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Visible-Light Photochromism of Triarylamine- or Ferrocene-Bound Diethynylethenes that Switches Electronic Communication between Redox Sites and Luminescence

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Abstract: Redox-active ferrocene- and triarylamine-terminated diethynylethene derivatives have been synthesized and their photochromic properties and switching behavior based on through-bond electronic communication between the two redox sites, as well as their emissions, have been examined. Both bis(ferrocenylethynyl)ethene **1** and bis(triarylaminoethynyl)ethene **2** show visible-light photochromism induced by donor–acceptor charge-transfer (CT) transitions from the ferrocene or triarylamine to the diethynylethene moieties. The reversibility and quantum yields of the photochromism of **2** ($\Phi_{E\rightarrow Z}=6.1\times10^{-2}$, $\Phi_{Z\rightarrow E}=1.4\times10^{-2}$) are far higher than those of **1** ($\Phi_{E\rightarrow Z}=8.6\times10^{-6}$, $\Phi_{Z\rightarrow E}=2.5\times10^{-6}$). The higher efficiency in **2** may be attributed to the absence of the heavy atom effect and of a low-lying ^{3}LF state, which are characteristic of ferrocenyl compounds. This proposition is further supported by the fact that bis(ferrocenylbuta-1,3-diynyl)ethene **3**, which, unlike **1**, is free from steric interference between the two ferrocenyl groups in the *Z* form, does not show a significant improvement in its photoisomerization quantum yields ($\Phi_{E\rightarrow Z}=6.2\times10^{-5}$, $\Phi_{Z\rightarrow E}=3.4\times10^{-5}$). The visible-light photochromism of **1** and **2** is accompanied by a switch in the strength of the electronic communication between the two redox sites in their mixed-valence states ($\Delta E^{0\prime}$ values are 70 and 48 mV for (*E*)-**1** and (*Z*)-**1**, and 74 and 63 mV for (*E*)-**2** and (*Z*)-**2**). In the case of **2**, further evaluations were carried out through intervalence charge-transfer (IVCT) band analyses and DFT calculations. We have also demonstrated that steric repulsion between the methyl ester moieties in the *Z* form is implicated in the reduction in the through-bond electronic communication. Compound **2** exhibits photoluminescence, which is more efficient in the *E* form than in the *Z* form, whereas **1** and **3** show no photoluminescence.

Keywords: electrochemistry. · electronic communication · luminescence · oxidation · photochromism

Introduction

The exploration of electronic communication through organic π-bridges in mixed-valence compounds is of great importance in clarifying electron-transfer and -transport issues.[1] Above all, control of this electronic communication by means of external stimuli (photons,[2] protons,[3] ions,[4] etc.) has attracted much attention because these kinds of systems can constitute molecular devices in themselves,[5] as well as models for switchable molecule-based electronic circuits,[6] in which the π-bridges may be regarded as conductive nanowires. Among the potential systems that may be controlled by external stimuli, photocontrollable ones are the most favorable in terms of their practicable reversibility. Ethynylethene, which can be regarded as the fundamental building block of polydiacetylene,[7] is suitable for investigations of the type described above because it has a highly extended π-system, reversible and efficient *Z*/*E* photochromism, both isomers are thermally stable, and it is amenable to synthetic diversity.[8] We have found a new class of diethynylethene frameworks, namely dimethyl 2,3-bis(ethynyl)fumarate/maleate, to represent excellent photochromic and acceptor fragments.[9] In combination with ferrocene, which is a good donor and shows rather intense electronic communication through π-bridges,[10] the unique system (*E*)/(*Z*)-**1**, dimethyl 2,3-bis(ferrocenylethynyl)fumarate/maleate (Figure 1), was established to produce an optical switch in the electronic

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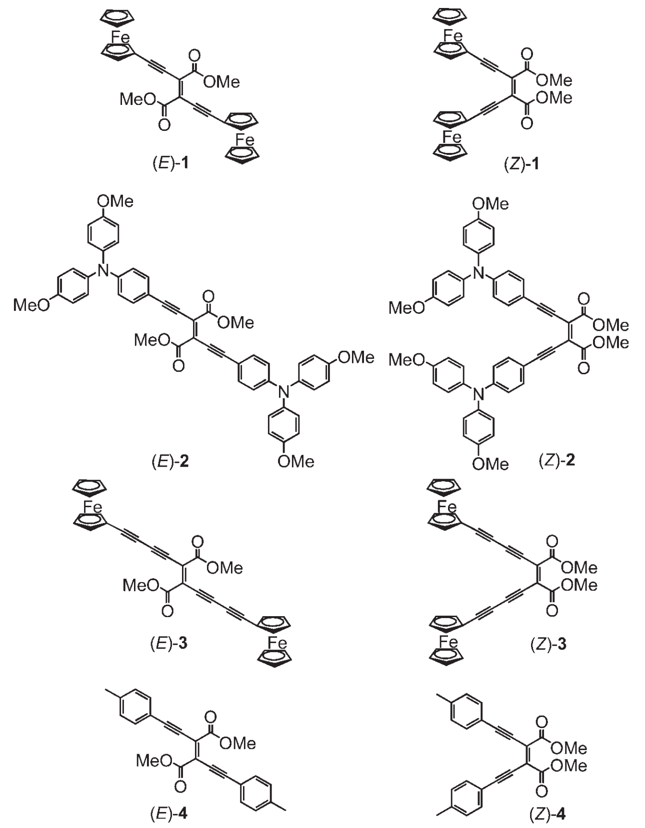

Figure 1. Diethynylethenes **1**–**4**.

communication with photoisomerization triggered by the excitation of a donor–acceptor charge-transfer (CT) band in the visible region, as reported previously in a short communication.[9]

Thus far, a considerable number of metal (organometallics and transition metal complexes,[11,12] nanoparticles,[13] surfaces[14])–organic photochromic ensembles have been reported, in which the photochromic abilities are suppressed through electron- or energy-transfer quenching processes. Compound **1** also suffers from this kind of drawback, with quite low quantum yields for the *Z*/*E* photoisomerization ($\Phi_{E\rightarrow Z}=8.6\times10^{-6}$, $\Phi_{Z\rightarrow E}=2.5\times10^{-6}$),[9] which we ascribe to the quenching ability of the ferrocenyl moieties based on the heavy atom effect of the Fe^{II} ion[15a] and a low-lying ^{3}LF state.[15] Moreover, **1** lacks an *E*-rich photostationary state (PSS), although we have confirmed the existence of both $E\rightarrow Z$ and $Z\rightarrow E$ photoisomerization pathways.[9]

