

## Visible-Light Photochromism of Bis(ferrocenylethynyl)ethenes Switches Electronic Communication between Ferrocene Sites\*\*

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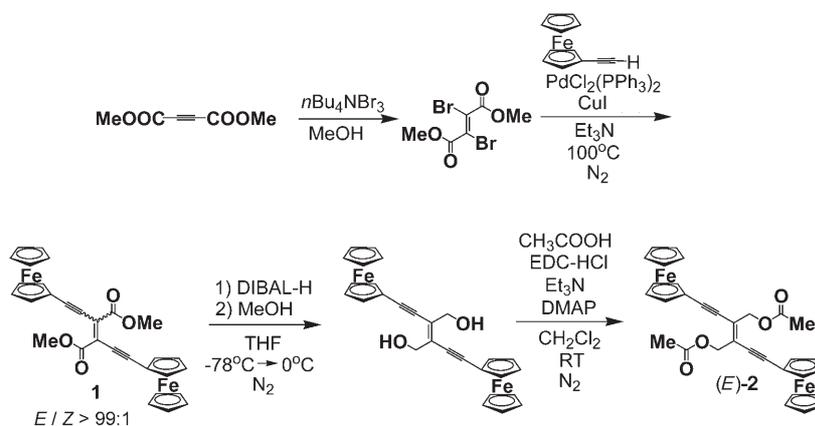
Ferrocene has many attractive features, such as excellent reversible redox properties, high solubility in organic media, and high modifiability with organic chemical methods,<sup>[1]</sup> and it remains a promising molecular fragment for molecular devices. Related to the redox properties, intramolecular mixed-valence interactions between multiple ferrocene sites have been regarded as a key to the realization of molecular electronics, such as molecular quantum cellular automata (QCA),<sup>[2]</sup> and the fundamental evaluation of their ability as molecular electronic wires.<sup>[3]</sup>

Ferrocene exhibits an excellent affinity for organic  $\pi$ -bridge systems, with strong electronic coupling between the Fe d orbitals and the  $\pi$  orbitals of the cyclopentadienyl ring and  $\pi$  bridges. This mutual interaction can yield an intramolecular mixed-valence interaction<sup>[4]</sup> and a charge-transfer (CT) band in the visible region.<sup>[5–7]</sup> This CT transition from ferrocene d orbitals to the LUMO of either the acceptor group<sup>[5]</sup>

or the  $\pi^*$  orbital of the bridge<sup>[6]</sup> is key to the excellent nonlinear optical properties of ferrocene(donor)–acceptor combinations<sup>[5]</sup> and, for example, the green-light-induced *trans*-to-*cis* isomerization of the azobenzene moiety in ferrocenylazobenzenes.<sup>[6]</sup>

To our knowledge, light-triggered electronic communication between ferrocenes has never been reported before. In the present study, we adopted an ethynylethene  $\pi$  framework<sup>[8]</sup> as a bridge fragment, which undergoes *Z*–*E* photoisomerization on the central C–C double bond. The greatest benefit of introducing this class of photochromic compounds is the thermal stability of the *Z* and *E* isomers,<sup>[8]</sup> which is important in terms of their applications as, for example, molecular switching devices. Additionally, the possibility of modifying substituents on the central C–C double bond is also likely to be important in terms of tuning the photoisomerization behavior and mixed-valence communication by the electronic perturbation of the  $\pi$  system. These properties of ethynylethene are superior to those of other photochromic species such as the azo group. Our attempts at quantitative analysis of the mixed-valence interaction in *cis*-azoferrocene have not been successful because of the low stability of the *cis* isomer.<sup>[9,10]</sup>

Herein, we report two types of ferrocene-conjugated ethynylethenes, (*E*)-**1** and (*E*)-**2** (Scheme 1), which differ in the presence of a  $\pi$  or  $\sigma$  substituent on the central double bond. Their photophysical properties also contrast with each other: (*E*)-**1** showed visible-light photochromism, whereas



