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Photochromism of diarylethenes having nitronyl nitroxides

Kenji Matsuda * and Masahiro Irie *

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, and CREST, Japan Science and Technology Corporation, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

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Abstract

The photoreactivities of photochromic diarylethenes having nitronyl nitroxide radicals were studied in terms of the measurement of the quantum yields and the conversions in the photostationary state. © 2000 Elsevier Science Ltd. All rights reserved.

Photochromic compounds have been recognized as candidates for optoelectronic materials, such as optical memory media or switches.[1–3] Diarylethenes, especially, are the most promising because of their thermal stability of both isomers even at 100°C, high fatigue resistance (>10^4 coloration/decoloration cycles), and very rapid response time (~1 ps).[4] For this application one of the basic requirements is the control of photoreactivity. The quantum yield of the cycloreversion reaction of diarylethenes was reported to be changed by the introduction of electron-donating substituents.[5] During the course of our studies of photoswitching of the magnetic interaction between organic radicals connected by dithienylethene,[6] we found that the photoreactivity of the dithienylethene was influenced by incorporating nitronyl nitroxide radicals. Since photochromic compounds with unpaired electrons have not yet been reported, the effect on the photoreactivity is interesting. In this paper, the photoreactivities of the radical-containing diarylethenes were studied by quantum yields and conversion rates.

Nitronyl nitroxide is a typical organic radical that is stable at room temperature in the air. The systems which we examined are shown in Scheme 1. The photoreactivities of radical-substituted **3** and **5** were compared with 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene **1**.

Compound **1** was formylated by dichloromethyl methyl ether (1 equiv. for monoformylation and 15 equiv. for diformylation) and aluminum chloride (1 equiv. for monoformylation and 4 equiv. for diformylation) in dry nitrobenzene to give mono- and diformyl derivatives. The mono- and diformyl derivatives were refluxed in methanol with 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (2.5 equiv.) in the presence of K_2CO_3 (2.5 equiv.) then oxidized with sodium periodate (3 equiv.) in dichloromethane and water to give nitronyl nitroxides **3** and **5**. Dark-blue plate crystals of **3** and **5** were obtained by

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* Corresponding authors.

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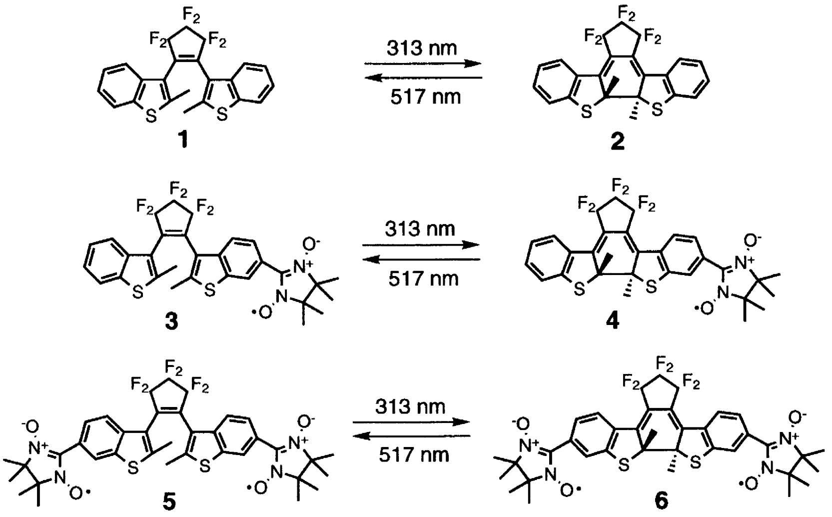


Scheme 1.

recrystallization from hexane–CH_2Cl_2.[7] Compounds **3** and **5** were stable in the air and showed ESR spectra of 5 lines and 9 lines, respectively, at room temperature in benzene solution.