Triarylamine derivatives display redox[16] and electronic communication[4,17] behavior quite similar to that of ferrocene derivatives, which is based on an *n* orbital on the central N atom. It is the absence/presence of the heavy-atom effect and of the low-lying quenching ^{3}LF excited state that define the critical difference between triarylamine and ferrocene. This difference is strongly reflected in their photochemical behavior. For example, triarylamine-based dyes tend to be highly emissive from singlet excited states,[18] whereas ferrocenyl compounds seldom show luminescence.[10] In this decade, a substantial number of reports have been published on triarylamine-based mixed-valence species[4,17] because a wide range of π-bridges may be introduced, giving rise to intense, well-isolated intervalence charge-transfer (IVCT) bands; however, no system has yet been produced with an optical switch in the electronic communication between triarylamine sites.

Against the background described above, we report herein on (*E*)/(*Z*)-**2**, or dimethyl 2,3-bis(*N*,*N*-di-4-methoxyphenyl-4-aminophenylethynyl)fumarate/maleate (Figure 1), which displays efficient and reversible visible light *Z*/*E* photochromism that is accompanied by changes in the strengths of the fluorescence and electronic communication between the two triarylamine sites. Electrochemical, IVCT, and DFT calculation analyses have been employed to evaluate this electronic communication. We also discuss steric repulsion between the methyl ester moieties in the *Z* form, which plays a role in reducing the electronic communication. Possible obstruction between the two ferrocenyl groups in the *Z* form (Figure S1) may be invoked in order to account for the low photoisomerization quantum yields of **1**. Therefore, to further justify the contribution of the electronic structure of the triarylamine to the drastic increase in the photoisomerization efficiency of **2**, we examined the photochromic behavior of (*E*)/(*Z*)-**3**, or dimethyl 2,3-bis(ferrocenylbuta-1,3-diynyl)fumarate/maleate (Figure 1), which has longer diyne bonds to circumvent this kind of steric hindrance (Figure S1).

Results and Discussion

Characterization: The *E*/*Z* configurations of **1**–**4** were determined as follows. For (*E*)-**2**, a single-crystal X-ray structure analysis was carried out (Figure 2), as was also the case for (*E*)-**1** and (*Z*)-**1**.[9] For (*Z*)-**2**, (*E*)-**3**, and (*E*)-**4**, the *E*/*Z* configurations were verified by checking the C=O vibrations in their IR spectra (Figure S2). The two C=O bonds give rise to symmetric and antisymmetric harmonic vibrations through the central C=C bond. In (*E*)-**1** and (*E*)-**2**, both of which have *Ci* symmetry in the crystal phase, only the antisymmetric vibration is allowed, whereas in (*Z*)-**1**, in which the inversion symmetry is lost, two signals are seen as a result of both vibrations. (*Z*)-**2**, (*E*)-**3**, and (*E*)-**4** also conform to these trends. (*Z*)-**3** and (*Z*)-**4** were generated in photoirradiation experiments (see later) and were identified from their ^{1}H NMR spectra without isolation.

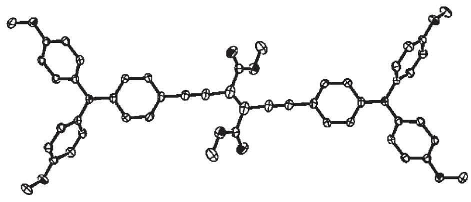

Figure 2. ORTEP drawing of (*E*)-**2** with thermal ellipsoids drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

Electronic spectra: Figure 3a shows the electronic spectra of the *E* forms of **1**–**4** in dichloromethane. In the UV region, each of the compounds shows an intense π–π* band characteristic of ethynylethene derivatives,[8] whereas unique visible bands are observed for all but (*E*)-**4**, which does not contain a donor moiety. Incidentally, tris(4-methoxyphenyl)amine only shows absorptions below 400 nm,[19] while ferrocene absorbs faintly in the visible region.[15] By means of time-dependent density functional theory (TD-DFT) calculations, these visible bands could be assigned to CT transitions from the HOMO, the out-of-phase combination of the ferrocene($d_{x^2-y^2}$) or triarylamine(n) with a contribution from the diethynylethene(π), to the LUMO, the diethynylethene(π*) (Figure 3b–d; Figures S3, S5, and S7 in the Supporting Information). These results do not contradict previous data for ferrocene-[20] and triarylamine-based[18] π-conjugated donor–acceptor pigments. It may be noted that there should exist another higher-lying CT band, from HOMO-1 or HOMO-2, the in-phase combination of the two redox sites, to the LUMO in (*E*)-**1**, (*E*)-**2**, and (*E*)-**3** (Figure 3b–d; Figures S3, S5, and S7); however, the higher CT transition is, in principle, Laporte-forbidden in *Ci*-symmetric *E* forms. The lower CT band in (*E*)-**2** is far more intense than that in (*E*)-**1**, reaching $\varepsilon_{\max} \approx 5\times10^4\,\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$. (*E*)-**3** showed enhanced molar absorptivities and redshifts for both its π–π* and lower CT bands compared with those of (*E*)-**1**, which may be attributed to the extension of the π-conjugation.

Figure 4 shows overlays of the electronic spectra of the *E* and *Z* forms of **1**–**4** in toluene. (*Z*)-**2** shows increased molar absorptivity on the short-wavelength side of the CT bands compared with (*E*)-**2**, whereas **1** and **3** do not show such reversals. In the *Z* form, the higher CT transition should be allowed due to the loss of inversion symmetry. According to the TD-DFT calculations, the *E*-to-*Z* conformational change in triarylamine-containing **2** is accompanied by a substantial increase in the oscillator strength of the higher CT transition, with a significant decrease in that of the lowest CT transition (Figure S4). In contrast, in ferrocene-containing **1** and **3**, the rise of the higher CT band is not so pronounced as to cause the reversal of the absorption in the visible region (Figures S6 and S8).