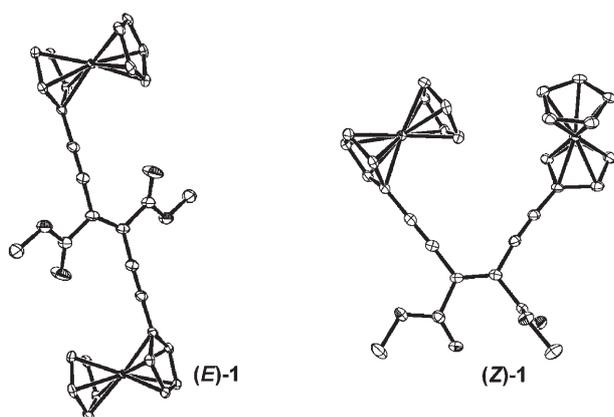
**Scheme 1.** Syntheses of (*E*)-**1**, (*Z*)-**1**, and (*E*)-**2**. EDC-HCl = 1-ethyl-3-(dimethylaminopropyl)-carbodiimide hydrochloride; DIBAL-H = diisobutylaluminumlithium hydride; DMAP = 4-(*N,N*-dimethyl)aminopyridine.

(*E*)-**2** did not show any photochromic behavior. Also discussed is the decrease in the strength of the mixed-valence interaction between the two ferrocene moieties accompanying *E*→*Z* isomerization in **1**. Compounds (*E*)-**1** and (*E*)-**2** were synthesized according to the procedure outlined in Scheme 1. The *Z* isomer of **1** was obtained as a minor by-product during the synthesis of (*E*)-**1**.<sup>[11]</sup> The absolute configurations of (*E*)-**1** and (*Z*)-**1** were confirmed by single-crystal X-ray analysis (Figure 1).<sup>[12]</sup> The configuration of **2** (*E*) was assigned with the aid of IR spectroscopy, by comparison of the absorptions derived from the carbonyl and C–C triple bonds of **2** with those of (*E*)-**1** and (*Z*)-**1**.

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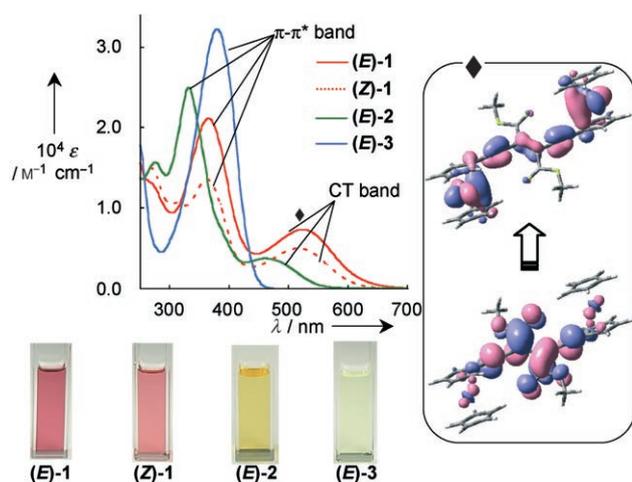
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**Figure 1.** ORTEP drawings of (*E*)-1 and (*Z*)-1 with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted.

Both (*E*)-1 and (*E*)-2 displayed electronic absorption bands in the visible region, together with the  $\pi$ - $\pi^*$  band in the UV region (Figure 2). On the other hand, the analogues (*E*)-3 (*p*-tol-C $\equiv$ C-(COOMe)C=C(COOMe)-C $\equiv$ C-*p*-tol) and (*E*)-4

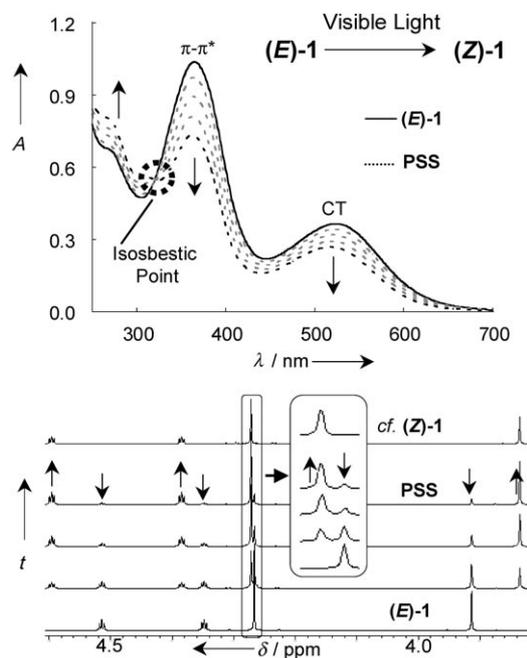


**Figure 2.** Electronic spectra of (*E*)-1, (*Z*)-1, (*E*)-2, and (*E*)-3 in dichloromethane, the main transition in the CT band of (*E*)-1 (marked with  $\blacklozenge$ ), and photos of each compound in dichloromethane.

