

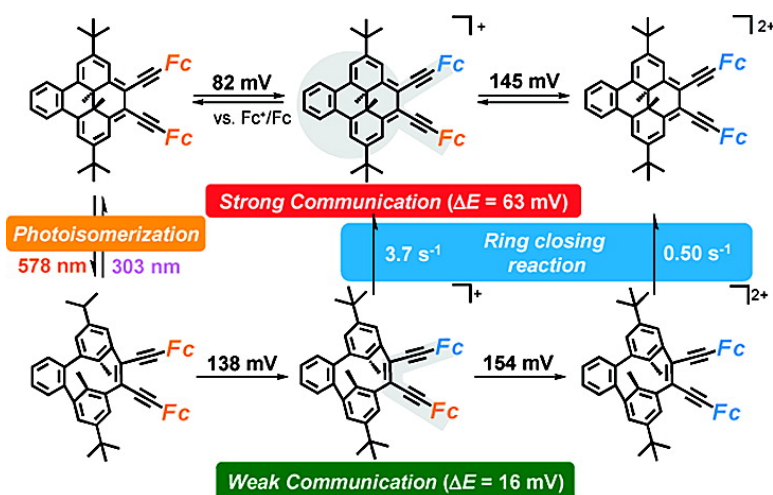
Communication

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Redox-Assisted Ring Closing Reaction of the Photogenerated Cyclophanediene Form of Bis(ferrocenyl)dimethyldihydropyrene with Interferrocene Electronic Communication Switching

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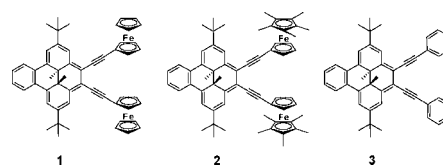
Various new phenomena appear in photochromic metal complexes in which an organic photochromic molecular moiety is attached to a metal complex moiety, caused by the electronic and steric interactions of both moieties.^{1,2} For example, ferrocene-attached azobenzene has shown reversible isomerization during irradiation with a single green light source, assisted by the redox reaction;^{2a–c} spiropyran a change in the stability of the metastable merocyanine form caused by the redox reaction;^{2d} and diethynylethene^{2e} a change in the electronic communication between two ferrocene moieties by the photoisomerization of the diethynylethene moiety. In this study, we connected two ferrocene moieties to dimethyldihydropyrene (DHP) (Chart 1) and produced a reversible photoswitching of the electronic communication between the ferrocene moieties. We also found a rare example of an indirect redox-assisted ring closing reaction of the photogenerated cyclophanediene (CPD) form of DHP (Scheme 1). There have been reported several redox-assisted ring closing reactions of a DHP moiety^{3a} and others.^{3b–d} However, the present system is unique because the ring closing is triggered by oxidation of not the DHP moiety but the ferrocene moiety.

DHP is a valuable photochromic molecule with reversible redox properties and a large π -conjugated planar structure, causing its conversion to an open and less π -conjugated CPD structure upon irradiation with visible light, with an isomerization ratio of almost 100%.⁴ The reverse conversion occurs upon irradiation with UV light or heating.⁴ Its intriguing electronic properties make DHP a promising molecular component in the photoswitching molecular devices,⁵ and alternation of the electronic structure of DHP by photoisomerization will make the photoswitching of the electronic communication between redox-active sites possible because the photocontrol of molecular wire conductivity is one of the most important issues in molecular switching devices.^{1,6,7} For this purpose, we designed bis(ferrocenylethynyl)dimethyldihydropyrene (**1**) and bis(pentamethylferrocenylethynyl)dimethyldihydropyrene (**2**) in the first series of complexes in which the DHP moiety and two redox-active ferrocene moieties were connected by a π -conjugated ethynyl moiety.

