Supporting Information

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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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Figure S1. Possible collision between the ferrocenyI groups in (Z)-1, and collision-free (Z)-2 and (Z)-3. The ferrocenyl and triarylamine groups are rotated along the C≡C bonds from the optimized structures of Z forms.
Figure S2. IR spectra of diethynylethenes in a KBr pellet around the signals derived from the C=O bonds.
Figure S3. Experimental (toluene solution) and simulated electronic spectra of (E)-2, and main transitions in $\pi$-$\pi^*$ and CT bands.
Figure S4. Experimental (toluene solution) and simulated electronic spectra of \((Z)-2\), and main transitions in \(\pi-\pi^*\) and CT bands.
Figure S5. Experimental (toluene solution) and simulated electronic spectra of (E)-1, and main transitions in $\pi-\pi^*$ and CT bands.
Figure S6. Experimental (toluene solution) and simulated electronic spectra of (Z)-1, and main transitions in $\pi-\pi^*$ and CT bands.
Figure S7. Experimental (toluene solution) and simulated electronic spectra of (E)-3, and main transitions in $\pi-\pi^*$ and CT bands.
Figure S8. Experimental (toluene solution) and simulated electronic spectra of (Z)-3, and main transitions in $\pi-\pi^*$ and CT bands.
Figure S9. Closeup of the $^1$H NMR spectrum of 2 around the signals derived from the methyl ester moieties in the PSS upon irradiation with light at 578 nm in toluene-d$_8$. 
Figure S10. Time-course plot for the determination of $\Phi_{E \rightarrow Z}$ and $\Phi_{Z \rightarrow E}$, and experimental data and parameters in 2 (for light at 546 nm). See ref[1] for the numerical treatment.
Figure S11. Time-course plot for the determination of $\Phi_{E \rightarrow Z}$ and $\Phi_{Z \rightarrow E}$, and experimental data and parameters in 2 (for light at 405 nm). See ref[1] for the numerical treatment.
Figure S12. UV/Vis (a) and $^1$H NMR (b) spectral changes of (E)-1 upon irradiation with 546 nm and 578 nm in dichloromethane and [D$_2$]dichloromethane. The percentages given in (a) indicate the proportion of Z isomer in each state.
Figure S13. Time-course plot for the determination of $\Phi_{E \rightarrow Z}$ and $\Phi_{Z \rightarrow E}$, and experimental data and parameters in 1 (for light at 546 nm). See ref[1] for the numerical treatment.
Figure S14. Time-course plot for the determination of $\Phi_{E \rightarrow Z}$ and $\Phi_{Z \rightarrow E}$, and experimental data and parameters in 3 (for light at 578 nm). See ref[1] for the numerical treatment.
Figure S15. UV/Vis (a) and $^1$H NMR (b) spectral changes of (E)-4 upon irradiation with light at 436 nm in toluene and toluene-d$_8$. The percentages given in (a) indicate the proportion of Z isomer in each state.
Figure S16. Time-course plot for the determination of $\Phi_{E \rightarrow Z}$ and $\Phi_{Z \rightarrow E}$, and experimental data and parameters in 4 (for light at 436 nm). See ref[1] for the numerical treatment.
Figure S17. Experimental and simulated cyclic voltammograms, and parameters for the simulations: (a) (E)-2; (b) (Z)-2.
Figure S18. Experimental and simulated cyclic voltammograms, and parameters for the simulations of the redox waves of decamethylferrocene, which was added in the solutions used for the measurements shown in Figures 9 and S17: (a) (E)-2; (b) (Z)-2.
Figure S19. (a) Cyclic voltammograms of \((E)-1\) and \((Z)-1\) (1.2 mM) in 0.1 M \(^{8}\text{Bu}_4\text{NBF}_4\)-dichloromethane at a sweep rate of 100 mVs\(^{-1}\). (b),(c) Experimental and simulated cyclic voltammograms, and parameters for the simulations: (b) \((E)-1\); (c) \((Z)-1\).
Figure S20. Experimental and simulated cyclic voltammograms, and parameters for the simulations of the redox waves of decamethylferrocene, which was added in the solutions used for the measurements shown in Figure S19: (a) (E)-I; (b) (Z)-I.
Figure S21. Curve fitting of the electronic spectra of (E)-2\textsuperscript{+} in dichloromethane and parameters for Gaussians.

\[
\text{[Gaussian]} = \epsilon_{\text{max}} \exp\left[-\frac{(\nu - \bar{\nu}_{\text{max}})^2}{2\sigma^2}\right]
\]

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<th>Gaussian #1 [triarylaminium-localized π-π\textsuperscript{*}]</th>
<th>$\epsilon_{\text{max}} / \text{M}^{-1}\text{cm}^{-1}$</th>
<th>$\bar{\nu}_{\text{max}} / \text{cm}^{-1}$</th>
<th>$\sigma / \text{cm}^{-1}$</th>
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<th>Gaussian #2 [CT from the bridge(π) to the triarylaminium(n)]</th>
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<th>Gaussian #3 [IVCT]</th>
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<td>$6.954 \times 10^3$</td>
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Figure S22. Curve fitting of the electronic spectra of $(Z)$-2$^-$ in dichloromethane and parameters for Gaussians.

\[ [\text{Gaussian}] = \varepsilon_{\text{max}} \exp \left[ -\frac{(\nu - \nu_{\text{max}})^2}{2\sigma^2} \right] \]
Figure S23. Energy levels of HOMO and HOMO-1 in (E)-2 and (Z)-2 estimated in DFT calculations.
References