(*p*-tol-C $\equiv$ C-(CH<sub>2</sub>OAc)C=C(CH<sub>2</sub>OAc)-C $\equiv$ C-*p*-tol), which lack the ferrocene moieties, showed only the  $\pi$ - $\pi^*$  band. Such dual absorptions were previously seen in ferrocene-containing pigments, which are excellent nonlinear optical materials,<sup>[5b]</sup> and in our azo precursors.<sup>[6,9,10]</sup> Time-dependent density functional theory (TD-DFT) calculations indicate that these bands in the visible region are assignable to CT-like transitions from the ferrocene *d* to the ethynylethene  $\pi^*$  orbitals (Figure 2), with some contribution by the enyne bridge, which again showed the same features as in two previous studies.<sup>[5b,6]</sup> Lower extinction coefficients ( $\epsilon$ ) were observed for both the  $\pi$ - $\pi^*$  and CT bands in (*Z*)-1 compared to those in (*E*)-1. With regards to (*E*)-2, a decrease in  $\epsilon$  and a blue shift in the CT band were found (Figure 2).

Irradiation of (*E*)-1 in dichloromethane with a mixture of green (546 nm) and yellow (578 nm) light from a superhigh-pressure Hg lamp<sup>[13]</sup> led to excitation of the CT band, with a

stepwise decrease observed in the  $\pi$ - $\pi^*$  band, as is typical in the *E*-to-*Z* transformation,<sup>[8]</sup> as well as in the CT band with time (Figure 3). In addition, one isosbestic point was observed which confirmed the absence of side reactions such as decomposition. A one-step reaction from the *E* to *Z* form was observed by <sup>1</sup>H NMR spectroscopy (Figure 3). The

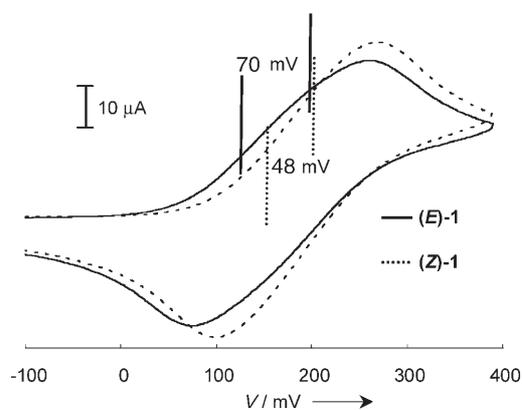


**Figure 3.** Time-course UV/Vis (upper) and <sup>1</sup>H NMR (lower) spectral changes of (*E*)-1 upon irradiation with light at 546 nm and 578 nm in dichloromethane and [D<sub>2</sub>]dichloromethane. PSS = photostationary state.

proportion of *Z* isomer in the photostationary state was calculated to be 89% based on the ratio of the integrals. This value is much higher than the percentage found for azo compounds<sup>[6,14]</sup> upon excitation of the CT transition from the metal moiety to the  $\pi^*$  orbital of the azo moiety. The quantum yields in toluene upon irradiation with green light at 546 nm<sup>[15]</sup> were found to be  $\Phi_{E \rightarrow Z} = 1.7 \times 10^{-5}$  and  $\Phi_{Z \rightarrow E} = 0.47 \times 10^{-5}$ .<sup>[16,17]</sup> Additionally,  $\pi$ - $\pi^*$  excitation with UV light at 365 nm also afforded *E*→*Z* isomerization, which is an intrinsic property in ethynylethenes.<sup>[8]</sup>

In contrast, (*E*)-2 showed no photochemical response to excitation of the CT band in the visible region or to excitation of the  $\pi$ - $\pi^*$  band in the UV region, as confirmed also by <sup>1</sup>H NMR spectroscopy. If we consider the photoisomerization behavior together with the differences in the electronic spectra, it can be concluded that the substituents attached directly to the central double bond contribute greatly to the photochemical properties in our ferrocene-conjugated ethynylethene system. This speculation is well supported by the photochemical responses of the analogues that lack the ferrocene moieties. For example, (*E*)-3 showed *E*→*Z* photoisomerization upon excitation of the  $\pi$ - $\pi^*$  band, just as (*E*)-1. On the contrary, (*E*)-4 revealed no photochromic behavior just as (*E*)-2, but instead it underwent photochemical degradation.

