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The One-Electron Transfer Induced Photocycloreversion of Stilbazolium Cyclodimers

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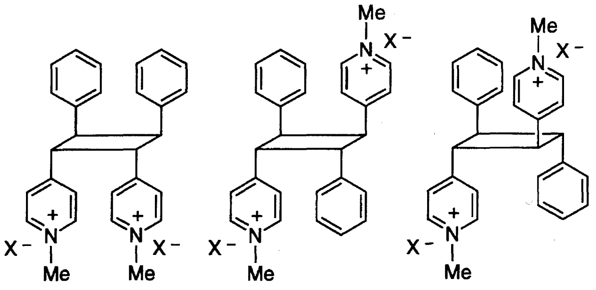
The irradiation of iodide salts of stereo isomeric stilbazolium cyclodimers in their CT bands (ca. 355 nm) resulted in a one-electron transfer induced photocycloreversion, which led to the formation of stilbazolium ions; the quantum yields (Φ) being highly sensitive to their structures, i.e., the Φ for *syn*-Head-to-Head (*syn*-HH) was found to be 0.35, for *syn*-Head-to-Tail (*syn*-HT) 0.0026, and for *anti*-Head-to-Head (*anti*-HH) 0.00095, respectively. This reaction shows a distinct contrast to photocycloreversion by irradiation at 255 nm, which resulted in a highly efficient, but nonselective, splitting, the Φ's being in the range of 0.3—0.8. In the photosensitized cycloreversion of methyl sulfate salts of dimers using 9, 10-dimethoxyanthracene (DMA) as a sensitizer, the quantum efficiencies show a structural dependence similar to the above case of irradiation at their CT bands. Cosensitization with DMA and 1-cyanonaphthalene as an electron mediator resulted in relative quantum yields showing a close coincidence to the yields in the irradiation of the CT band, i.e., 254 : 2.6 : 1 for *syn*-HH, *syn*-HT, and *anti*-HH, respectively. This implies that the one-electron transfer mechanism can be initiated both by CT band irradiation as well as DMA sensitization. It can be concluded that the structural dependence of the quantum efficiencies is attributed to the through-bond interaction of two pyridinium rings, which facilitates the splitting of the C–C bond in the cyclobutane ring.

The photochemical cycloreversion of cyclobutanes initiated by a one-electron transfer is a remarkable and interesting phenomenon from both biological[1—9] and photochemical points of view.[10—15] A number of reaction pathways for the reversion have been proposed. In biological studies, dramatic results have been seen in the photoreactivation of damaged DNA. For example, pyrimidine dimers formed by UV irradiation may be split by the one-electron transfer from the DNA photolyases. The photosplitting of dimethylthymine dimers using *N*,*N*-dimethylaniline as the electron donor was examined as a model study; this reaction proved to occur very rapidly (over 10^6 s^{-1}).[6a] Here, a clarification of the origin of the one-electron reductive cleavage is presented. In contrast, it is reasonable to assume that the oxidative cleavage is easily promoted by a decrease in the electron density of the C–C bond of cyclobutane.

In the present article, we have reported on a novel photosensitized one-electron reductive splitting of cyclobutane compounds possessing two pyridinium rings, that is, the stereoisomers of stilbazolium cyclodimers, *syn*-head-to-head (*syn*-HH), *syn*-head-to-tail (*syn*-HT), and *anti*-head-to-head (*anti*-HH), as shown in Chart 1. The present investigations will provide an alternative example of C–C bond scission in a reduced form of cyclobutane with the pyridinium substituent, presenting a comprehensive understanding of the mechanisms involved in this reaction. One-electron reductive cycloreversions have been carried out by CT excitation and sensitization with 9,10-dimethoxyanthracene (DMA) and 1-cyanonaphthalene (CN).



syn-HH *syn*-HT *anti*-HH

$X^- = I^-$ or $MeSO_4{}^-$

Chart 1.

