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Effect of Imino Nitroxyl and Nitronyl Nitroxyl Groups on the Photochromic Reactivity of Diarylethenes

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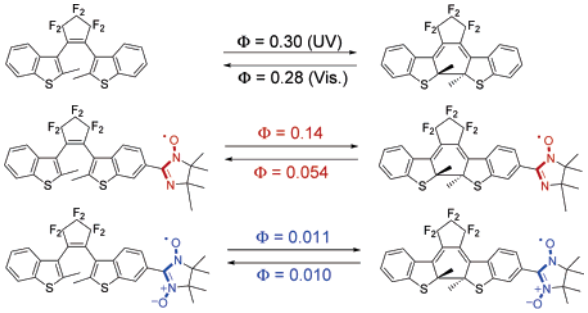
ABSTRACT



Diarylethene derivatives having imino nitroxide and nitronyl nitroxide have been prepared to examine the effect of the radical substituents on the photochromic reactivity of 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene. These radical substituents reduce the quantum yields of both cyclization and cycloreversion reactions. The nitronyl nitroxyl moiety is more effective to suppress the reactivity in comparison with the imino nitroxide moiety.

Photochromic compounds have been extensively studied for optoelectronic devices, such as optical data storages, displays, and switches.[1] Among the compounds, diarylethene derivatives are the most promising candidates for the technological applications because of their thermal and photo stability.[2] Diarylethene derivatives having a radical moiety at each end of the molecule have been investigated as effective photoswitches of intramolecular magnetic interactions.[3]

Although several photochromic molecules having radical substituents are synthesized, such as derivatives of 9,10-diphenyl anthracene,[4] azobenzene,[5] naphthopyran,[6] and arylimine,[7] the effect of radical substituents on the photochromic reactivity has not yet been clarified. In this paper, we examine the effect of the radical substituents on the reactivity of diarylethenes based on the absorption spectra, quantum yield, and conversion under irradiation with UV light.

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Figure 1 shows diarylethenes **1a**−**6a** which are discussed in this paper. Diarylethenes **2a**, **4a**, and **5a** are new

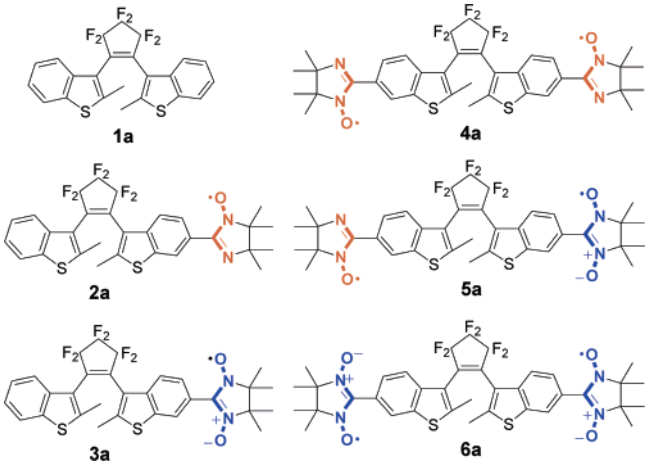

Figure 1. Diarylethene diradicals **2a**−**6a** that are derivatives of bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene **1a**.

compounds, and compounds **1a**,[8] **3a**,[3b] and **6a**[3a] are known compounds. The effect of nitronyl and imino nitroxyl substituents on the photochemical reactivity was examined. Compound **2a** was synthesized from **3a** by the treatment with sodium nitrite. Compounds **4a** and **5a** were synthesized by the oxidation of 1,2-bis[6-(1,3-dihydroxy-4,4,5,5-tetramethylimidazolidin-2-yl)-2-methyl-1-benzothiophen-3-yl]hexafluorocyclopentene using sodium metaperiodate. For all compounds, the structures were confirmed by ESR and high-resolution mass spectroscopy.