We evaluated the mixed-valence interaction by studying the splitting between the two redox potentials,  $\Delta E^0$ , as determined from cyclic voltammograms of (*E*)-**1** and (*Z*)-**1** measured in dichloromethane containing  $n\text{Bu}_4\text{NBF}_4$  ( $0.1 \text{ mol dm}^{-3}$ ). The result showed a larger  $\Delta E^0$  value in (*E*)-**1** (70 mV) than in (*Z*)-**1** (48 mV) (Figure 4).<sup>[18]</sup> This is



**Figure 4.** Cyclic voltammograms of (*E*)-**1** ( $1.2 \times 10^{-3} \text{ mol dm}^{-3}$ ) and (*Z*)-**1** ( $1.2 \times 10^{-3} \text{ mol dm}^{-3}$ ) in dichloromethane containing  $n\text{Bu}_4\text{NBF}_4$  ( $0.1 \text{ mol dm}^{-3}$ ) at a sweep rate of  $100 \text{ mV s}^{-1}$ . The potential was measured relative to the ferrocenium/ferrocene couple.

consistent with the fact that  $\pi$  conjugation, namely through-bond interaction,<sup>[4]</sup> is stronger in the *E* form and spatial interaction<sup>[19]</sup> is negligible because the two redox sites are well separated even in (*Z*)-**1** (Fe–Fe 6.17 Å), as indicated by the single-crystal X-ray structural analysis (Figure 2).

In summary, the perturbation by the transition-metal complex (ferrocene) by the organic photochromic framework (ethynylethene) and vice versa in the system reported here were both sophisticatedly utilized to attain visible-light photochromism that causes a change in electronic communication between the ferrocene sites. This result is expected to contribute to the development of well-defined supramolecular devices.

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 [12] Intensity data were collected at 113(2) K on a RIGAKU Mercury CCD using monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). (*E*)-**1**:  $\text{C}_{30}\text{H}_{24}\text{O}_4\text{Fe}_2$ ,  $M_r = 560.19$ ,  $P2_1/c$ ,  $a = 15.739(8) \text{ \AA}$ ,  $b = 7.404(4) \text{ \AA}$ ,  $c = 10.196(5) \text{ \AA}$ ,  $\beta = 95.294(3)^\circ$ ,  $V = 1183(1) \text{ \AA}^3$ ,  $Z = 2$ ,  $\mu = 1.263 \text{ mm}^{-1}$ , unique reflections = 2696 [ $R(\text{int}) = 0.0176$ ],  $R_1 = 0.0269$  [ $I > 2.00\sigma(I)$ ],  $wR_2 = 0.0646$  [ $I > 2.00\sigma(I)$ ]. (*Z*)-**1**:  $\text{C}_{30}\text{H}_{24}\text{O}_4\text{Fe}_2$ ,  $M_r = 560.19$ ,  $P\bar{1}$ ,  $a = 9.968(5) \text{ \AA}$ ,  $b = 11.115(6) \text{ \AA}$ ,  $c = 12.022(6) \text{ \AA}$ ,  $\alpha = 111.838(7)^\circ$ ,  $\beta = 92.640(6)^\circ$ ,  $\gamma = 96.769(6)^\circ$ ,  $V = 1222(1) \text{ \AA}^3$ ,  $Z = 2$ ,  $\mu = 1.223 \text{ mm}^{-1}$ , unique reflections = 5353 [ $R(\text{int}) = 0.0176$ ],  $R_1 = 0.0337$  [ $I > 2.00\sigma(I)$ ],  $wR_2 = 0.0935$  [ $I > 2.00\sigma(I)$ ]. CCDC 600138 ((*E*)-**1**) and 600139 ((*Z*)-**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).  
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