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Electrochemical Cyclization/Cycloreversion Reactions of Diarylethenes

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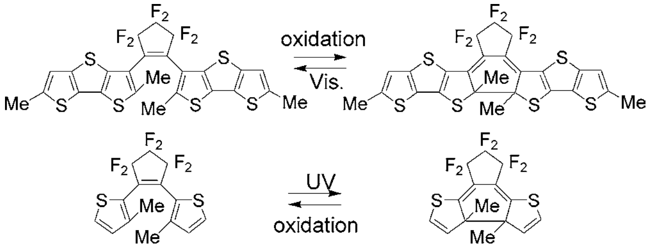
ABSTRACT



Electrochemical oxidation of diarylethene derivatives induced cyclization or cycloreversion reactions. The reaction mechanism was studied with CV, absorption spectra, and theoretical calculation.

Diarylethenes undergo reversible electrocyclic reactions upon alternate irradiation with UV and visible light.[1,2] Such electrocyclic reactions can be induced not only upon photoirradiation but also by electrochemical reduction or oxidation.[3] Fox reported the electrochemical cyclization of fulgide,[4] and Kawai and Branda recently reported the cycloreversion[5] and cyclization[6] of diarylethenes. The electrochemical reactions are being used for molecular switching[7] and also can be potentially applied to molecular-scale electronic switches.[8] The structural requirements and the mechanism of the reactions, however, have not yet been well understood. To reveal the mechanism, the oxidative cyclization and cycloreversion of some diarylethene derivatives were studied, and the basic requirement for the reactions was proposed.

The following three diarylethenes, 1,2-bis(2,6-dimethyldithieno[3,2-*b*;2′,3′-*d*]thiophen-3-yl)perfluorocyclopentene **1a**,[9] 1-(2-methyl-benzothiophen-3-yl)-2-(1,2-dimethylindol-3-yl)-

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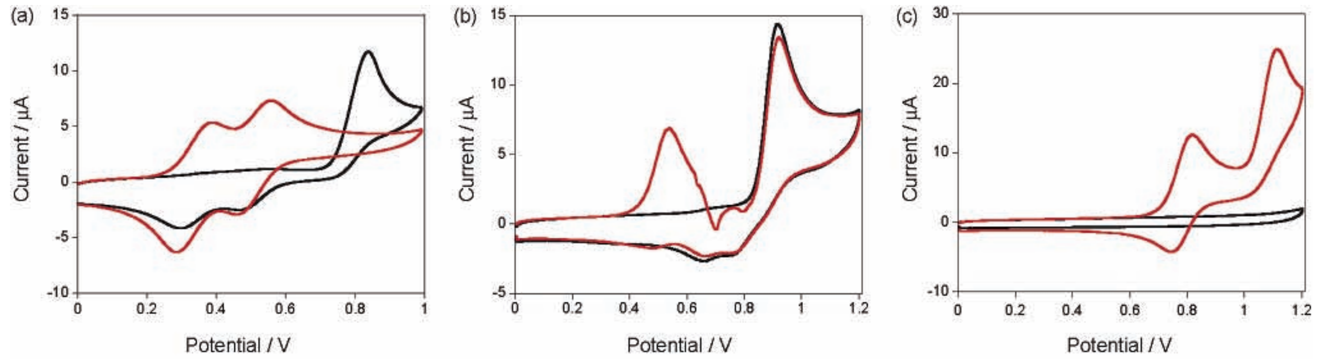
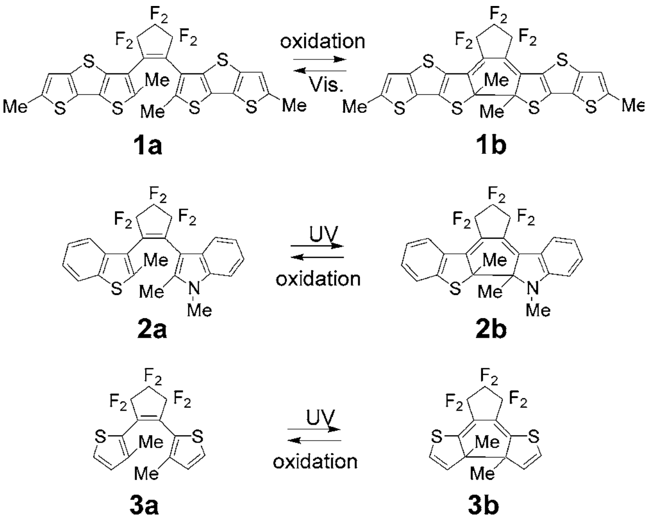