All of the compounds exhibited slight blueshifts in their π–π* and CT bands in the *Z* forms (Figure 4). It has been reported that ethynylethene derivatives without steric hindrance do not display such blueshifts upon *E*-to-*Z* isomerization.[8c,d] Figure 5 shows the optimized structures of (*E*)-**4** and (*Z*)-**4**. The *E* form has a coplanar structure, whereas in the *Z* form the two methyl ester moieties are substantially tilted because of their mutual steric repulsion. This series of results indicates that the structural hindrance of the methyl ester moieties in the *Z* form, which is common to all of the

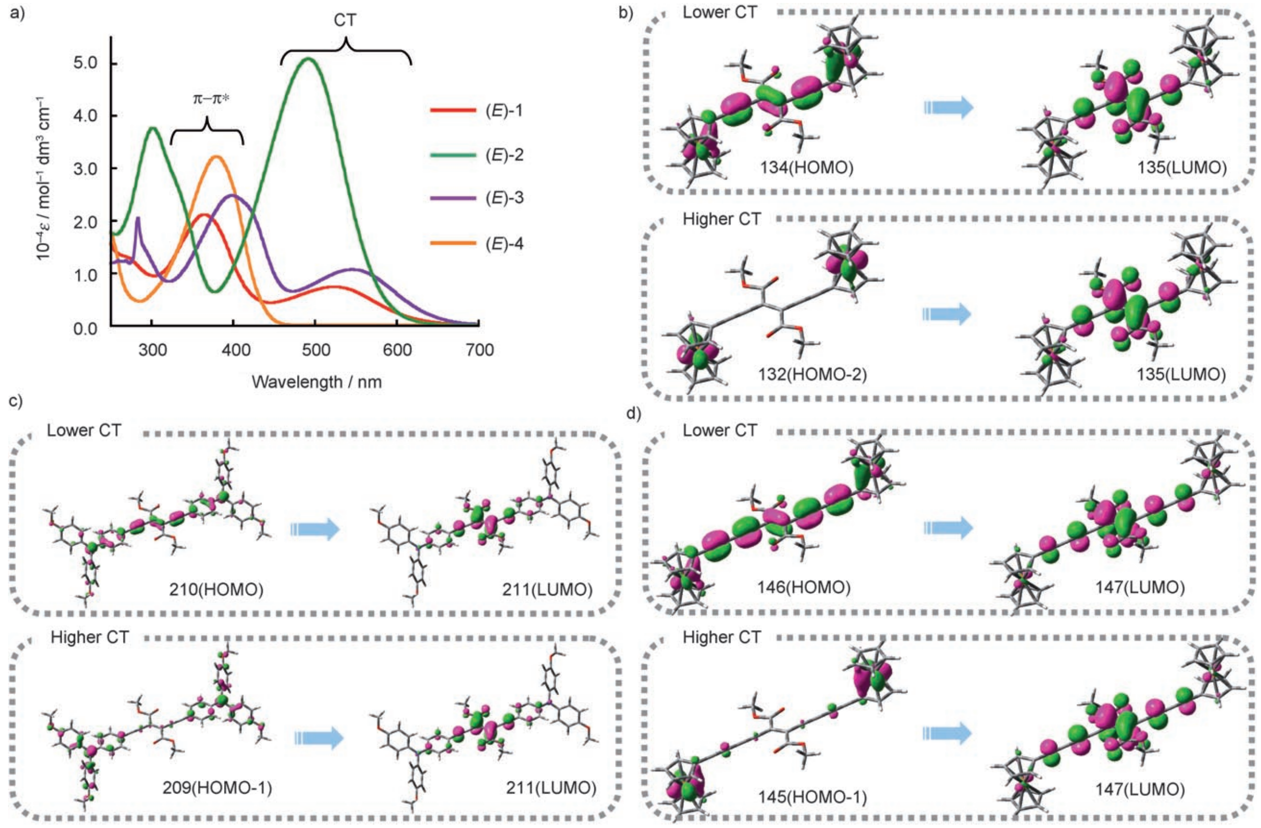

Figure 3. a) Electronic spectra of (*E*)-**1** to (*E*)-**4** in dichloromethane. b)–d) Main transitions in the lower and higher CT bands: b) (*E*)-**1**; c) (*E*)-**2**; d) (*E*)-**3**.

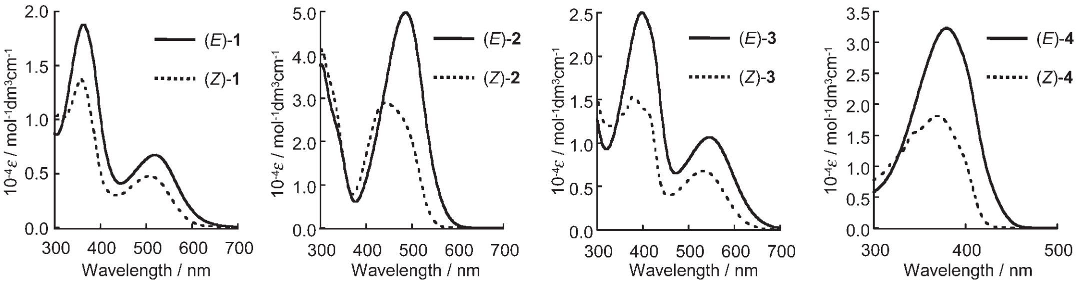

Figure 4. Overlays of the electronic spectra of the *E* and *Z* forms of **1**–**4** in toluene. Those of the *Z* forms were measured directly for **1**, and calculated mathematically from photoirradiation experiments described in a later section.

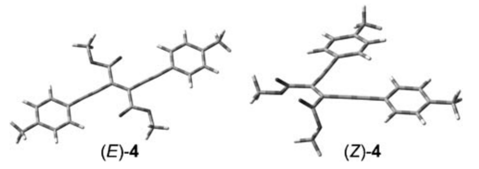

Figure 5. Optimized structures of (*E*)-**4** and (*Z*)-**4**.

compounds considered here, is sufficiently pronounced to disturb the π-conjugation.