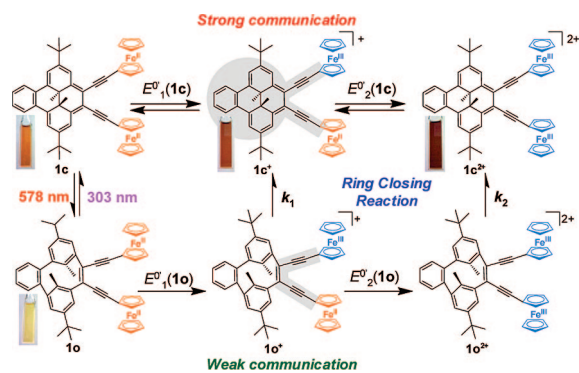
Complex **1** was prepared by Stille coupling of a dibromo-DHP derivative^{4d} and tributylstannyethynylferrocene using Pd(PPh₃)₄ as the catalyst in DMF at 95 °C. The complex was characterized by NMR, IR, ESI-MS, elemental analyses, and single-crystal X-ray crystallography (Figure 1a). Its NMR signals and X-ray structure indicate that **1** exists only as the closed form, **1c**. **2** and bis(phenylethynyl)dimethyldihydropyrene (**3**) were prepared by a similar method and fully characterized (see Supporting Information).

A solution of **1c** in dichloromethane was brownish red, exhibiting broad absorption from 250 to 650 nm (Figure S1). The absorption bands were assigned with reference to the absorption spectrum of **3** and theoretical TD–DFT calculations (Figures S1–S3 and Table

Chart 1



Scheme 1



S3). The intense bands around 420 nm were attributed to a DHP π – π^* band. The broad shoulder of **1c** from 450 to 650 nm was different in shape from that of **3**, which has only a π – π^* band. TD–DFT calculations indicated that the additional bands of **1** were primarily attributable to a CT-like transition (from the hybrid of ferrocene *d* and DHP π to DHP π^*) and a DHP π – π^* band.

Irradiation of **1c** in THF with yellow (578 nm) light, the wavelength of which corresponded to the visible π – π^* band of the DHP moiety, caused a stepwise decrease in the spectrum in the visible region and an increase in the UV region with one isosbestic point (Figure 1b). This spectroscopic behavior is characteristic of DHP-to-CPD isomerization, producing the open form, **1o**, with a less π -conjugated structure.⁴ In the ¹H NMR spectral change in THF-*d*₈ (Figure S4), protons of the methyl group, which stands up from the DHP plane, were significantly shifted to the lower-field region after irradiation, which is direct evidence of DHP ring opening.⁴ The photoisomerization ratio of **1o** was 97% in the photostationary state. Irradiation of **1o** in THF with UV (303 nm) light gave an absorption spectrum exactly the same as the original spectrum of **1c** (Figure 1b), indicating that **1** undergoes reversible photochromism (Figure S5).

A cyclic voltammogram (CV) of **1c** in Bu₄NClO₄–dichloromethane showed two separated reversible redox waves corresponding to ferrocenium/ferrocene, followed by one reversible redox wave corresponding to DHP⁺/DHP (Figure 2a). The difference between

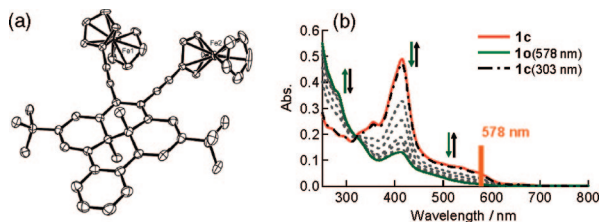


Figure 1. (a) ORTEP view of **1** with thermal ellipsoids set at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. (b) UV-vis absorption spectral changes of **1** in THF upon excitation at 578 nm (from **1c** to **1o**) and 303 nm (from **1o** to **1c**).

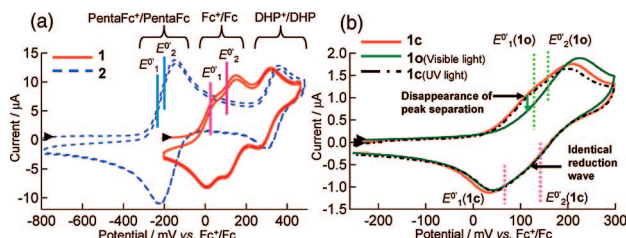
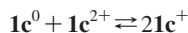