Figure 1. Cyclic voltammograms of (a) **1a** (black) and **1b** (red); (b) **2a** (black) and **2b** (red); (c) **3a** (black) and **3b** (red). Measurements were performed in dichloromethane (1×10^{-3} M) for **1** and acetonitrile (1×10^{-3} M) for **2** and **3** (0.1 M TBAP) on a platinum electrode (vs Fc/Fc^{+}). Scan rates were 100 mV/s.

Scheme 1 Photoelectrochromism of Diarylethene **1**, **2**, and **3**



perfluorocyclopentene **2a**,[10] and 1,2-bis(3-methyl-2-thienyl)-perfluorocyclopentene **3a**,[11] were prepared according to the reported procedures (Scheme 1). These compounds underwent photochromic reactions in solution as already reported in the literature.

Figure 1 shows cyclic voltammograms (CV) of **1a**, **1b**, **2a**, **2b**, **3a**, and **3b**. The closed-ring isomers were isolated by HPLC. The closed-ring isomer **1b** shows oxidation waves at 0.39 and 0.56 V and reduction waves at 0.46 and 0.28 V. When **1a** was oxidized at 0.84 V, reduction peaks appeared at 0.75, 0.46, and 0.28 V. The peak height at 0.84 V suggests that the oxidation wave includes both the first and the second oxidation processes. The reduction peaks at 0.46 and 0.28 V corresponds to the closed-ring isomer **1b**. In the second cycle of the CV measurement, oxidation peaks at 0.39 and 0.56 V were observed along with the peaks at 0.84 V. When **1a** was oxidized with $FeCl_3$, the closed-ring isomer **1b** was formed (Figure S3 in Supporting Information). Formation of a *cis*-type compound was not discerned. This result indicated that oxidation of the open-ring isomer **1a** gave the closed-ring isomer **1b**.

To confirm the oxidative cyclization reaction of **1a**, the radical cation of **1a** was produced by γ-irradiation in 1-chlorobutane at 77 K and its reaction was followed. It is well-known that solute mono-radical cation is produced in alkyl halide matrices with high energy radiation.[12] Upon irradiation with γ-rays new absorption peaks due to the radical cation of **1a** appeared at 428 and 650 nm at 77 K. When the sample was warmed to room temperature, the absorption bands due to the radical cation disappeared and an absorption due to the closed-ring isomer appeared at 615 nm. The result confirms that the oxidation of **1a** induces the cyclization reaction.

The open-ring isomer **2a** showed an oxidation wave at 0.92 V. On the other hand, the closed-ring isomer **2b** showed an oxidation wave at 0.54 and 0.92 V. The second oxidation wave at 0.92 V is consistent with the oxidation wave of the open-ring isomer **2a**. As the scan speed gets faster, the second wave intensity gets smaller compared with the first wave intensity. This voltammogram suggests that **2b** undergoes an oxidative cycloreversion reaction. This oxidative cycloreversion reaction of **2b** was also performed chemically. When $FeCl_3$ (1 equiv) was added to the closed-ring isomer **2b**, the open-ring isomer **2a** was obtained. When 0.1 equiv of $FeCl_3$ was used, the ratio of the open-ring isomer was 46%, suggesting that the reaction is catalytic. No side reaction was observed.

