Photochromism

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Photoelectrocatalysis to Improve Cycloreversion Quantum Yields of Photochromic Dithienylethene Compounds**

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Photochromic *cis*-1,2-dithienylethene (DTE) compounds exhibit a reversible interconversion between the open and closed forms under alternating photoirradiation. DTEs could be potentially used for molecular photonic applications because the photochromism of DTEs has advantageous characteristics, such as fatigue resistance, short response time, and reversibility.[1] In particular, the photochromism is thermally irreversible, enabling high fidelity recording of information based on a variety of signals, including fluorescence,[2] conductivity,[3] and chiroptical responses.[4] This thermal irreversibility is attributable to the huge ground-state thermodynamic barrier between the open and closed forms of DTEs; this barrier is due to the symmetry constraint as dictated by the Woodward–Hoffmann rule. For instance, the barrier height of *cis*-1,2-di(3-thienyl)ethene is as high as 46 kcal mol^{-1}.[5] The barrier height is significantly lower in the photoexcited state (i.e., $\Delta E^* < \Delta E_0$ in Figure 1a), thus enabling chromic interconversion.[5,6] In this context, photochromism can be referred to a process in which photoexcitation provides an excited-state reaction path, thus allowing a smaller energy barrier.

In contrast to photochromic cyclization,[7] photochromic cycloreversion of DTEs is very inefficient. Typically, for cycloreversion the photochromic quantum yields ($\Phi_{C\rightarrow O}$) are 10^{-2}–10^{-1}-fold smaller than those for cyclization,[1b,8] and high-power irradiation sources or long irradiation time is required. This inefficiency arises because there is an activation energy to access the conical intersections from the closed form (i.e., ΔE^* in Figure 1a) and also because there is branching at the conical intersections to both open and closed forms in the adiabatic potential energy surface (broken arrows in Figure 1a).[5,6,9] There have been several approaches to improve the $\Phi_{C\rightarrow O}$. Irie and co-workers accomplished a $\Phi_{C\rightarrow O}$ as high as 0.5 ± 0.1 by multiphoton excitation.[10] Alternatively, Scandola and co-workers employed triplet sensitization to achieve a $\Phi_{C\rightarrow O}$ value of 0.51.[11] These methods take advantage of the higher excited state or the triplet state having smaller activation barriers (ΔE^*). Despite of these achievements, however, the application of these methods are limited because of the requirement of sophisticated laser sources or judicious ordering among electronic states of DTEs and the triplet sensitizer. Furthermore, because the direction and efficiency of the photochromic reaction depends strongly on the electronic structure of DTEs,[8,12] synthetic attempts to increase multiphoton absorption cross sections or to conjugate triplet sensitizers might offset the overall efficiency.

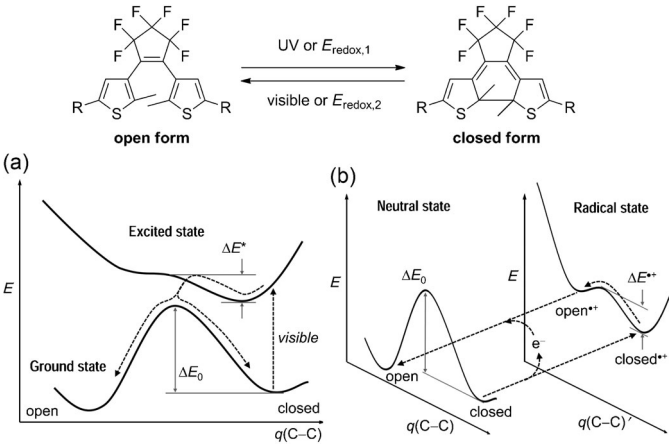

Figure 1. Schematic representation of cycloreversion in the photochromism (a) and the electrochromism (b) of DTE compounds.

