Photoelectric Signal Conversion by Combination of Electron-Transfer Chain Catalytic Isomerization and Photoisomerization on Benzodimethyldihydropyrenes

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S *Supporting Information*

ABSTRACT: Photochromic benzocyclophanediene showed oxidation-triggered isomerization to form benzodimethyldihydropyrene. The isomerization proceeded via an autocatalytic reaction system, which could be combined with the photochromic nature of the molecule to establish a new photoelectric signal conversion system.

Irradiation can induce changes of molecular structure, and hence color changes, in photochromic molecules, which form different metastable isomers.[1,2] Such photoisomerization accompanies the change of the molecule's electronic structure and physical properties, including luminescence,[3] magnetism,[4] conductivity,[5] and wettability;[6] therefore, these molecules have attracted much attention as promising components for photocontrolled molecular memories and switches. The use of photochromic molecules in electronic devices requires the controlling or monitoring of their isomer state via electrical methods (using either potential or current), as is common in semiconductor devices. The isomeric state of the molecules should be monitored by the electrode potential, and it could be controlled by electrical stimuli (i.e., the intermolecular addition or removal of electrons). In this sense, the elucidation of a correlation between the photochromic and redox behaviors (i.e., the photo- and electroresponsive abilities) of the molecules is important to establish a dual electro- and photoresponsive system.[7]

Benzodimethyldihydropyrene (BzDHP, **1c**; **c** indicates a closed π-conjugated structure) is a purple-colored photochromic molecule. It undergoes reconstruction of the π-conjugation on the molecular skeleton upon irradiation with visible light to transform into noncolored benzocyclophanediene (BzCPD, **1o**; **o** indicates an open π-conjugated structure).[8,9] The reverse **1o**-to-**1c** isomerization can proceed under ultraviolet (UV) irradiation or heat treatment. Our previous work studied the photochemical and electrochemical properties of BzDHP with ferrocenyl substituents.[10] We reported that the oxidation of the ferrocene moiety caused isomerization from the open form of the ion to the closed form. The oxidation was suggested to be followed by an intramolecular electron transfer from the cyclophanediene (CPD) moiety to the oxidized ferrocene moiety. The generated CPD+ moiety was thermally unstable, and immediately isomerized to the dimethyldihydropyrene cation (DHP+) structure. The intramolecular electron transfer was a key event in the isomerization reaction, which was expected to occur owing to

the ferrocene and the CPD moieties showing close redox potentials in the open form of the structure. These results prompted us to develop electrically stimulated isomerization in a simpler photochromic molecule: unsubstituted **1o**. The redox potential of **1o** is close to that of **1c**, which should allow oxidation-triggered **1o**-to-**1c** isomerization via intermolecular electron transfer.[11]

We report herein the electrochemical and photochemical properties of **1c** and its analog, **2c** (Scheme 1).[12,13] Oxidation-

Scheme 1. Photo- and Electron-Transfer Chain Catalytic Isomerization 1c and 2c to their respective 1o and 2o Open Form
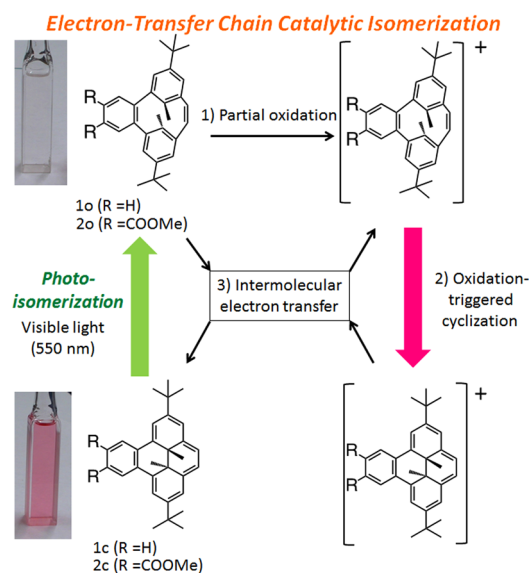
triggered **1o**-to-**1c** isomerization was observed, and the autocatalytic nature of the reaction system was revealed: the isomerization could be completed with only 0.3 equiv oxidant. Isomerization of the analog, **2o**, via a similar reaction system was quicker. These findings allowed us to develop a novel photoelectric signal conversion system.