Figure 2 shows the absorption spectral changes of diarylethenes **1**−**6**. Upon irradiation with 313 nm light, all compounds underwent photochromic reactions in ethyl acetate solution. The pale orange solution **2a** turned red-purple with the retention of isosbestic point at 307 and 326 nm. The color change is due to the formation of the closed-ring isomer **2b**. This red-purple color disappeared upon irradiation with visible light. Pale orange solution **3a** turned red-purple, and dark brown solution **5a** turned purple. Table 1 summarizes the absorption maxima of the open-ring isomers **1a**−**6a** and the conversion ratios under irradiation with 313 nm light. The conversion ratio at the photostationary state was determined by comparing the absorbance of the closed-ring isomer with that in the photostationary state. Upon irradiation with 517 nm light, the closed-ring isomers **1b**−**6b** underwent cycloreversion reaction to **1a**−**6a**. The absorption maximum showed slight bathochromic shifts upon increasing π-conjugated chain length.

The quantum yields of compounds **2**, **4**, and **5** were measured in ethyl acetate using **1** as a reference.[3b] The results are shown in Table 1 with data of the other diarylethene diradicals. The conversion can be expressed by eq 1, where ϵ_a and ϵ_b are absorption coefficients at irradiated wavelength and $\Phi_{a\rightarrow b}$ and $\Phi_{b\rightarrow a}$ are cyclization and cycloreversion quantum yields. The calculated conversion ratios well agreed with the experimental data.

$$\text{conversion}_{a\rightarrow b} = \frac{\Phi_{a\rightarrow b}\epsilon_a}{\Phi_{a\rightarrow b}\epsilon_a + \Phi_{b\rightarrow a}\epsilon_b} \qquad (1)$$

The cyclization and cycloreversion quantum yields of radical-substituted diarylethenes **2**−**6** are smaller than the