While the CV measurement of the open-ring isomer **3a** showed no peaks between 0 and 1.2 V, the voltammogram

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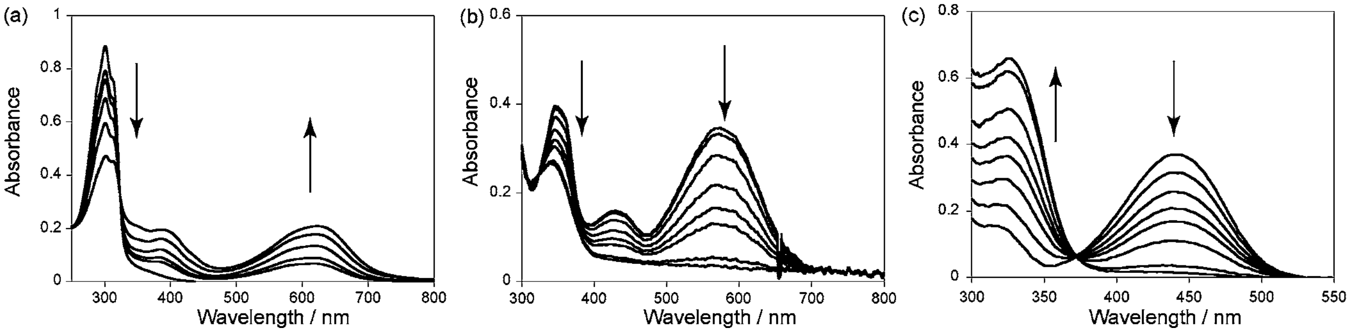


Figure 2. (a) Change of the absorption spectrum of **1a** by electrolysis at 0.75 V (Ag/Ag$^+$) (acetonitrile, 2 × 10^{-5} M). Open-ring isomer **1a**, after electrolysis for 5, 10, 30, 60, and 120 min. (b) Change of the absorption spectrum of **2b** by electrolysis at 0.75 V (Ag/Ag$^+$) (acetonitrile, 5 × 10^{-4} M). Closed-ring isomer **2b**, after electrolysis for 1, 2, 3, 4, 5, 10, and 20 min. (c) Change of the absorption spectrum of **3b** by electrolysis at 0.90 V (Ag/Ag$^+$) (acetonitrile, 1 × 10^{-3} M). Closed-ring isomer **3b**, after electrolysis for 5, 10, 15, 20, 30, 60, and 120 min.

of the closed-ring isomer **3b** showed oxidation peaks at 0.82 and 1.11 V and reduction peaks at 1.1 and 0.74 V. Since the open-ring isomer did not show any peaks, the CV measurement cannot give any information concerning the oxidative reactions.

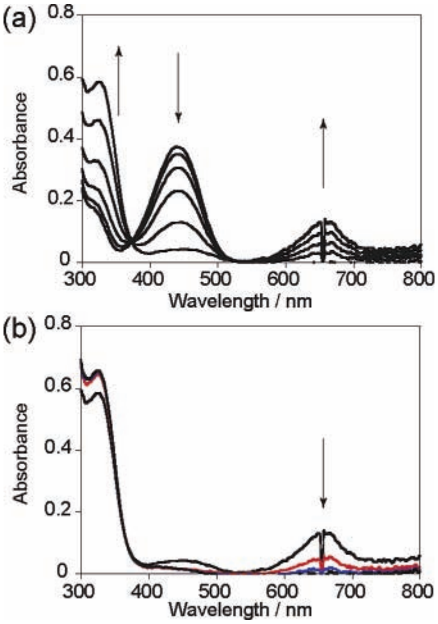
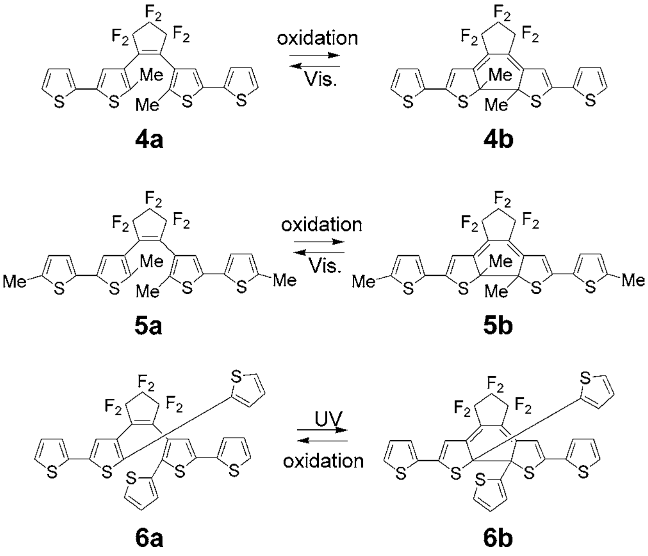