Photoisomerization: In toluene, excitation of the CT bands of (*E*)-**2** with light at 578 nm caused a UV/Vis spectral change with isosbestic points (Figure 6a), which was reflected in a drastic color change (Figure 6c). This reaction was further tracked by means of ^{1}H NMR spectroscopy, which revealed one-step *E*-to-*Z* photoisomerization (Figure 6b and Figure S9). The proportions of the *Z* isomer reached >99 % (irradiation with light at 578 nm) and 97 % (irradiation with light at 546 nm), as calculated on the basis of the relative integrals of the ^{1}H NMR spectra. Time-course UV/Vis spectral changes (Figure S10) revealed the quantum yields for the photoisomerization of **2** to be larger than those of **1** (Figures S12 and S13) by almost four orders of magnitude (Table 1). These values for **2** are also superior or similar to those for the organic analogue **4** upon excitation of the π–π* bands (Table 1, Figures S15 and S16).

Table 1. Photoisomerization quantum yields of **1**–**4** in toluene.

	$10^2\Phi_{E\to Z}$	$10^2\Phi_{Z\to E}$	Irradiation [nm][a]
1	0.00086	0.00025	546
2	4.4	0.89	546
	6.1	1.4	405
3	0.0062	0.0034	578
4	1.2	1.2	436[b]

[a] Excitation of the CT bands. [b] Excitation of the π–π* bands.

It is noteworthy that upon irradiation with light at 405 nm, at which the absorption of (*Z*)-**2** increased com-

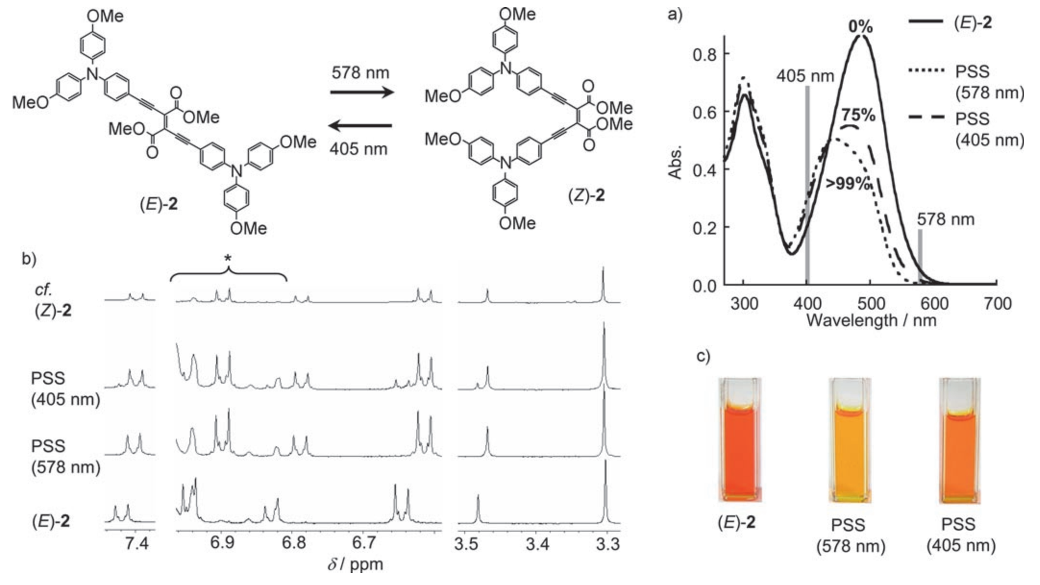

Figure 6. a) UV/Vis and b) ^{1}H NMR spectral changes of (*E*)-**2** in toluene and [D$_8$]toluene, respectively, upon irradiation with light at 578 and 405 nm. The percentages given in a) indicate the proportion of the *Z* isomer in each state. The asterisk in b) indicates the presence of signals derived from the solvent. The scale for the methoxy protons is reduced to one-third of that for the aromatic protons. c) Photograph of (*E*)-**2** before and after irradiation with light at 578 or 405 nm.

pared with that of (*E*)-**2** as shown in Figure 4, the PSS moved in the *E*-richer direction compared with what was found upon irradiation with light at 578 nm, again with high efficiency (Table 1, Figure 6, and Figure S11). Such switching behavior has never been observed for **1**, for which there is no reversal of the absorption in the visible region in the *Z* form (Figure 4).

Compound **3** is free from the steric congestion between its ferrocenyl groups in the *Z* form (Figure S1). When (*E*)-**3** in toluene was irradiated with light at 578 nm, one-step UV/Vis and ^{1}H NMR spectral changes similar to those noted for (*E*)-**1** (Figure S12) were observed, indicating *E*-to-*Z* photoisomerization (Figure 7). The proportion of the Z isomer in the PSS was 79 % (Figure 7), and the quantum yields of the photoisomerization were only slightly higher than those in the case of **1** (Table 1 and Figure S14). It is also noteworthy that, in contrast to **1**, compound **3** did not show an *E*-richer PSS.

This series of results indicates that the far higher photoisomerization quantum yields observed for **2** as compared to those found for **1** is not attributable to the steric issue (Figure S1), but to the difference in the electronic structures between triarylamine and ferrocene, that is, the absence or existence of the heavy atom effect[15a] and a low-lying ^{3}LF state.[15] This proposition is further supported by the fact that stilbene derivatives modified with organic substituents such as nitro and dialkylamino groups show relatively high photoisomerization quantum yields from both their singlet and triplet excited states,[21] whereas styrylferrocene undergoes significantly less efficient photoisomerization, which is ascribed to fast internal conversion and intersystem crossing from singlet excited states to photoisomerizable triplet excited states, and subsequent effective deactivation via the ^{3}LF channel.[11]

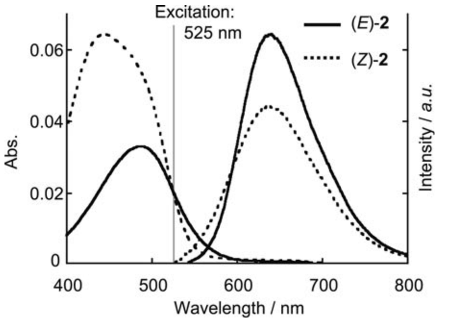

Figure 8. Absorption and fluorescence spectra of (*E*)-**2** and (*Z*)-**2** in toluene at ambient temperature upon excitation of the CT bands. At the excitation wavelength (525 nm), both samples have identical optical densities.