It has been recently reported that photochromic DTEs undergo cycloreversion in their oxidized states.[13] The electrochromism features high conversion yields and enables dual chromism because the oxidation reaction is independent of the excited-state electronic structure of DTEs.[14] Recent mechanistic studies suggest that the electrochromic cycloreversion involves a radical cation of the closed form as a reactive intermediate.[13a,e,f] Spontaneous cycloreversion of the intermediate produces a radical cation of the open form; this radical cation is neutralized by the neutral closed form. This electrochromism is catalytic because the last step regenerates the reactive intermediate.[13b]

The electrochromism involves radical intermediates possessing significantly lower barrier energies (i.e., $\Delta E^{\bullet+} < \Delta E_0$ in Figure 1b),[14a] an effect similar to photoexcitation in the

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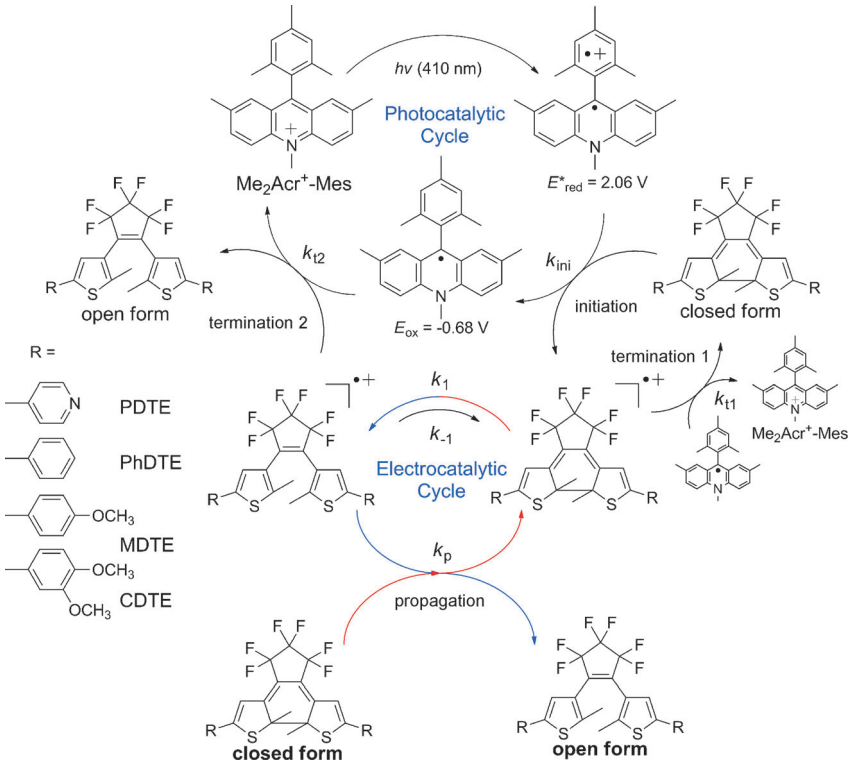
photochromism. This similarity stimulated us to develop a photoelectrocatalytic strategy to improve the efficiency of the cycloreversion. The idea is to employ a photoredox catalyst that triggers catalytic electrochromism (Scheme 1). Photoexcitation of 9-mesityl-10-methylacridinium ion (Acr^+-Mes) transiently generates the long-lived electron-transfer (eT) state ($Acr^{\bullet}$-$Mes^{\bullet+}$) having high oxidation power.[15] An



Scheme 1. Mechanism of the photoelectrocatalytic cycloreversion of DTE compounds.