Figure 1 shows cyclic voltammograms of **1o**, **1c**, **2o**, and **2c**. A reversible redox wave was shown by **1c** at $E^{0'}$ = 0.01 V vs ferrocenium/ferrocene, and by **2c** at $E^{0'}$ = 0.16 V. Electron-
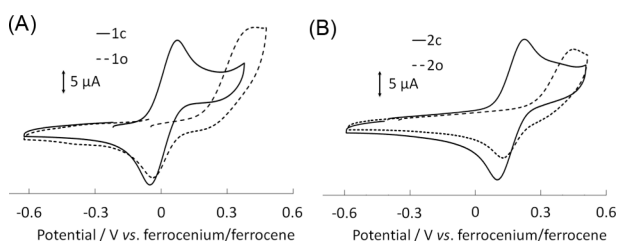
Figure 1. Cyclic voltammograms of (A) **1c** (solid line) and **1o** (dashed line) and (B) **2c** (solid line) and **2o** (dashed line) in 0.1 M Bu$_4$NClO$_4$-dichloromethane at 298 K.

withdrawing methyl ester groups in **2c** decreased the electron density on the DHP skeleton to shift more positively $E^{0\prime}$. **1o** showed an irreversible oxidation peak attributed to **1o**$^+$/**1o** at E_{pa} = 0.39 V, suggesting that the oxidation accompanied a structural transformation or chemical reaction. The reduction peak current was observed at E_{pc} = −0.02 V, a potential similar to that of **1c** (E_{pc} = −0.04 V). Similar irreversible redox behavior was shown by **2o** (E_{pa} = 0.44 V and E_{pc} = 0.14 V). The results indicate the conversion of the open forms (**1o** and **2o**) to the closed forms (**1c** and **2c**) by oxidation, as discussed below. Simulations of the cyclic voltammograms of **1o** and **2o** suggest reaction rates over 10 M^{-2} s^{-2}.

To identify the chemical process that occurred after the oxidation of **1o**, UV−vis spectra were measured for **1c** and **1o** and their respective 1e$^-$-oxidized species **1c**$^+$ and **1o**$^+$. The cations were chemically prepared by adding 1 equiv [(4-BrC$_6$H$_4$)$_3$N][SbCl$_6$] oxidant to dichloromethane solutions of the neutral species (Figure 2). **1c**$^+$ displayed a characteristic
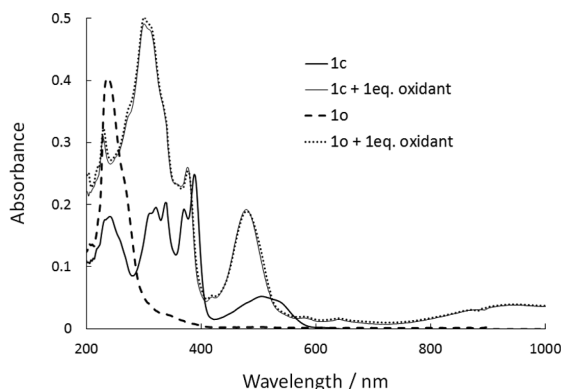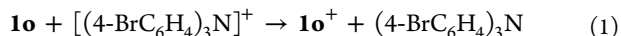

Figure 2. UV−vis-NIR spectra of **1c** and **1o** with and without oxidant.

broad absorption band in the near-infrared (NIR) region that was not shown by **1c**. The addition of oxidant to a solution of **1o** immediately changed the spectrum to become very close to that of **1c**$^+$. These spectroscopic and electrochemical results indicate the oxidation-triggered isomerization of **1o** to **1c**$^+$. A possible intermediate, **1o**$^+$, was not detected, suggesting that **1o**$^+$ was not energetically favorable and that the conversion to **1c**$^+$ was immediate. **2** showed similar spectroscopic characteristics to **1**: the 1e$^-$ oxidation of **2o** yielded a spectrum nearly identical to that of **2c**$^+$ (see Supporting Information, SI), indicating rapid **2o**$^+$-to-**2c**$^+$ isomerization. The reaction can be represented as the following equations:

$$\mathbf{1o} + [(4\text{-}BrC_6H_4)_3N]^+ \rightarrow \mathbf{1o}^+ + (4\text{-}BrC_6H_4)_3N \qquad (1)$$

$$\mathbf{1o}^+ \rightarrow \mathbf{1c}^+ \qquad (2)$$

$$\mathbf{1c}^+ + \mathbf{1o} \rightarrow \mathbf{1c} + \mathbf{1o}^+ \qquad (3)$$