Fluorescence spectra: At ambient temperature, both (*E*)-**2** and (*Z*)-**2** show emissions with wavelength maxima at 639 nm and 637 nm, respectively, upon excitation at the CT bands (Figure 8). Relatively large Stokes shifts are observed in both isomers, which are typical of fluorescence from ^{1}CT excited states in donor–acceptor-type triarylamine-based dyes.[18] The efficiency of the fluorescence is higher in (*E*)-**2** than in (*Z*)-**2**. In contrast, both **1** and **3**, containing ferrocenyl units, show no emission.

Electrochemistry: The electronic communication between the two triarylamine sites in the mixed-valence states in (*E*)-**2** and (*Z*)-**2** was evaluated by means of cyclic voltammetry. Figure 9 and Figure S17 show cyclic voltammograms and their simulations for (*E*)-**2** and (*Z*)-**2** in 0.1 M $n\mathrm{Bu_4NBF_4}$ in dichloromethane. The voltammograms of both isomers were simulated with two one-electron reversible processes, attributable to the stepwise redox changes of the two triarylamine sites.[4,17] The separation between the two redox potentials, $\Delta E^{0\prime}$, was larger in the *E* form (74 mV for (*E*)-**2** and 63 mV

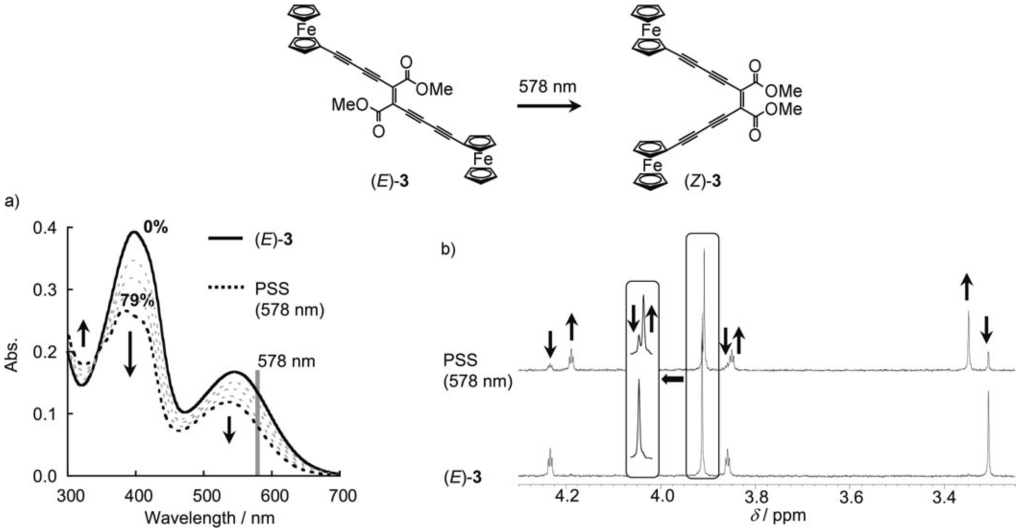

Figure 7. a) UV/Vis and b) ^{1}H NMR spectral changes of (*E*)-**3** in toluene and [D$_8$]toluene, respectively, upon irradiation with light at 578 nm. The percentages given in a) indicate the proportion of the *Z* isomer in each state.

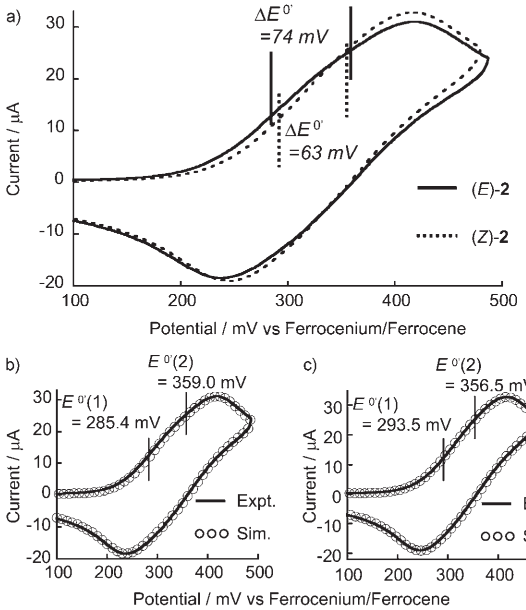

Figure 9. a) Cyclic voltammograms of (*E*)-**2** and (*Z*)-**2** (1.1 mM) in 0.1 M $n\mathrm{Bu_4NBF_4}$ in dichloromethane at a sweep rate of 100 mV s^{-1}. b),c) Experimental and simulated cyclic voltammograms: b) (*E*)-**2**; c) (*Z*)-**2**. See Figures S17 and S18 for details of the parameters used for the simulations.

for (*Z*)-**2**), as was also the case for **1** (70 mV for (*E*)-**1** and 48 mV for (*Z*)-**1**; Figure S19).[9] Since, in the present cases, the through-space distances between the two redox sites are obviously far shorter in the *Z* forms (11.9 Å for (*E*)-**1** and 7.5 Å for (*Z*)-**1**; 17.4 Å for (*E*)-**2** and 10.8 Å for (*Z*)-**2**, the Fe–Fe or N–N distances of the neutral species based on DFT calculations), $\Delta E^{0'}$ should be dominated by the through-bond communication, rather than the through-space coulombic repulsion and direct contact between the redox sites.[22] The weaker through-bond communication in the *Z* forms is attributable to the disruption of the π-conjugation by the steric repulsion between the methyl ester moieties, which clearly arises in both **1** and **2** (Figures 4 and 5).

Electronic spectra of monocationic (*E*)-2 and (*Z*)-2: Taking advantage of the fact that mixed-valence compounds based on triarylamines tend to show intense and well-resolved IVCT bands compared with those based on organometallics and transition metal complexes,[17] we also subjected (*E*)-**2** and (*Z*)-**2** to IVCT analyses with chemical oxidation. Tris(4-bromophenyl)ammonium hexachloroantimonate ($E^{0'}$ = 0.70 V vs ferrocenium/ferrocene in dichloromethane[23]) was used as an oxidant, considering the oxidation potentials of the triarylamine moieties in (*E*)-**2** and (*Z*)-**2**. The oxidizing reagent (0.1 equiv) was added to neutral (*E*)-**2** and (*Z*)-**2** in dichloromethane, such that the ratios between the monocation and dication exceeded 100 according to K_{comp} calculated from the electrochemical data given above.