Results and Discussion

Photocycloreversion of Stilbazolium Cyclodimers by CT Excitation. The irradiation of a solution of isomeric stilbazolium cyclodimers, i.e., *syn*-HH, *syn*-HT, or *anti*-HH in acetonitrile (1—2×10^{-3} mol dm^{-3}) under an argon atmosphere resulted in the quantitative formation of a mixture of *E*- and *Z*-stilbazolium monomers (Stz). At the initial stage of photoreaction, the product was exclusively *E*-Stz followed by isomerization to *Z*-isomer by a secondary photochemical reaction. Table 1 summarizes the quantum yields for the formation of total Stz by irradiation at 255±5 and 355±5 nm for methyl sulfate and iodide salts, respectively. For the iodide

Table 1. Quantum Yields for the Cycloreversion of Stilbazolium Dimers by $\pi\pi^*$ or CT Excitation

Dimers	Quantum yield[a)]/Φ 255±5 nm[b)]	Quantum yield[a)]/Φ 355±5 nm[c)]
syn-HH	0.82 (2.7)	0.35 (365)
syn-HT	0.66 (2.2)	0.0026 (2.7)
anti-HH	0.30 (1)	0.00095 (1)

a) The values in parentheses are the relative quantum yields. b) Acetonitrile solutions of the dimer methyl sulfate salts (1.0×10^{-3} mol dm^{-3}) were irradiated at 255±5 nm ($\pi\pi^*$ excitation) under Ar. c) Acetonitrile solutions of dimer iodide salts (2.0×10^{-3} mol dm^{-3}) were irradiated at 355±5 nm, i.e., CT bands, under Ar. The values were corrected for differences in the absorption intensities of the CT bands between the three dimers.

salts ($X^- = I^-$), irradiation of their CT bands at 355±5 nm showed their relative quantum efficiencies to be remarkably disparate, i.e., 365 : 2.7 : 1 for *syn*-HH, *syn*-HT, and *anti*-HH, respectively. It should be noted that the quantum yields were found to be extremely sensitive to their isomeric structures. On the other hand, the methyl sulfate salts ($X^- = CH_3SO_4^-$) of the dimers exhibited no CT band at all around 350 nm, and direct irradiation at 255±5 nm resulted in a highly efficient cycloreversion, the quantum yields (Φ) being in the relatively narrow range of 0.3—0.8.

Figure 1 shows the absorption spectra of the iodide and methyl sulfate salts of the *syn*-HH cyclodimer in acetonitrile. Similar absorption spectra were also obtained with the other cyclodimers, i.e., *syn*-HT and *anti*-HH. The iodide salts exhibit strong absorption maxima at around 250 nm with a log ε of 4.58 to 4.61 along with weak maxima at around 350 nm with a log ε of 2.41 to 2.90. The former strong absorption can be attributed to the $\pi\pi^*$ band, while the latter can be assigned to the intramolecular charge-transfer (CT) band between the pyridinium cation and the iodide anion,[16,17)] which could no longer be observed in water, while absorption at a longer wavelength could not be observed in the corresponding methyl sulfate salts.

It is clear that cyclobutane rings are cleaved in a concerted or homolytic stepwise manner upon $\pi\pi^*$ excitation of the aromatic moieties of the cyclodimers due to the *anti*-bonding character of the cyclobutane C–C bonds by irradiation at 250 nm. The quantum yields for these dimers were significantly high in the range of 0.3—0.8. In contrast, cycloreversion by CT excitation at 355 nm was found to be profoundly sensitive to the structure of the cyclodimers. It is evident that CT excitation induces an electron transfer from the iodide ion to the pyridinium cation,[17)] and the cyclodimers are subsequently cleaved by one-electron reduction. It should be noted that the resulting relative efficiencies of *syn*-HH ≫ *syn*-HT > *anti*-HH could be observed in the DMA photosensitized cycloreversion.

DMA Photosensitized Cycloreversion. Solutions of stilbazolium cyclodimer (1.0×10^{-3} mol dm^{-3}) in acetonitrile including 9,10-dimethoxyanthracene (DMA, 3.0×10^{-4} mol dm^{-3}) were irradiated at 400±5 nm under an Ar atmosphere. All of the dimers were then cleaved to produce Stz (exclusively *E*-isomer). However, a remarkable difference could be seen in the quantum yields for the formation of Stz among the cyclodimers, as shown in Table 2. Significantly, *syn*-HH was cleaved more than 40 times as efficiently as *syn*-HT and *anti*-HH, similar to the results for CT excitation, while controlled experiments in the absence of DMA showed no formation of Stz.