exoergic eT from DTE to the $Mes^{\bullet+}$ moiety of $Acr^{\bullet}$-$Mes^{\bullet+}$ initiates the electrochromic ring opening of DTE in competition with the back eT (BeT) from the $Acr^{\bullet}$ moiety to the radical cation of the closed form (termination 1). The eT from a closed form of neutral DTE to the open-form radical cation completes cycloreversion to regenerate the closed-form radical cation; this is the propagation step of the electrocatalytic chain mechanism in Scheme 1.[16] The chain process is terminated by BeT from the $Acr^{\bullet}$ moiety to the open-form radical cation (termination 2). This strategy benefits from the catalytic nature of the electrochromism; in contrast to the photon-stoichiometric photochromism, the photon economy gains a leverage effect, thus leading to a greatly improved $\Phi_{C\rightarrow O}$. In addition, decoupling the photoexcitation component (photoredox catalyst) from the cycloreversion component (DTE) evokes excellent fatigue resistance (see the Supporting Information, Figure S1). Herein, we describe the proof-of-concept experiment for the photoelectrocatalytic cycloreversion of DTEs. A $\Phi_{C\rightarrow O}$ value as high as 0.54 was accomplished.

Four DTE compounds (PDTE, PhDTE, MDTE, and CDTE; Scheme 1),[17] each having different terminal aryl rings were used for the photoelectrocatalytic ring opening. Spectroscopic and electrochemical data of the DTE compounds are listed in the Supporting Information, Table S1. Figure 2a shows UV/Vis absorption spectra of acetonitrile solutions of 2,7-dimethyl-9-mesityl-10-methylacridinium (Me_2Acr^+-Mes) perchlorate[18] and the open (PhDTEo) and the closed (PhDTEc) forms of PhDTE. The spectrum of Me_2Acr^+-Mes featured vibronic absorption bands at 405–450 nm, where both PhDTEc and PhDTEo had negligible absorption. Monochromatized 410 nm photoirradiation of a CH_3CN solution containing 1 mM of Me_2Acr^+-Mes and 1 mM of PhDTEc led to complete ring opening of PhDTEc, as determined from the UV/Vis absorption and ^1H NMR spectra (Figure 2b and the Supporting Information, Figure S2). The absorption bands of Me_2Acr^+-Mes were intact during the cycloreversion of PhDTEc, thus indicating the catalytic role of Me_2Acr^+-Mes. Indeed, full cycloreversion was achieved in the presence of catalytic amounts of Me_2Acr^+-Mes (0.1–1 equiv; see the Supporting Information, Figure S3). $\Phi_{C\rightarrow O}$ values, determined by standard ferrioxalate actinometry (see the Supporting Information), increased in proportion with the concentration of $PhDTE_C$ (the Supporting Information, Figure S4). The photoaction spectrum plotting the ratio of $\Phi_{C\rightarrow O}$ in the presence of 1 mM of Me_2Acr^+-Mes to $\Phi_{C\rightarrow O}$ in the absence of 1 mM of Me_2Acr^+-Mes (i.e., $\Phi_{C\rightarrow O}(Me_2Acr^+\text{-Mes})/\Phi_{C\rightarrow O}(\text{no catalyst})$) as a function of the photoirradiation wavelength is shown in Figure 2a. This spectrum overlaps with the high-order vibronic absorption bands of Me_2Acr^+-Mes, thus implying that cycloreversion of PhDTEc was due to photoexcitation of Me_2Acr^+-Mes.

Under the optimized conditions ($\lambda_{ex} = 410$ nm and CH_3CN solutions containing 1 mM of photoredox catalyst and 1 mM of DTE), we determined the photoelectrocatalytic $\Phi_{C\rightarrow O}$ of PDTE, PhDTE, MDTE, and CDTE. Two different 9-mesityl-10-methylacridinium ion derivatives, Me_2Acr^+-Mes and Acr^+-Mes, were employed as photoredox catalysts. The photoelectrocatalytic $\Phi_{C\rightarrow O}$ values are summarized in Table 1, which reveals that there is one order of magnitude enhancement of $\Phi_{C\rightarrow O}$ relative to the conventional photochromic $\Phi_{C\rightarrow O}$ (control). The largest $\Phi_{C\rightarrow O}$ value is 0.54, which is comparable to the values obtained by multiphoton excitation[10] and triplet sensitization.[11] It should also be emphasized that our method does not require expensive laser sources and sophisticated energy alignments.