Figure 3. (a) Change of the absorption spectrum of **3b** by electrolysis at 1.0 V (Ag/Ag$^+$) (acetonitrile, 1 × 10^{-3} M). Closed-ring isomer **3b**, after electrolysis for 1, 2, 3, 4, and 5 min. (b) Change of the absorption spectrum of **3b** after measurement of (a). Initial, 30 s (red), 60 s (blue), 120 s.

Figure 2 shows the absorption spectral changes along with the electrolysis of **1**, **2**, and **3**. Upon electrolysis of the solution of the open-ring isomer **1a** in acetonitrile at 0.75 V (vs Ag/Ag$^+$) the absorption band at 615 nm increased with retention of the isosbestic point at 323 nm. The solution turned blue immediately. The absorption maximum was identical with the reported absorption maximum of the closed-ring isomer **1b** (612 nm).[9] When the solution was irradiated by visible light, the blue color disappeared. This suggests that the electrochemically generated blue color is due to the closed-ring isomer **1b**. Electrolysis was also performed for **2b** and **3b**. The decoloration was observed by the electrolysis at 0.75 and 0.90 V for **2b** and **3b**, respectively; **1a** underwent oxidative cyclization and **2b** and **3b** underwent oxidative cycloreversion.

Scheme 2



In the case of **3b**, during the electrolysis, a new band (λ_{max} = 667 nm) appeared (Figure 3a) and diminished after the electrolysis was stopped (Figure 3b). When 1-chlorobutane solution containing **3b** was irradiated with γ-rays at 77 K, new peaks due to the radical cation were observed at 656 and 906 nm (see Supporting Information). The new band at around 660 nm can be assigned as the radical cation of

Table 1. Total Energy of Cation Radicals, Energy Gaps, and Electrochemical Reactivity

	total energy of neutral form (Hartree)		total energy of cation radical (Hartree)				
entry	open-ring isomer	closed-ring isomer	open-ring isomer	closed-ring isomer	Δ*E* (C$^+$−O$^+$) (kcal/mol)	oxidative cyclization	oxidative cycloreversion
1	−3948.901778	−3948.896007	−3948.661507	−3948.678297	−10.54	yes	no
2	−1976.423011	−1976.397020	−1976.174954	−1976.163379	+7.26	no	yes
3	−1972.779483	−1972.736046	−1972.507535	−1972.484241	+14.62	no	yes
4	−3076.314470	−3076.296699	−3076.069224	−3076.074760	−3.47	yes	no
5	−3154.897794	−3154.881261	−3154.661352	−3154.666091	−2.97	yes	n/a
6	−4101.261222	−4101.218712	−4101.027948	−4101.001624	+16.52	n/a	yes

3b. It was suggested the electrochemical cycloreversion reaction proceeds via a cation radical of the closed-ring isomer.