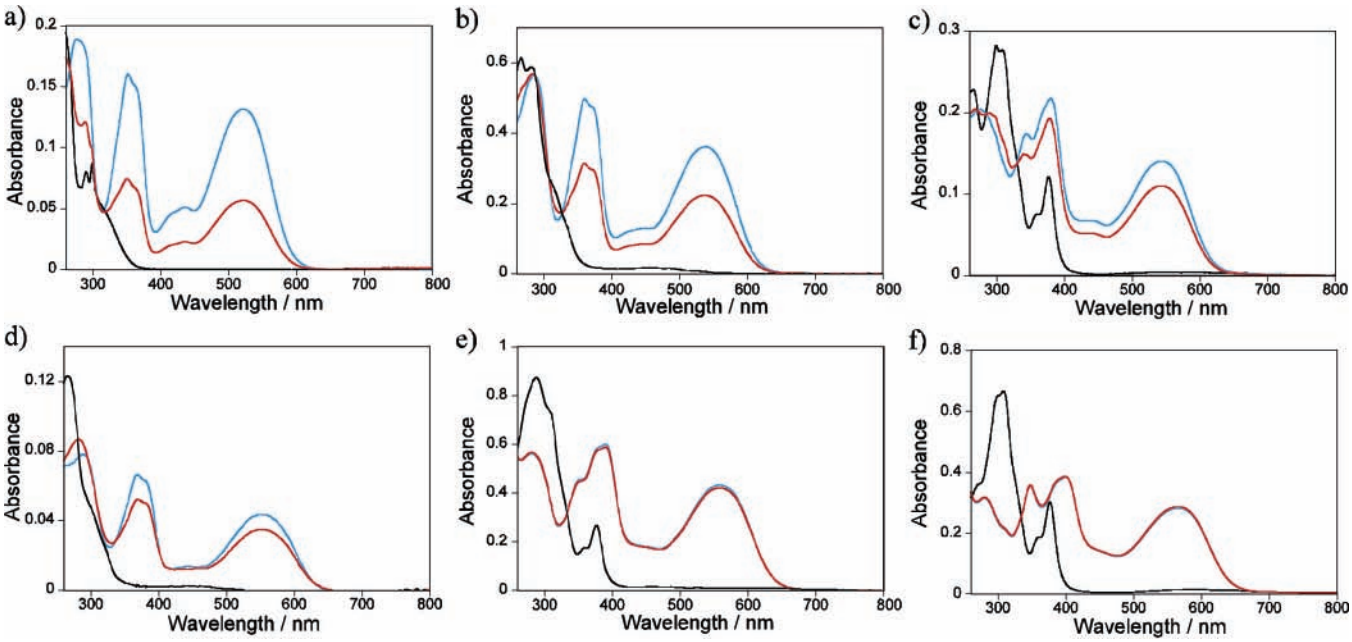

Figure 2. Absorption spectral change of (a) **1a** (~1.2×10^{-5} M), (b) **2a** (~2.8×10^{-5} M), (c) **3a** (~9.7×10^{-6} M), (d) **4a** (~3.8×10^{-6} M), (e) **5a** (~2.7×10^{-5} M), and (f) **6a** (~1.7×10^{-5} M) in ethyl acetate solution by photoirradiation: open-ring isomer (black line); closed-ring isomer (blue line); photostationary state under irradiation with 313 nm light (red line).

Table 1. Absorption Maxima and Coefficients of **1**−**6** and the Quantum Yields and Conversions in Ethyl Acetate

	λ_{max}/nm ($\epsilon \times 10^3$/M^{-1} cm^{-1})		quantum yield		
	a	**b**	$\Phi_{a\rightarrow b}$ (313 nm)	$\Phi_{b\rightarrow a}$ (517 nm)	conversion (calcd)
1[a]	258 (16)	351 (12), 523 (10)	0.31	0.28	0.43 (0.50)
2	267 (20), 320 (sh), 460 (sh)	360 (16), 537 (11)	0.14	0.054	0.61 (0.77)
3[a]	297 (20), 377 (10), 600 (0.35), 645 (0.35)	380 (23), 543 (15)	0.011	0.010	0.79 (0.71)
4	265 (34), 300 (sh), 450 (sh)	381 (20), 551 (14)	0.078	0.012	0.85 (0.89)
5	289 (34), 376 (11), 450 (sh), 596 (0.41), 648 (0.40)	390 (23), 558 (15)	0.041	0.0010	1.00 (0.99)
6[a]	309 (34), 377 (16), 598 (0.63), 646 (0.63)	400 (20), 565 (15)	0.040	0.0010	1.00 (0.99)

[a] Taken from ref 3b.

value of **1**. The cyclization quantum yields of monoiminonitroxyl-substituted **2a** and diiminonitroxyl-substituted **4a** are 47% and 19% of that of nonsubstituted diarylethene **1**. This result indicates that the quantum yields are reduced depending on the number of radical moieties. The cyclization quantum yields of monoiminonitroxyl-substituted **2a** and mononitronylnitroxyl-substituted **3a** are 47% and 3.5% of that of **1**. This result suggests that nitronyl nitroxyl radical is more effective to suppress cyclization reaction in comparison with imino nitroxyl radical.

The main cause of the suppression of the cyclization reaction is considered to be the energy transfer from the diarylethene core to the radical substituents. Therefore the absorption of these radicals were investigated.[9] Absorption spectra of **3a**, **5a**, and **6a** have absorption band around 360 nm, while the band is not discerned in **1a**, **2a**, and **4a**. Figure 3 shows the absorption spactra of *p*-bromophenyl nitronyl nitroxide **7** and *p*-bromophenyl imino nitroxide **8**. Nitronyl nitroxide has a strong absorption band at 367 nm (ϵ = 16 000) and imino nitroxide has a weak absorption band at 311 nm (ϵ = 4000). These absorption bands are assigned to $\pi-\pi^*$ transitions. The absorption bands in the visible region are assigned to n$-\pi^*$ transitions. The absorption characteristics were reproduced by time-dependent density-functional theory (TD-DFT) calculations with UB3LYP functional and 6-31G basis set.[10] The calculation indicated that nitronyl nitroxide has a 360 nm absorption band with an *f* value of 0.0699 and imino nitroxide has a 338 nm absorption band with an *f* value of 0.0144. The radical moieties are considered to act as the energy acceptors. Since the cyclization reaction is reported to be very fast (<2 ps),[11] the cyclization was not completely quenched. The energy transfer from diarylethene core to nitronyl nitroxyl radical is more effective than the energy transfer to imino nitroxyl radical.