Figure 10a shows the electronic spectra of monocationic (*E*)-**2** and (*Z*)-**2**. As in previous reports, each spectrum can be deconvoluted with three Gaussians (Figure 10b, c; Figures S21 and S22), which, in order of energy, may be attributed to a triarylammonium-localized π–π* band,[17a] a CT band from the diethynylethene(π) to the triarylammonium(*n*),[17h] and an IVCT band,[17] respectively. The symmetrical IVCT bands indicate that both (*E*)-$\mathbf{2}^+$ and (*Z*)-$\mathbf{2}^+$ conform to Robin and Day class II,[24] rather than class III, or lie at the border of classes II and III.[1c,d,17a,25] It is worth noting that there is a substantial difference in the strengths of the IVCT bands between (*E*)-$\mathbf{2}^+$ and (*Z*)-$\mathbf{2}^+$.

When a Gaussian-shaped curve is employed for the IVCT band, the off-diagonal matrix coupling element H_{ab} can be obtained from Hush's equation [Eq. (1)][26]:

$$H_{\mathrm{ab}} = 2.06\times10^{-2}R^{-1}(\varepsilon_{\max}\bar{\nu}_{\max}\bar{\nu}_{1/2})^{1/2} \qquad (1)$$

where $\varepsilon_{\max}$, $\bar{\nu}_{\max}$, $\bar{\nu}_{1/2}$, and R are the molar extinction coefficient and wavenumber at the absorption maximum, the full-width at half-maximum of the IVCT band, and the distance between the two redox sites, respectively. Application of Equation (1) with the $\varepsilon_{\max}$, $\bar{\nu}_{\max}$, and $\bar{\nu}_{1/2}$ values derived from the curve fittings (Figures S21 and S22), and R from the N–N distances of the neutral species from the DFT calculations, gave a slightly larger H_{ab} for the *E* form (534 cm^{-1} for (*E*)-$\mathbf{2}^+$ and 529 cm^{-1} for (*Z*)-$\mathbf{2}^+$). It should be noted that there is a high possibility of a larger underestimation of H_{ab}, which results from a greater overestimation of R in (*E*)-$\mathbf{2}^+$

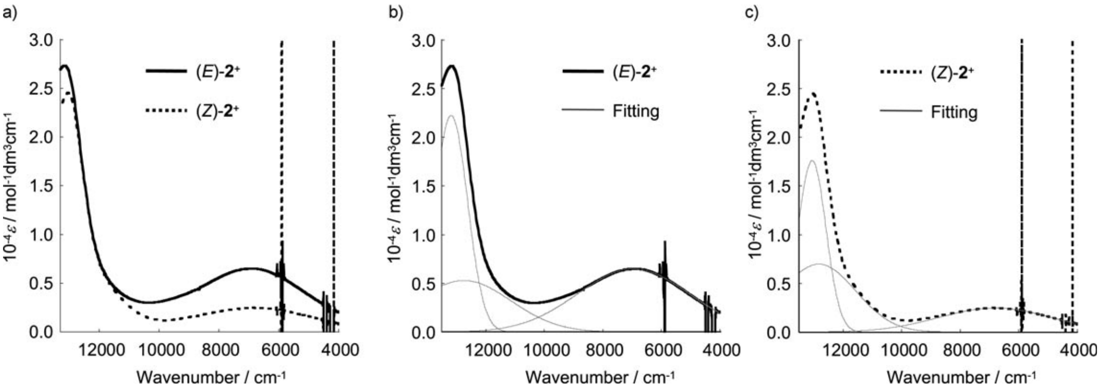

Figure 10. a) Overlay of the electronic spectra of (*E*)-$\mathbf{2}^+$ and (*Z*)-$\mathbf{2}^+$ in dichloromethane. b),c) Curve fitting with three Gaussians: b) (*E*)-$\mathbf{2}^+$; c) (*Z*)-$\mathbf{2}^+$. See Figures S21 and S22 for details of the parameters used for the fittings.

than in (Z)-$\mathbf{2}^{+}$. The determination of R is one of the most difficult problems in the application of Hush's equation, because stronger delocalization of the surplus charge over the redox sites and π-bridge produces a shorter effective charge-transfer distance.[27] The electrochemical data indicate that the delocalization over the two triarylamine sites is larger in the *E* form (Figure 9). The disruption of the π-conjugation in the *Z* form by the steric repulsion of the methyl ester moieties (Figures 4 and 5) suggests that the delocalization over the diethynylethene π-bridge is also greater in the *E* form. In addition, the vector connecting the two redox centers is almost directed along the diethynylethene π-bridge in the *E* form, whereas in the *Z* form there is a large discrepancy. This topological difference also leads to a more pronounced reduction of R in the *E* form by delocalization over the diethynylethene π-bridge.

Coropceanu et al. have suggested[17c,h,28] that the extent of the electronic communication can be evaluated from MO calculations on neutral species according to Koopman's theorem:

$$H_{ab} = 1/2(\varepsilon_{\mathrm{HOMO}} - \varepsilon_{\mathrm{HOMO-1}}) \tag{2}$$

where $\varepsilon_{\mathrm{HOMO}}$ and $\varepsilon_{\mathrm{HOMO-1}}$ denote the energy levels of the HOMO and HOMO-1, respectively, of the neutral species. Assignment of the results of the DFT calculations afforded a larger value for the *E* form (1524 cm^{-1} for (E)-$\mathbf{2}^{+}$ and 1286 cm^{-1} for (Z)-$\mathbf{2}^{+}$) (Figure S23). This trend is consistent with our experimental results and discussion.