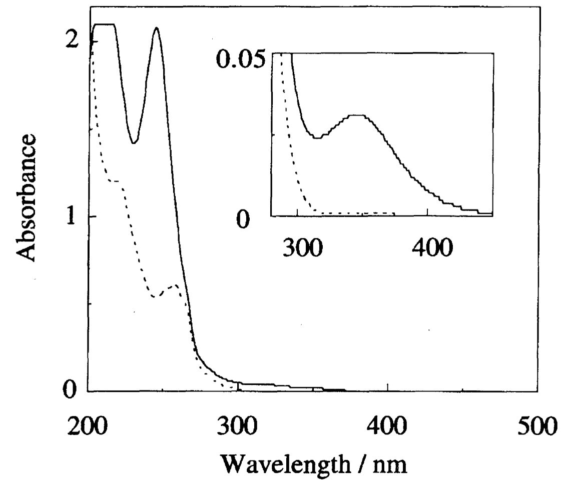


Fig. 1. The UV and visible absorption spectra of 5.0×10^{-5} mol dm^{-3} *syn*-HH salts in acetonitrile. Solid and dotted curves indicate the spectra for $X^- = I^-$ and $MeSO_4^-$, respectively. The inset represents their magnified spectra.

It was found that the DMA fluorescence with a λ_{max} at 440 nm in acetonitrile was efficiently quenched by all of the cyclodimers. The quenching rate constants (k_q) estimated from the Stern–Volmer plots of the fluorescence quenching experiments were found to be about 10^{10} M^{-1} s^{-1}, as shown in Table 3, indicating that the excited singlet state of DMA was quenched by all of the dimers at a diffusion-controlled rate. Free-energy changes (ΔG_{et}) in one-electron transfer from the excited singlet DMA to the dimers were calculated by employing the reduction potentials of −0.98 for *syn*-HH, −1.32 for *syn*-HT, and −1.27 V vs. SCE for *anti*-HH, respectively. The obtained ΔG_{et} values given in Table 3 indicate that one-electron transfer processes are highly exoergonic for the three dimers, and proceed at a diffusion-controlled rate. The estimation was found to be in good agreement with the results of the fluorescence-quenching experiments, and it was evident that cycloreversions are initiated by a one-electron transfer from the excited singlet DMA to the cyclodimers.

Cosensitized Cycloreversion Mediated by Cyanoaromatics. It is generally accepted that the radical ion species generated by photoinduced charge separation may be deactivated by a rapid back electron transfer in the solvent cage usually resulting in low quantum yields of product formation. To address such deactivation, the effect of cosensitized cycloreversion was investigated for DMA photosensitization utilizing cyanoaromatics as the electron mediator. Here, the significant effects seen in the structural variation of the cyclodimers can be realized by minimizing the effect of the back electron transfer, which competes with the

Table 2. Photosensitized Cycloreversion of Stilbazolium Dimers[a)]

Sensitizer	Mediators[a)]	Cyclodimers	Quantum yield/Φ	
			Observed values	Relative values
DMA	—	*syn*-HH	0.033	44
		syn-HT	0.0013	1.7
		anti-HH	0.00075	(1)
DMA	CN	*syn*-HH	0.33	254
		syn-HT	0.0034	2.6
		anti-HH	0.0013	(1)
DMA	DCB	*syn*-HH	0.024	62
		syn-HT	0.00075	1.9
		anti-HH	0.00039	(1)
DMA	DCN	*syn*-HH	0.034	89
		syn-HT	0.00031	0.82
		anti-HH	0.00038	(1)

a) Acetonitrile solutions of DMA (3.0×10^{-4} mol dm^{-3}) and cyclodimers (1.0×10^{-3} mol dm^{-3}, methyl sulfate salts) were irradiated at 400±5 nm under Ar. For the cosensitized reaction, various cyanoaromatics were added (5.0×10^{-4} or 2.5×10^{-4} mol dm^{-3}) to act as the electron mediator; CN: 1-cyanonaphthalene; DCB: 1,4-dicyanobenzene; DCN: 1,4-dicyanonaphthalene.