The photochromism of diarylethenes **3** and **5** was studied. Fig. 1 shows the photochromic interconversion between **3** and **4**, and **5** and **6**. The ethyl acetate solution of **3** (3.4×10^{-6} M) was irradiated with 313 nm light. Upon irradiation the intense absorption at 543 nm grew and after 30 min it reached the photostationary state. The color of the solution was changed from pale blue to red purple. Clear isosbestic point was observed at 330 nm. Then the sample was irradiated with 578 nm light for 10 min. The spectrum converted back to the original one with retention of isosbestic point at 330 nm. Although the radical moiety has absorption around 550–700 nm, the existence did not prohibit the photochromic reaction. Similar photochromic behavior was also observed starting from closed-ring form **4**. Upon irradiation with 578 nm light the absorption at 543 nm almost disappeared. After that the solution was irradiated with 313 nm light. In the photostationary state the ratio of the closed-ring form was 79%.

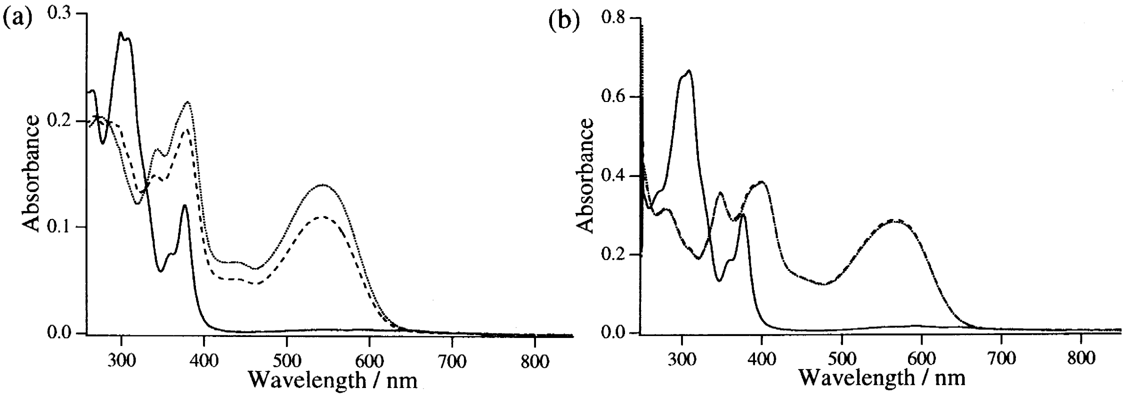


Fig. 1. Absorption spectra of ethyl acetate solution of (a) monoradical **3** and **4** (9.7×10^{-6} M) and (b) diradical **5** and **6** (1.7×10^{-5} M). (—) Open-ring form, (· · · ·) closed-ring form, and (- - - -) in the photostationary state

The photochromism of **5** showed different photoreactivity.[6] The ethyl acetate solution of **5** (1.7×10^{-5} M) was irradiated with 313 nm light. The color change was similar to that of **3**. It took only 5 min to reach the photostationary state and it took as much as 60 min to convert back to the original state. In addition in the photostationary state, the ratio of the closed-ring form was almost 100%. For the practical usage of the photochromic material, high conversion is one of the important characteristics.

The quantum yields of the diarylethenes **3** and **5** were measured in ethyl acetate using **1** as reference.[8] The degree of conversion at the photostationary state was determined by comparing the UV–vis spectra of the closed-ring form isomers and the sample at photostationary state. The results are summarized in Tables 1 and 2. The conversion in the photostationary state can be expressed by ε values at the irradiation wavelength, ε_A and ε_B, and cyclization and cycloreversion quantum yields, $\Phi_{A\rightarrow B}$ and $\Phi_{B\rightarrow A}$, as shown in Eq. (1).

$$conversion_{A\rightarrow B} = \frac{\Phi_{A\rightarrow B}\varepsilon_A}{\Phi_{A\rightarrow B}\varepsilon_A + \Phi_{B\rightarrow A}\varepsilon_B} \tag{1}$$