Based on the reaction paths depicted in Scheme 1, the photoelectrocatalytic $\Phi_{C\rightarrow O}$ can be expressed as $\Phi_{C\rightarrow O} = \alpha\cdot((k_{ini}k_p)/(k_{t1}k_{t2}))(k_1/(k_1 + k_{-1}))$, where k_{ini}, k_1, k_{-1}, k_{t1}, k_{t2}, and k_p are rate constants for the initiation through oxidative eT (k_{ini}), ring opening (k_1) and ring closing (k_{-1}) between the radical intermediates, two termination processes through

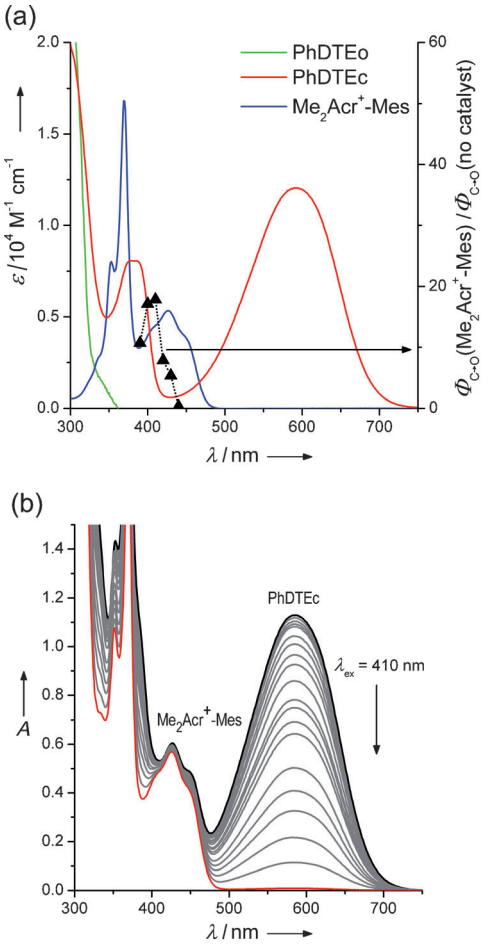


Figure 2. a) UV/Vis absorption spectra of 1 mM of Me_2Acr^+-Mes and the open (PhDTEo, 1 mM) and closed (PhDTEc, 1 mM) forms of PhDTE (CH_3CN, room temperature). The broken line with filled triangles (▲) is a photoaction spectrum plotting ratios of $\Phi_{C\rightarrow O}$ of PhDTEc in the presence of 1 mM of Me_2Acr^+-Mes to $\Phi_{C\rightarrow O}$ in the absence of 1 mM of Me_2Acr^+-Mes ($\Phi_{C\rightarrow O}(Me_2Acr^+\text{-Mes})/\Phi_{C\rightarrow O}$(no catalyst). b) Photoelectrocatalytic cycloreversion of 1 mM of PhDTEc under 410 nm photoexcitation of Me_2Acr^+-Mes (1 mM; deaerated CH_3CN).