The characteristic autocatalytic nature of the **1o**-to-**1c** isomerization was revealed by monitoring the change of the absorbance after adding 0.3 equiv oxidant to a dichloromethane solution of **1o** (Figure 3A). Peaks at 400 and 500 nm
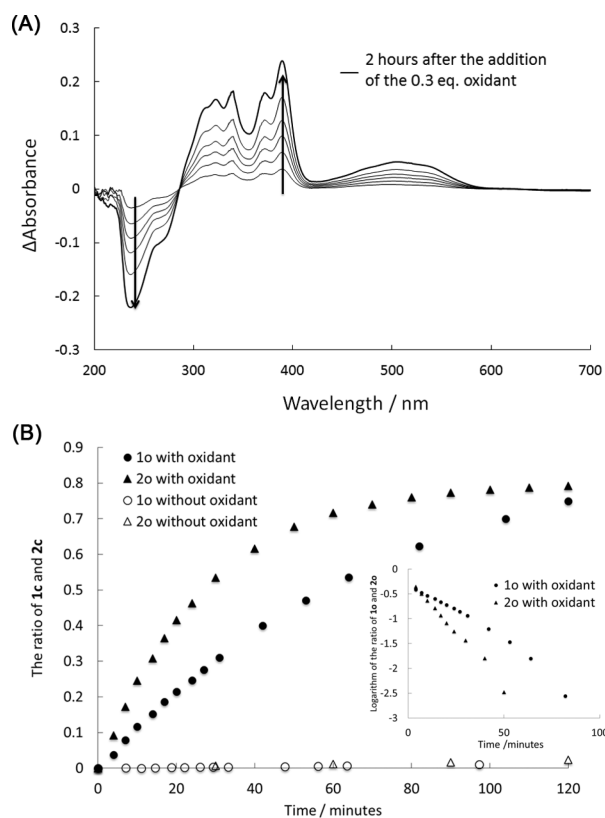

Figure 3. (A) Gradual changes of Δabsorbance after the addition of 0.3 equiv of [(4-BrC$_6$H$_4$)$_3$N][SbCl$_6$] to 0.1 M dichloromethane solution of **1o** at 298 K. (B) Time dependence of ratio of **1c** and **2c** with and without oxidant. Inset shows the time dependence of the logarithm of the ratio of **1o** and **2o** with and without oxidant.

attributable to **1c** appeared as the reaction proceeded, and the peak at 240 nm attributable to **1o** decreased. The spectrum obtained 2 h after the addition of the oxidant was similar to that expected from an ~3:7 ratio mixture of **1c** and **1c**$^+$, indicating that almost all the **1o** was converted to **1c**. It is expected that the saturated ratio of **1c** in Figure 3B should be 0.7, but in fact the small excess over the 0.7 was observed. It was due to the partial reduction of **1c**$^+$. The catalytic oxidative isomerization of **1o** to **1c** was much quicker than the equivalent noncatalytic thermal isomerization, which took 4 days to complete. Time-dependent spectroscopy revealed that the catalytic amount of oxidant accelerated the isomerization of **1o** to **1c**; similar but faster catalytic isomerization was shown by **2o**.

The mechanism of the autocatalytic isomerization is explained as follows: **1o** is oxidized by [(4-BrC$_6$H$_4$)$_3$N][SbCl$_6$] to form **1o**$^+$ (eq 1), which is thermally unstable and isomerizes immediately to **1c**$^+$ (eq 2). These reactions were confirmed by UV−vis-NIR spectroscopy (Figure 2). The instability was suggested by DFT calculations, which revealed the ground-state energy of **1o**$^+$ to be 90.7 kJ mol^{-1} higher than that of **1c**$^+$ and revealed a difference of 86.1 kJ mol^{-1} between the ground-state energies of **2o**$^+$ and **2c**$^+$.[14] After the isomerism, **1c**$^+$ receives an