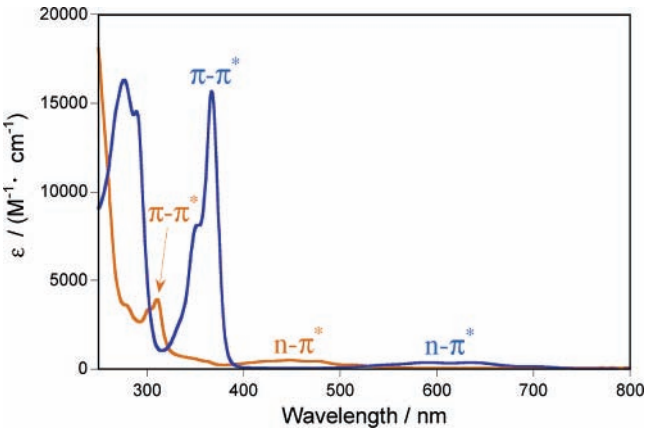

Figure 3. Absorption spectra of *p*-bromophenyl nitronyl nitroxide **7** (blue line) and *p*-bromophenyl imino nitroxide **8** (orange line) in ethyl acetate solution.

On the other hand, the suppression of the cycloreversion reactions cannot be explained by the energy transfer because the absorption bands of the closed-ring isomers have lower energy than the $\pi-\pi^*$ absorption band of the radicals. An important factor affecting the cycloreversion quantum yield is the resonant quinoid structures (Scheme 1). The cycloreversion quantum yields of **5b** and **6b** are exceptionally small. This is due to the formation of quinoid structures. In the study of biradicals and triradicals, nitronyl nitroxide is known to have stronger intramolecular magnetic interaction than imino nitroxide because of the formation of quinoidal structures.[12] In the case of **4** which has two imino nitroxyl moieties, contribution of the quinoid form is considered to be small. Therefore, imino nitroxide radical did not affect

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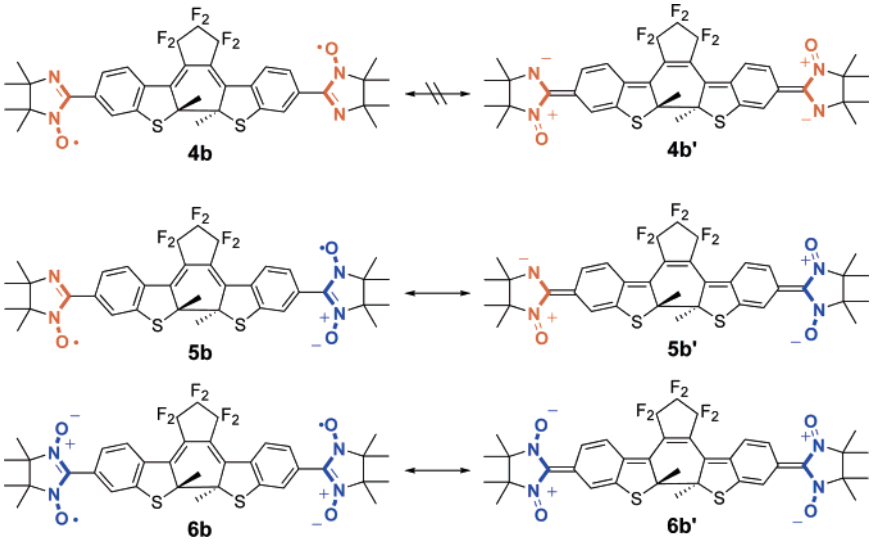
Scheme 1. Resonant Stabilization of the Closed-Ring Isomers **4b**, **5b**, and **6b** That Have Two Radical Substituents



the cycloreversion reaction. Nitronyl nitroxide has an allyl-like structure, so that the quinoidal structure cannot be dominant, but even a slight purturbation of the electronic structure affects the quantum yield significantly.

In conclusion, the excited-state energy transfer from the diarylethene core to the radical moieties reduced the cyclization reaction of diarylethene derivatives having radical substituents. Nitronyl nitroxyl radical is more effective to suppress the reactivity in comparison with imino nitroxyl radical. The cycloreversion reactions are also suppressed by the contribution of quinoidal structures. The present results are useful for the design of efficient photoactive organic magnetic materials.

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Supporting Information Available: Detailed synthetic procedures of **1a**−**6a**, **10a**, and **11a**, optimized Cartesian coordinates, and HPLC charts of **2a**, **4a**, and **5a**. X-ray structural data for **3a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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