Conclusions

We have created a new visible-light photochromic system, **2**, that can reversibly and efficiently undergo switching of its through-bond electronic communication between the two triarylamine sites and fluorescence intensity. Compounds **1**–**3** have two characteristic bands in the visible region, ascribed to CT transitions from the in-phase and out-of-phase combinations of the two triarylamine(*n*) or ferrocene(*d*) to the diethynylethene(π*). These compounds undergo *Z*/*E* photochromism upon excitation of their CT bands. The efficiency of the photochromism in fully organic **2** ($\Phi_{E\rightarrow Z}=6.1\times10^{-2}$, $\Phi_{Z\rightarrow E}=1.4\times10^{-2}$) is far higher than that in organometallic **1** ($\Phi_{E\rightarrow Z}=8.6\times10^{-6}$, $\Phi_{Z\rightarrow E}=2.5\times10^{-6}$) or in **3** ($\Phi_{E\rightarrow Z}=6.2\times10^{-5}$, $\Phi_{Z\rightarrow E}=3.4\times10^{-5}$). This series of results indicates that the difference in the electronic structures of triarylamine and ferrocene, rather than steric repulsion between the two ferrocenyl units in (Z)-**1**, is mainly responsible for the drastic difference in efficiency between **1** and **2**.

Compound **2** shows reversible *Z*/*E* switching behavior in response to irradiation at 578 nm and 405 nm, which is unattainable with ferrocene-containing compounds **1** and **3**. This phenomenon stems from the dramatic changes in the strengths of the two CT bands between (E)-**2** and (Z)-**2**.

We have also demonstrated that both isomers of **2** show fluorescence in fluid solution, the efficiency of which is higher in the *E* form.

The strength of the electronic communication between the redox sites in **1** and **2** has been quantitatively evaluated from cyclic voltammograms and their simulations, with weaker through-bond interactions being identified in both *Z* forms. This phenomenon stems mainly from steric hindrance between the methyl ester moieties and the resulting distortion of the π-system, which is reflected in blueshifts in the electronic spectra and in the DFT calculations. Further evaluations for **2** by IVCT analyses and DFT calculations are consistent with the electrochemical data.

The results reported herein have been obtained through sophisticated considerations of both electronic and structural aspects of functional molecular fragments, as well as how these act in unison. This work and its concept constitute a paradigm for the construction of molecular devices, as well as providing models for photoswitchable molecular electronic circuits.

Experimental Section

Dimethyl 2,3-dibromofumarate,[29] (E)-**1**,[9] (E)-**4**,[9] *N,N*-di-4-methoxyphenyl-4-ethynylphenylamine,[30] and ethynylferrocene[10d] were prepared according to previous reports. Et_3N was distilled and stored over KOH pellets. THF was distilled from metallic Na and benzophenone. Other chemicals were used as purchased unless otherwise stated.

Dimethyl 2,3-bis(*N,N*-di-4-methoxyphenyl-4-aminophenylethynyl)fumarate [(*E*)-2]: Et_3N (40 mL) was added to a mixture of dimethyl 2,3-dibromofumarate (400 mg, 1.3 mmol), CuI (27 mg), $[PdCl_2(PPh_3)_2]$ (100 mg), and *N,N*-di-4-methoxyphenyl-4-ethynylphenylamine (940 mg, 2.8 mmol) under a nitrogen atmosphere. The pale-yellow suspension was heated to 100 °C, whereupon it turned deep-red in color. After the mixture had been heated under reflux for 2 h, it was allowed to cool to ambient temperature, whereupon dichloromethane was added to quench the reaction. The deep-red suspension was filtered through Celite, and the filtrate was concentrated to dryness in vacuo. The deep-red residue was purified by column chromatography on basic alumina (activity grade II–III), eluting with hexane/dichloromethane 1:1. The deep-red fraction was collected and concentrated to furnish (E)-**2** as a deep-red solid (770 mg, 73 %). Recrystallization from dichloromethane/hexane with protection from light produced deep-red crystals of (E)-**2**. ^{1}H NMR (500 MHz, [D$_8$]toluene): $\delta=7.42$ (d, $J=9.2$ Hz, 4H), 6.96–6.93 (m, 8H), 6.83 (d, $J=9.1$ Hz, 4H), 6.64 (d, $J=9.6$ Hz, 8H), 3.48 (s, 6H), 3.30 ppm (s, 12H); elemental analysis calcd (%) for $C_{50}H_{42}O_8N_2$: C 75.17, H 5.30, N 3.51; found: C 74.94, H 5.37, N 3.22.

Dimethyl 2,3-bis(*N,N*-di-4-methoxyphenyl-4-aminophenylethynyl)maleate [(*Z*)-2]: A solution of (E)-**2** (200 mg, 0.25 mmol) in toluene (120 mL) was irradiated for 24 h at 546 and 578 nm by means of a high-pressure Hg lamp equipped with a cut-off filter. After completion of the reaction was confirmed by TLC, the solution was concentrated and the residue obtained was purified by column chromatography on basic alumina (activity grade II–III) eluting with hexane/dichloromethane (1:1, v/v). The second red fraction was collected and concentrated to give (Z)-**2** (185 mg, 92 %) as a red solid. Recrystallization from dichloromethane/hexane with protection from light produced exclusively (Z)-**2** as a red powder. ^{1}H NMR (500 MHz, [D$_8$]toluene): $\delta=7.40$ (d, $J=9.2$ Hz, 4H), 6.90 (d, $J=9.5$ Hz, 8H), 6.79 (d, $J=9.2$ Hz, 4H), 6.61 (d, $J=9.6$ Hz, 8H), 3.47 (s, 6H), 3.30 ppm (s, 12H); elemental analysis calcd (%) for $C_{50}H_{42}O_8N_2$: C 75.17, H 5.30, N 3.51; found: C 75.03, H 5.55, N 3.35.