electron from neutral **1o** to yield neutral **1c** and **1o**$^+$ (eq 3). The generated **1o**$^+$ then isomerizes to **1c**$^+$ according to eq 2. Therefore, the reactions in eqs 2 and 3 can successively occur to convert all the **1o** to **1c**.[13] To test the electron-transfer reaction in eq 3, 0.3 equiv of **1c**$^+$ was added to a solution of **1o**, and the reaction was monitored by UV−vis spectroscopy. As expected, the absorbance peak derived from **1c** increased, and eventually almost all the **1o** was converted to **1c** (see SI). The logarithm of the ratio of **1o** increased in magnitude linearly with time (inset, Figure 3B), implying that the reaction was first order relative to **1o**. The concentration of **1c**$^+$ is thought to have remained constant. The reaction rate constant of the cyclization, k_{cyc}, was estimated to be 3.4×10^{-4} s^{-2} M^{-2}, two hundred times that of the reaction without oxidant ($k_{cyc} = 1.7 \times 10^{-6}$ s^{-2} M^{-2}).[15] These results support the intermolecular electron transfer of eq 3, indicating that **1c**$^+$ plays a key role in this chain reaction. The reaction rate constant of eq 2, k_2, was estimated by simulation of the cyclic voltammogram to be over 10 s^{-2} M^{-2}, three thousand times the value of k_{cyc}. This suggests that the intermolecular electron transfer is the rate-determining step. This electron-transfer reaction seems to have been energetically unfavorable due to the E_{pa} of **1o** being more positive than that of **1c**. The unfavorable energetic properties made this reaction the rate-determining step in the chain reaction. In this case, the sum of the differences of the Gibbs energies in the chain reaction, $\Delta G_{total} = \Delta G_{(2)} + \Delta G_{(3)}$ (where $\Delta G_{(2)}$ and $\Delta G_{(3)}$ indicate the differences of the Gibbs energies of eqs 2 and 3, respectively), was expected to be negative, because $\Delta G_{(2)}$ would be negative and large due to the highly unstable nature of **1o**$^+$. The DFT calculation supported these considerations: ΔG_{total} was estimated to be -31.6 kJ mol^{-1} in **1** and -31.3 kJ mol^{-1} in **2**. Electron-transfer chain catalytic cycloreversion reactions of photochromic diarylethene compounds are rarely reported, and this work is the first to describe the cyclization of DHP compounds.[16] The distinct character of the two reactions is represented by their Gibbs energy changes during the intermolecular electron transfer ΔG_{IET}, which is negative for the cycloreversion reaction of the diarylethene, indicating the energetic favorability of the process. However, $\Delta G_{IET} = \Delta G_{(3)}$ and is positive in the cyclization reaction of the BzDHP compounds. This study found that the electron-transfer chain catalytic isomerization proceeded even in the presence of energetically unfavorable electron transfer.

The rate of the electron-transfer chain catalytic isomerization was faster in **2o** than in **1o** as shown in Figure 3B. The difference in E_{pa} between the open and closed forms, ΔE_{pa}, was 0.10 V smaller for **2** than for **1**. Therefore $\Delta G_{(3)}$ of **2** is smaller than that of **1**.[17] This indicates that the intermolecular electron transfer (eq 3) favorably proceeded in **2o** than in **1o**, consistent with expectation that the intermolecular electron transfer was the rate-determining step in the chain reaction.[18]

The combination of catalytic isomerization with the photochromic properties of the molecules allowed us to establish a novel photoelectric signal conversion system. The photo signal was detected by the change in electrode rest potential (E_{rest}), which was operated through the photo-isomerization (**1c**-to-**1o**) and electroisomerization (**1o**-to-**1c**) of the molecules. E_{rest} was determined principally by the ratio of **1c**$^+$/**1c** according to the Nernst equation.[19,20] Irradiation with light-induced **1c**-to-**1o** isomerization, changing the **1c**$^+$/**1c** ratio, which could be detected in situ by monitoring E_{rest}.