Figure 2. Cyclic voltammograms of **1** and **2** (a) at $100 \text{ mV} \cdot \text{s}^{-1}$ in $0.1 \text{ M Bu}_4\text{NClO}_4\text{-CH}_2\text{Cl}_2$ at 298 K . Cyclic voltammogram of **1c** and **1o** (b) in the potential region for redox reaction of ferrocene moieties at $100 \text{ mV} \cdot \text{s}^{-1}$ in $0.1 \text{ M Bu}_4\text{NClO}_4\text{-1,3-dichloropropane}$ at 218 K . $E^{\circ}_1(\mathbf{1c}) = 82 \text{ mV}$, $E^{\circ}_2(\mathbf{1c}) = 145 \text{ mV}$, $E^{\circ}_1(\mathbf{1o}) = 138 \text{ mV}$; $E^{\circ}_2(\mathbf{1o}) = 154 \text{ mV}$, $k_1 = 3.7 \text{ s}^{-1}$, and $k_2 = 0.50 \text{ s}^{-1}$.

the two redox potentials of the ferrocene moieties, ΔE° ($=E^{\circ}_2 - E^{\circ}_1$), was 109 mV . The comproportionation constant, K_c , for the equilibrium,



which is a measure of the strength of the electronic communication and given by $K_c = \exp(\Delta E^{\circ} F/RT)$, was 57 , suggesting that the DHP moiety provides considerable electronic communication between the two ferrocene moieties in **1c**.⁸

In contrast, complex **2** exhibited no photoisomerization (Figure S6). This is probably because the stronger donor ability of pentamethylferrocene assists quenching the photoexcited state more efficiently than ferrocene.⁹ **2** did not show good electronic communication between its pentamethylferrocene moieties (ΔE° of 53 mV and K_c of 7.7 ; Figure 2a). This result suggests that fine-tuning the difference in redox potential between the DHP and ferrocene moieties is critical for the electronic interaction between the two moieties and has a large effect on their electrochemical properties.

1c underwent complete photoisomerization during irradiation with visible ($510\text{--}700 \text{ nm}$) light to form **1o**, and there was a difference in CV in $\text{Bu}_4\text{NClO}_4\text{-1,3-dichloropropane}$ at 218 K before and after photoisomerization (Figure 2b). **1c** showed two redox waves for the ferrocene moieties, and a simulation indicated ΔE° of 63 mV and K_c of 28 (Figure S8). Conversely, the CV of **1o** showed only one oxidation wave with no clear sign of peak separation, consistent with the less π -conjugated structure of CPD relative to that of DHP. However, the reduction wave was identical to that of **1c**, suggesting that a ring closing reaction occurred after the oxidation of the ferrocene moieties (Figure 2b). The redox reaction was simulated based on the mechanism shown in Scheme 1, and ΔE° was calculated to be 16 mV and K_c was 2.3 (Figure S9). The CV after a solution of **1o** was irradiated with UV (303 nm) light was similar to the original CV of **1c** (Figure 2b), indicating that the reversible CV changes and the strength of the electronic communication are caused by photoswitching between **1c** and **1o**.

The redox-assisted ring closing reaction was supported by more detailed measurements of CV and absorption spectral measurements. In the CV of **1o**, the redox wave attributed to the DHP moiety appeared after the oxidation of the ferrocene moieties in the first scan, and the characteristic features of the CV of **1c** were observed in the second scan (Figure S10). UV-vis-NIR spectra of **1o**⁺ and **1o**²⁺ in THF, generated by the chemical oxidation of **1o** with 1 and 2 equiv of oxidant, $[\text{Fc}(\eta^5\text{-C}_5\text{H}_4\text{Cl})_2]\text{PF}_6$, respectively, completely matched those of **1c**⁺ and **1c**²⁺, respectively (Figure S11). These results indicate that the ring closing reaction occurred in both the **1o**⁺ and **1o**²⁺ states.

In conclusion, bis(ferrocenyl)dimethyldihydropyrene (**1**), which is the first molecule in which DHP and metal complexes are connected through a π -conjugated ethynyl moiety, exhibits both reversible photochromic behavior and photoswitching of the electronic communication between the ferrocene moieties. **1** also shows a redox-assisted ring closing reaction (from **1o** to **1c**) with oxidation of only the ferrocene moieties. These findings should extend our understanding of photochromic metal complexes and will be useful in designing molecular switching devices based on DHP derivatives.

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Supporting Information Available: Synthetic procedures and characterization data for **1**, **2**, and **3**, simulated CVs of **1c** and **1o**, UV-vis-NIR absorption spectral changes in **1o** and **1c** upon the addition of oxidant, and theoretical calculation data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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