Table 1
Absorption maxima and coefficients of the open-ring isomers of **1**, **3**, and **5** and the quantum yields of cyclization reaction in ethyl acetate

	λ_{max} / nm (ε)	$\Phi_{open\rightarrow closed}$	Conversion (313 nm)
1	258 (16000)	0.31 (313 nm)	0.43
3	298 (29000)	0.011 (313 nm)	0.79
5	309 (34000)	0.040 (313 nm)	1.00

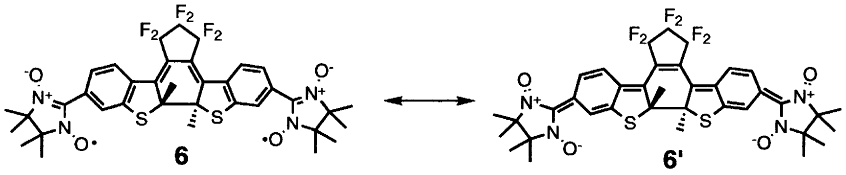
Table 2
Absorption maxima and coefficients of the closed-ring forms of **2**, **4**, and **6** and the quantum yields of cycloreversion reaction in ethyl acetate

	λ_{max} / nm (ε)	$\Phi_{closed\rightarrow open}$	Conversion (517 nm)
2	523 (10000)	0.28 (517 nm)	1.00
4	543 (15000)	0.010 (517 nm)	1.00
6	565 (15000)	0.0010 (517 nm)	1.00

The calculated conversions agreed well with the experimental values. The cyclization and cycloreversion quantum yields of monoradical **3** and **4** were about 1/30 of those of non-substituted diarylethenes **1** and **2**. This can be attributed to the energy transfer from diarylethene to the radical moiety. Although non-substituted open-ring form **1** exhibited fluorescence at around 435 nm, radical-substituted **3** and **5** were non-fluorescent, when excited at 313 nm in ethyl acetate. This suggests that excitation energy is transferred to the radical moiety.

The cycloreversion reaction of disubstituted compound **6** was further suppressed. The closed-ring isomer **6** has a resonant quinoid structure. The resonant quinoid structure **6′** stabilizes the closed-ring form isomer, but there is no such stabilization in open-ring isomer **5** or monosubstituted closed-ring isomer **4** (Scheme 2). This suppression of cycloreversion reaction resulted in high conversion from open-ring isomer **5** to closed-ring isomer **6**. Lehn et al. reported that closed-ring isomer of bisphenolic diarylethenes is electrochemically oxidized to the quinoid form, and its cycloreversion reaction is strongly suppressed.[9,10] In the present case, the contribution of the quinoid structure was relatively small. Therefore, the cycloreversion reaction took place, though the quantum yield was small.

In conclusion, we have studied the photoreactivities of diarylethenes having nitronyl nitroxide radicals. The quantum yields of both cyclization and cycloreversion reactions were suppressed by the introduction



Scheme 2.

of a nitronyl nitroxide radical to one of the aryl groups. The cycloreversion reaction of the disubstituted compound was further suppressed due to the contribution of the resonant quinoid structure in the closed-ring form isomer.

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7. Selected data for **3**: dark blue microcrystal; mp 218.5–219.0°C (decomp.); UV–vis (AcOEt) λ_{max} (ε) 298 (2.9×10^4), 360 (6.3×10^3), 377 (1.0×10^4), 548 (sh), 600 (3.5×10^2), 645 (3.5×10^2), 712 (sh); ESR (benzene) 1:2:3:2:1, 5 lines, g=2.007, a_N=7.3 G. Anal. found: C, 57.42; H, 4.11; N, 4.53%; calcd for $C_{30}H_{25}F_6N_2O_2S_2$: C, 57.78; H, 4.04; N. 4.49%. The data for **5** has been reported in Ref. 6.
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