A total of 0.1 equiv [$(4\text{-BrC}_6\text{H}_4)_3\text{N}$][SbCl$_6$] was added to a dichloromethane solution of **1c** to form 0.1 equiv **1c**$^+$. The

solution showed $E_{rest} = 0.20$ V vs Ag$^+$/Ag (Figure 4). Irradiation of the solution with visible light (>450 nm) positively shifted
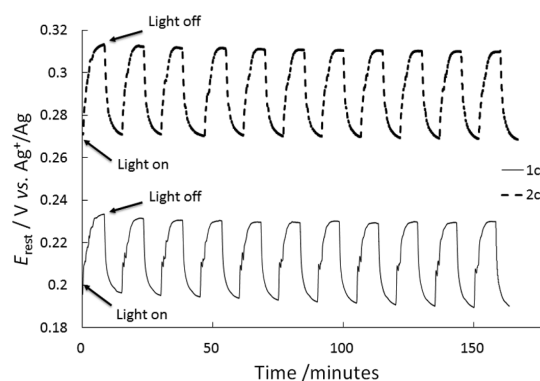

Figure 4. Changes in electrode rest potential (E_{rest}) of **1c** and **2c** with 0.1 equiv of [$(4\text{-BrC}_6\text{H}_4)_3\text{N}$][SbCl$_6$] in Bu$_4$NClO$_4$-dichloromethane at 298 K under intermittent >450 nm irradiation.

E_{rest} to 0.23 V. The initial potential E_{rest} was recovered after the irradiation had ceased. This behavior was repeatedly demonstrated over 10 cycles. These results are interpreted as follows. The visible irradiation converted **1c** into **1o**, increasing the **1c**$^+$/**1c** ratio. This eventually positively shifted E_{rest}. After the cessation of irradiation, the catalytic **1o**-to-**1c** isomerization was induced in the presence of **1c**$^+$, which led the **1c**$^+$/**1c** equilibrium to revert to its initial state, shifting E_{rest} negatively to its initial value.[21] During the visible irradiation, ~80% of the **1c** was isomerized to **1o**, which was estimated using the Nernst equation from the difference in E_{rest} before and after the irradiation (ΔE_{rest}).[20] The E_{rest} of **2c** changed between 0.27 and 0.31 V during the cycles, which is different to the range shown by **1c**, despite the two showing similar ΔE_{rest}. The results demonstrate a new photosensing system based on photo-isomerization and electron-transfer chain catalytic isomerization.

In conclusion, oxidation-triggered catalytic **1o**-to-**1c** isomerization was observed and explored. This electron-transfer chain catalytic isomerization, combined with the photochromic nature of the molecules, allowed the establishment of a new photoelectric signal conversion system in which the visible light signals are converted to the electrode rest potential via reversible isomerization.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental procedures and additional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(13) For details, see SI.

(14) Geometry of **1c**, **1o**, **2c**, and **2o** were fully optimized with the DFT method without the solvent effect. The B3LYP level of theory with the 6-31G basis set was used to model the compounds. Present calculations were implemented with the Gaussian09 program package.

(15) When the 0.05 equiv oxidant was added to the solution of **1o**, k_{cyc} was decreased to 4.2×10^{-5} s^{-2} M^{-2}, supporting the first-order nature of the reaction (see SI).

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(17) Activation energy for eq 3 would also be smaller in **2** than **1**, considering that the structural changes of the molecules in the reaction are not much different in **1** and **2**.

(18) Internal reorganization energies for eq 3 were estimated to 91.6 and 92.2 kJ/mol for **1** and **2**, respectively (for details, see Figure S6). Similarity of the values suggests that the external reorganization would affect the intermolecular electron transfer.

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(20) The E_{rest} is estimated according to Nernst equation as shown below:

$$E_{rest} = E_0 - \frac{RT}{F} \ln \frac{[\mathbf{1c}]}{[\mathbf{1c^+}]}$$

where E_0: the standard electrode potential; R: the gas constant; T: the absolute temperature; F: the Faraday constant; $[\mathbf{1c}]$: the concentration of **1c** in solution; $[\mathbf{1c^+}]$: the concentration of **1c$^+$** in solution; $[\mathbf{1c}]/[\mathbf{1c^+}]$ is approximately estimated from E_{rest}. We note that the observed E_{rest} would be influenced by the other experimental factors, such as the presence of **1o**.

(21) In the 10 cycles responses the small degradation was observed, which was thought to be caused by the decomposition of **1c$^+$**.