To investigate the energetic requirement for the oxidative cyclization/cycloreversion reactions, DFT calculation was performed to obtain the total energies of the cation radicals (UB3LYP/6-31G*) and neutral forms (B3LYP/6-31G*) for both the open- and the closed-ring isomers.[13] Zero-point energy correction was included. For references, 1,2-bis(2-methyl-5-(2-thienyl)-3-thienyl)perfluorocyclopentene **4a**,[6] 1,2-bis(2-methyl-5-(5-methyl-2-thienyl)-3-thienyl)perfluorocyclopentene **5a**,[6] and 1,2-bis(2,5-di(2-thienyl)-3-thienyl)perfluorocyclopentene **6a**[5b] were also calculated (Scheme 2). Branda et al. reported that **4** and **5** undergo oxidative cyclization[6] reactions and **6** undergoes oxidative cycloreversion reaction.[5b] The total energies, the energy gaps, and electrochemical reactivities are shown in Table 1. The representative energy diagram for **1** and **2** are shown in Figure 4. For all compounds, in the neutral form, the open-ring isomers are more stable than the closed-ring isomer.

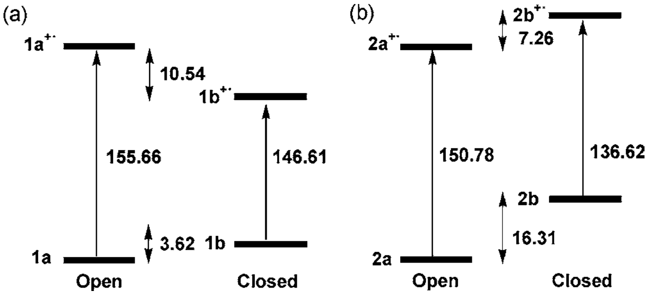


Figure 4. Schematic diagram of the energy potentials of (a) **1a**, **1b**, **1a**$^{+\bullet}$, **1b**$^{+\bullet}$ and (b) **2a**, **2b**, **2a**$^{+\bullet}$, **2b**$^{+\bullet}$. The energy unit is kcal/mol. Zero-point energy correction was included.

In the case of **2**, **3**, and **6**, the cation radicals of the open-ring isomers are more stable than the closed-ring isomers, so the oxidative cycloreversion reaction is thermodynamically allowed. On the other hand, the cation radicals of the closed-ring isomer **1b**$^{+\bullet}$, **4b**$^{+\bullet}$, and **5b**$^{+\bullet}$ are more stable than the open-ring isomers **1a**$^{+\bullet}$, **4a**$^{+\bullet}$, and **5a**$^{+\bullet}$. In these cases the oxidative cyclization is thermodynamically allowed. Although the activation energy was not taken into account by this treatment, the calculated result explains the reactivity of the radical cations of the open- and the closed-ring isomers. When Δ*E* (C$^+$−O$^+$) is plus, oxidative cycloreversion is allowed, and when Δ*E* (C$^+$−O$^+$) is minus, oxidative cyclization is allowed. As shown in Figure 4b, in the case of cycloreversion reaction, the reduction of **2a**$^{+\bullet}$ to **2a** can reoxidize **2b** to **2b**$^{+\bullet}$ because the energy gap between **2a**$^{+\bullet}$ and **2a** is larger than the energy gap between **2b**$^{+\bullet}$ and **2b**. This can explain the chain reaction.

The energy diagrams suggest that there are two possibilities in the reaction along with the oxidation of the diarylethene derivatives: oxidative cyclization of the open-ring isomers and the oxidative cycloreversion of the closed-ring isomers. These two cases can be distinguished by the energy of the radical cations of the open- and the closed-ring isomers. This explanation indicates that the oxidative cyclization and cycloreversion reactions are quite general phenomena and those two phenomena should be complimentary.

In conclusion, we have found that the diarylethene derivatives undergo oxidative cyclization reactions when the radical cations of the closed-ring isomers are more stable than the open-ring isomers and also that the diarylethenes undergo oxidative cycloreversion reactions when the radical cations of the open-ring isomers are more stable than the closed-ring isomers. The proposed mechanism can generally explain the oxidative cyclization and cycloreversion reactions of diarylethene derivatives.

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Supporting Information Available: Experimental procedures, absorption spectrum of **3b** after γ-irradiation, X-ray crystallographic structure of **1a**, HPLC chart of **1a** upon oxidation, optimized Cartesian coordinates, and NMR and HRMS spectra of **1a**, **2a**, and **3a**. X-ray structural data for **1a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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