solution (1×10^{-5} M) at room temperature upon irradiation with UV (A, B) and visible light (C, D), respectively.

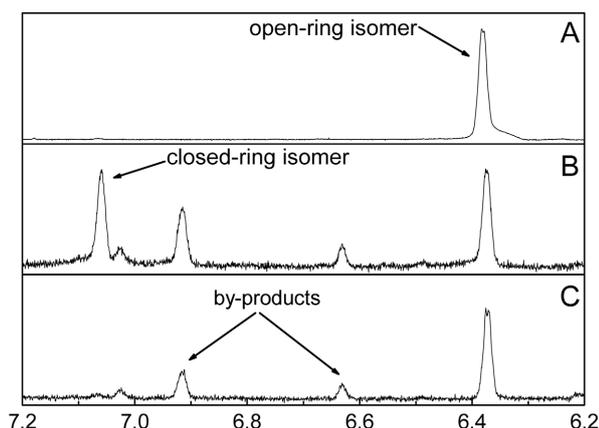


Figure 2. ^1H NMR spectra of the thiophene protons of DMTF04; (A) open-ring isomer (B) after UV irradiation for 20hr and (C) after visible irradiation in CDCl_3 (5×10^{-2} M) at room temperature.

DMTF04. In the spectrum of the open-ring isomer, the singlet peak appears at 6.39 ppm.⁵ Upon irradiation with 312 nm, a new singlet peak of the closed-ring isomer appears at 7.28 ppm. The intensity of the two signals indicates that the relative population of the open and closed-ring isomer is around 50 : 50. In addition, we observed two new peaks at 6.9 and 6.6 ppm. These peaks didn't disappear even after visible light irradiation, which implies that the new peaks are related with by-products rather than the closed-ring isomer. The fatigue properties of DMTF6 are consistent with that of the reported structure.⁷ It is unexpected that the by-products were more efficiently produced from DMTF04 than from DMTF6. Scheme 1 illustrates the photochromic reaction of DMTF04 and their possible side reactions upon UV illumination.^{7,8}

To understand the kinetics of photoreaction for DMTF04, we employed fluorescence spectroscopy instead of absorption spectroscopy because of the overlap of the absorption bands of the by-product with its closed-ring isomer. Figure 3A shows the fluorescence spectrum of o-DMTF04 (solid line) and c-DMTF04 (dashed line). Similar to the case of 1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (BTFO4)⁵ and 1,2-bis(6-acetyl-2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (DABTFO4),⁹ the fluorescence quantum yield of DMTF04 is increased upon photocyclization. Figure 3B represents the fluorescence intensity changes of DMTF04 monitored at 470 nm upon continuous UV illumination (312 nm) as a function of time. Initial increase in the fluorescence intensity is related to the photocyclization and the decay may be related to the irreversible formation of the by-products. DMTF04 was quantitatively converted to the by-product upon 312 nm illumination with a time constant of 8 min. Since there is no fluorescence after 50 minute, we can assume that the fluorescence quantum yield of the by-product is extremely low compared with c-DMTF04. This result opens up the possible application of DMTF04 in permanent optical recording based on the non-reversible photochromic conversion of DMTF04. Either by fluores-

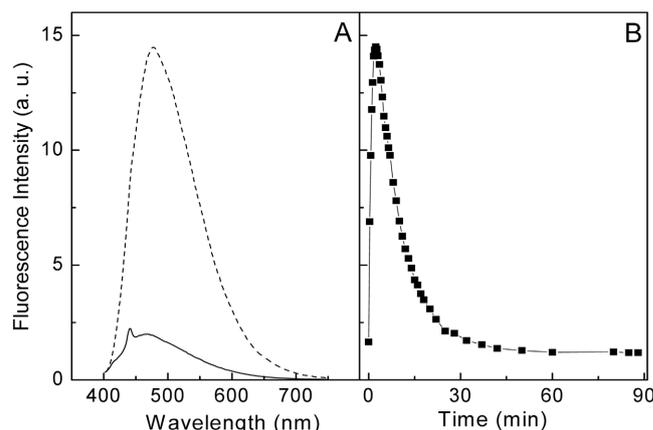


Figure 3. (A) Fluorescence spectra of o-DMTF04 (solid line) and c-DMTF04 (dashed line) in ethyl acetate solution (1×10^{-5} M) (B) The fluorescence intensity changes of DMTF04 monitored at 470 nm as a function of time upon continuous UV illumination.

cence or absorption change, one can read information recorded on a media containing DMTF04.

In summary, we have synthesized and characterized the photophysical and fatigue properties of DMTF04. The results have shown that the photo-stability of DMTF04 was significantly decreased compared with the unoxidized DMTF6. The possible application of DMTF04 would be the development of permanent recording material based on a non-reversible photochromic conversion.

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- DMTF04**-open-ring isomer: m.p. 168 °C (decompose) ^1H NMR (CDCl_3 , 300 MHz) δ : 6.38 (s, 2H), 2.22 (s, 6H), 2.00 (s, 6H). HRMS (m/z); calcd. for $\text{C}_{17}\text{H}_{14}\text{F}_6\text{O}_4\text{S}_2$; 460.0238, found 460.0237., closed-ring isomer: ^1H NMR (CDCl_3 , 300 MHz) δ : 7.06 (s, 2H), 2.37 (s, 6H), 1.68 (s, 6H).
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