1-Ferrocenyl-4-triisopropylsilylbuta-1,3-diyne: Triisopropylsilylacetylene (22 mL, 0.11 mol), [$PdCl_2(PPh_3)_2$] (838 mg, 1.2 mmol), and CuI (460 mg, 2.4 mmol) were suspended in a mixture of THF (100 mL) and Et_3N (100 mL) under an aerobic atmosphere. A solution of ethynylferrocene (5.0 g, 0.024 mol) in THF (120 mL) was added dropwise to this suspension over 5 min. After stirring the brown suspension for 1 h, diethyl ether (300 mL) was added. The resulting mixture was then filtered through Celite. After evaporation of the volatiles in vacuo, the dark-brown residue obtained was purified by column chromatography on alumina (activity grade II–III) eluting with hexane. The first orange fraction was collected and concentrated to give 1-ferrocenyl-4-triisopropylsilylbuta-1,3-diyne as a dark-brown oil, which subsequently crystallized (2.2 g, 24 %). ^{1}H NMR (500 MHz, [D_1]chloroform): $\delta = 4.50$ (dd, $J = 1.8$, 1.8 Hz, 2H), 4.26 (s, 5H), 4.24 (dd, $J = 1.8$, 1.8 Hz, 2H), 1.12–1.10 ppm (m, 21H); elemental analysis calcd (%) for $C_{23}H_{30}FeSi$: C 70.76, H 7.75; found: C 70.61, H 7.82.

Ferrocenylbuta-1,3-diyne: Under a nitrogen atmosphere, 1-ferrocenyl-4-triisopropylsilylbuta-1,3-diyne (404 mg, 1.0 mmol) was dissolved in THF (90 mL). A solution of Bu_4NF in THF (1.1 mL, 1.1 mmol) and a few drops of water were added to the solution. After stirring the mixture for 5 min, the reaction was quenched by the addition of water and diethyl ether. The organic phase was separated, and washed with water and brine. The brown ethereal solution was dried over Na_2SO_4, diluted with 1,4-dioxane (100 mL), and then concentrated in vacuo until the diethyl ether and THF were removed. The resulting solution of 1-ferrocenylbuta-1,3-diyne in 1,4-dioxane was used directly in the next reaction because of the low stability of this compound in concentrated solution or in the solid state.

Dimethyl 2,3-bis(ferrocenylbuta-1,3-diynyl)fumarate [(*E*)-3]: Under a nitrogen atmosphere, [$PdCl_2(PPh_3)_2$] (16 mg), CuI (16 mg), and 2,3-dibromofumarate (150 mg, 0.49 mmol) were suspended in a solution of 1-ferrocenylbuta-1,3-diyne (1.0 mmol) in 1,4-dioxane (100 mL) and Et_3N (30 mL). The suspension was refluxed for 1 h, whereupon the color changed from orange to purple. The mixture was then cooled to ambient temperature, whereupon dichloromethane was added to quench the reaction. The suspension was filtered through Celite, and the filtrate was concentrated in vacuo. The black residue was then purified by column chromatography on alumina (activity grade II–III) eluting with hexane/dichloromethane 3:2. Recrystallization from hexane/dichloromethane produced tiny deep-purple crystals of (*E*)-**3** (54 mg, 18 %). ^{1}H NMR (500 MHz, [D_8]toluene): $\delta = 4.23$ (dd, $J = 1.8$, 1.8 Hz, 4H), 3.91 (s, 10H), 3.86 (dd, $J = 1.8$, 1.8 Hz, 4H), 3.31 ppm (s, 6H); elemental analysis calcd (%) for $C_{34}H_{24}O_4Fe_2$: C 67.14, H 3.98; found: C 66.98, H 4.20.

Single-crystal X-ray structure analysis: Intensity data were collected at 120(1) K on a Bruker SMART APEX using monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å). (*E*)-**2**: $C_{50}H_{42}O_8N_2$, $M_r = 798.88$, $P2_1/c$, $a = 10.870(2)$, $b = 12.875(3)$, $c = 14.823(3)$ Å, $\beta = 97.135(4)°$, $V = 2050.4(7)$ Å^3, $Z = 2$, $\mu = 0.088$ mm^{-1}, unique reflections = 4711 [$R(\text{int}) = 0.0417$], $R_1 = 0.0507$ [$I > 2.00\sigma(I)$], $wR_2 = 0.1207$ [$I > 2.00\sigma(I)$]. The structure was solved with SHELXS-97[31] and refined against F^2 using SHELXL-97.[32]

CCCDC 661918 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.

DFT calculations: The three-parameterized Becke-Lee–Yang–Parr (B3LYP) hybrid exchange-correlation functional[33] was employed. As basis sets, LANL2DZ[34] was used for **1** and **3**, 6–31G** for **2**, and 6-311G** for **4**. The geometries were optimized with symmetry constraints. TD-DFT calculations were executed under the same conditions as listed above. Solvent effects were not considered in any of the processes. This series of calculations was implemented with the Gaussian 03 program.

Photoirradiation: A high-pressure Hg lamp (Ushio Inc.) served as the photon source, with certain bright lines being selected by means of a monochromator (CT-10T, JASCO Inc.). Photon fluxes were measured with Q8230 and Q82311, a semiconductor photon counter set-up supplied by Advantest Corporation. The quantum yields of the photoisomerizations were calculated according to the procedure reported by Zimmerman et al.[35] None of the compounds showed any significant difference in their photochemical behavior between aerobic and anaerobic conditions.

Electrochemistry: Electrochemical data were acquired with an ALS-650B voltammetric analyzer (BAS Inc.). A series of measurements was carried out in a standard one-compartment cell, using 3 mm ϕ glassy carbon (Tokai Carbon Co., Ltd.) as a working electrode, platinum wire (The Nilaco Corporation) as a counter electrode, and an Ag/Ag$^+$ reference electrode. As an internal standard, decamethylferrocene ($E^{0\prime} = -551$ mV vs Fc$^+$/Fc under our measurement conditions) was added after each measurement, and its redox wave was used to determine the solution resistance and double-layer capacitance (Figures S18 and S20). DigiSim 3.03b (BAS Inc.) was used to simulate the voltammograms. nBu$_4$NBF$_4$ (Sigma–Aldrich Co.) was recrystallized from EtOH. Dichloromethane (HPLC grade, Kanto Chemicals Co., Inc.) was used as received. Ferrocene (Kanto Chemicals Co., Inc.) was recrystallized from dichloromethane/hexane. Decamethylferrocene was synthesized according to a previous report.[36]

Apparatus: UV/Vis spectra were measured with Jasco V-570 and Hewlett–Packard 8453 UV/Vis spectrometers, IR spectra with a Jasco FT/IR-620v spectrometer, ^{1}H NMR spectra with a Bruker DRX 500 (500 MHz) spectrometer, and fluorescence spectra with a Hitachi F-4500 spectrofluorimeter.

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