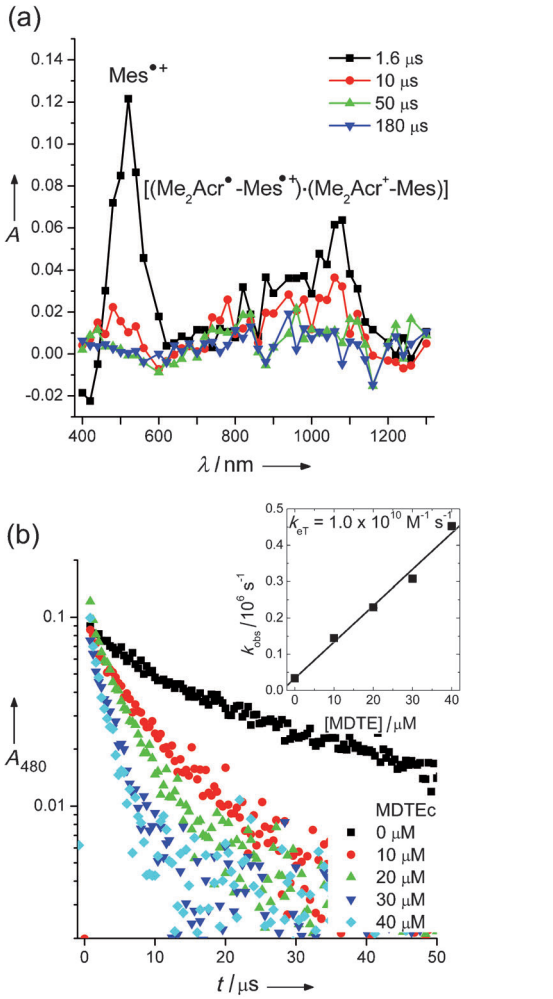


Figure 3. a) Transient absorption spectra of 100 μM of Me_2Acr^+-Mes (deaerated CH_3CN) in the presence of 20 μM MDTEc after nanosecond photoexcitation at $\lambda_{ex}=430$ nm. b) Decay traces of the 480 nm absorption band at different concentrations of MDTEc (0–40 μM). Inset graph is a plot of k_{obs} versus [MDTEc], where k_{obs} is the decay rate of the 480 nm band.

Table 1: Cycloreversion quantum yields of DTE compounds.[a]

	PDTE	PhDTE	MDTE	CDTE
Me_2Acr^+-Mes	0.54	0.29	0.17	0.17
Acr^+-Mes	0.29	0.22	0.11	0.14
no catalyst[b]	0.062	0.016	0.048	0.023

[a] Determined by standard ferrioxalate actinometry (6.0 mM $K_3[Fe(C_2O_4)_3]$, $\Phi=1.1$ at 410 nm). Conditions: $\lambda_{ex}=410$ nm (8.3×10^{-10} einstein s^{-1}), 1 mM of photoredox catalyst and 1 mM of DTE in deaerated CH_3CN. [b] Quantum yields in the absence of the photoredox catalyst. Conditions: $\lambda_{ex}=410$ nm (8.3×10^{-10} einstein s^{-1}) and 1 mM of DTE in deaerated CH_3CN.

reductive BeT (k_{t1} and k_{t2}), and propagation (k_p). α is a constant that accounts for molar absorbance and preserves the dimensionless nature of $\Phi_{C\rightarrow O}$. To determine k_{ini}, we acquired transient absorption spectra of Me_2Acr^+-Mes after nanosecond photoexcitation at $\lambda_{ex}=430$ nm (Figure 3a). The transient absorption spectra comprised two bands at 480 and 1070 nm, which correspond to the radical cation of the mesityl group ($Mes^{\bullet+}$), and a dimer of the eT state and the neutral species (i.e., $[(Me_2Acr^{\bullet}\text{-}Mes^{\bullet+})\cdot(Me_2Acr^+\text{-}Mes)]$), respectively.[19] The decay rate of the 480 nm absorption band increased in the presence of increasing amounts of MDTEc (Figure 3b). This increase is due to eT from MDTEc to the Mes^+ moiety with a large positive driving force of $-\Delta G_{eT}=e[E^*_{red}(Me_2Acr^+\text{-}Mes)-E_{ox}(MDTEc)]=1.34$ eV. The electron transfer rate (k_{eT}) was determined to be $1.0\times10^{10}\,M^{-1}s^{-1}$ (Figure 3b), which is close to that of the diffusion limited regime. Because k_{eT} values for the other combinations of DTEs and photoredox catalysts were in the range of 0.26–$1.0\times10^{10}\,M^{-1}s^{-1}$ (see the Supporting Information, Figure S5 and Table S2), it is inferred that k_{eT}, which corresponds to k_{ini}, is not a limiting parameter of $\Phi_{C\rightarrow O}$.

Once the radical cation of the closed form is generated by the photoinduced eT, it undergoes thermodynamically allowed ring opening. We previously determined the ring-opening rates (k_1) of the radical intermediates and found that

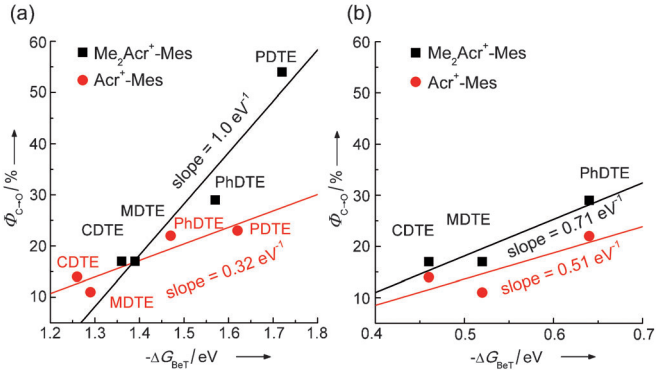


Figure 4. Plots of $\Phi_{C\rightarrow O}$ as a function of the driving force for the BeT ($-\Delta G_{BeT}$) through the termination (a) and propagation (b) processes.

k_1 increased in proportion with the electron density of DTEs, whereas the rate for the reverse reaction (k_{-1}) exhibited an opposite trend.[17] As shown in Scheme 1, the cycloreversion step competes with the termination 1 step. The $\Phi_{C\rightarrow O}$ value increases with increasing driving force of BeT from the reduced photoredox catalyst to the radical cation of the closed form ($-\Delta G_{BeT} = e[E_{ox}(DTE_C) - E_{red}(catalyst)]$; E_{red}(catalyst) vs. SCE = −0.67 V (Me_2Acr^+-Mes) and −0.57 V (Acr^+-Mes))[18] (Figure 4a). This BeT process may be located in the Marcus-inverted region because of the large driving force. In such a case, the termination by BeT becomes slower with the increase of the driving force, thus resulting in an increase in the $\Phi_{C\rightarrow O}$ value although the rate of ring opening becomes slower. Similarly, the rate of BeT from the Acr• moiety to the open-form radical cation (termination 2) may also be slowed down with increasing driving force because the driving force of BeT to the open-form radical cation is larger than that to the closed-form radical cation (see the Supporting Information, Figure S6). The $\Phi_{C\rightarrow O}$ value also increases with increasing driving force of eT from the neutral closed form to the radical cation of the open form (propagation in Scheme 1; $-\Delta G_{BeT} = e[E_{ox}(DTE_O) - E_{ox}(DTE_C)]$) as shown in Figure 4b. In this case, the BeT may be in the Marcus-normal region because of the much smaller driving force than in the case of Figure 4a when the eT rate increases with increasing driving force. Thus, the highest $\Phi_{C\rightarrow O}$ value was obtained for PDTE because it undergoes the slowest termination 1 process and the fastest propagation process despite showing the slowest ring-opening rate. The $\Phi_{C\rightarrow O}$ value obtained for Me_2Acr^+-Mes is larger than that for Acr^+-Mes (Table 1); this finding is also ascribed to the larger deriving force of BeT from the Me_2Acr• moiety to the closed-form radical cation, thus resulting in a slower termination 1 in favor of cycloreversion.

To summarize, we developed a new method to achieve high cycloreversion quantum yields of photochromic DTE compounds. The method involved the electrocatalytic ring opening of DTEs by photoexcitation of the photoredox catalyst. The mechanistic studies established the BeT and eT from the neutral closed form of DTE compounds to the open-form radical cation as being key steps.

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