Table 3. One-Electron Transfer from Excited Singlet DMA to Stilbazolium Dimers

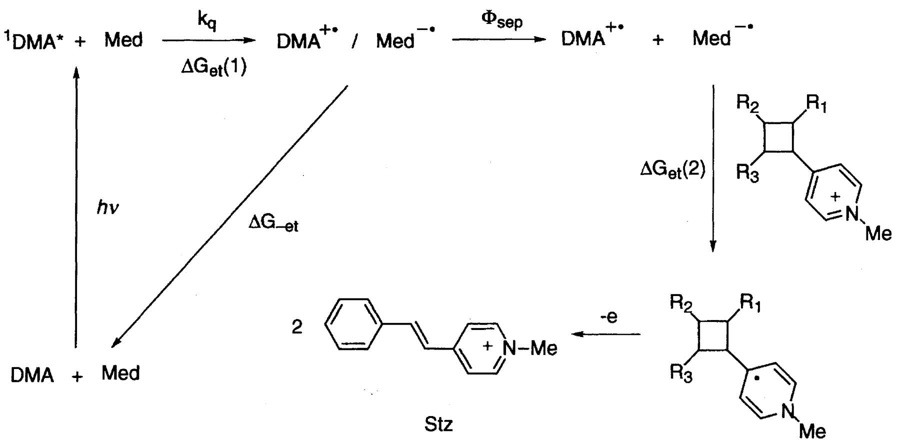
Dimers[a)]	$E_{1/2}$[b)]/V vs. SCE	k_q[c)]/M^{-1} s^{-1}	ΔG_{et}[d)]/eV
syn-HH	−0.98	1.1×10^{10}	−1.24
syn-HT	−1.32	1.2×10^{10}	−0.90
anti-HH	−1.27	1.2×10^{10}	−0.95

a) Stilbazolium dimers used here were methyl sulfate salts. b) The cyclic voltammograms of the stilbazolium dimers were irreversible and therefore the half-wave potentials were obtained by adding 0.0285 V to the cathodic peak potentials assuming that a one-electron reduction takes place. c) Calculated as τ_s of DMA = 16.9 ns.[22)] d) Calculated according to the Rehm–Weller equation, $\Delta G_{et} = (E^{ox} - E^{red}) - E_s$; the values of E^{ox} and E_s of DMA are 0.98 V[23)] (vs. SCE) and 3.2 eV,[24)] respectively.

C–C bond splitting. The cyanoaromatics used here were 1-cyanonaphthalene (CN), 1,4-dicyanonaphthalene (DCN), and 1,4-dicyanobenzene (DCB). The quantum yields for the formation of Stz were found to be significantly enhanced by the presence of the cyanoaromatics, as can be seen in Table 2. It is worth noting that the cycloreversion leading to Stz was remarkably accelerated by the addition of CN, but was rather retarded by the addition of DCB or DCN. Moreover, the effect of CN as the mediator was different for the three isomeric dimers; the splitting of the cyclobutane ring was enhanced 10 times for *syn*-HH, while just 2-3 times for *syn*-HT and *anti*-HH. The resulting relative quantum yields of 254 : 2.6 : 1 for *syn*-HH, *syn*-HT, and *anti*-HH, respectively, for cosensitization with DMA–CN were in good coincidence with those irradiated at their CT bands.

A vital role of cyanoaromatics in the cosensitization of the dimers with DMA is to mediate an electron from the DMA to the cyclodimers, as shown in Scheme 1. The present experiments demonstrate that cycloreversion involves a one-electron transfer to the cyclodimers, which gives a dimer radical cation by an electron transfer from the iodide with CT excitation at 355 nm or an intermolecular electron transfer by photosensitization with DMA. The one-electron transfer pathways can be reasonably well understood by a rather good superimposition of the relative reactivities between the intra- and intermolecular electron transfers. The electron-transfer pathways are also supported by an acceleration effect of CN in the cosensitization with DMA.

Table 4 lists the physical constants influencing the quantum yields for Stz formation in the cosensitization reactions. Electron transfers from the excited singlet DMA to all of the cyanoaromatics were found to proceed at a diffusion-controlled rate, judging from the values of k_q and ΔG_{et} (1). The most important factor which determines the efficiencies of the cosensitized cycloreversions is the efficiency (Φ_{sep}) for the formation of free-radical anions of the cyanoaromatics, Med$^{-\bullet}$. The values of Φ_{sep} were estimated from free-energy changes (ΔG_{-et}) for the back electron transfer calculated from the redox potentials of DMA and the cyanoaromatics, as shown in previous relevant literature.[18)] It can be seen that a cosensitization with the sensitizer and mediator is effective for the formation of free-radial ions in which the smaller is the exothermicity for the formation of ion pairs, the slower is the back electron transfer as a consequence of the inverted region effect. In fact, the combination of DMA and CN resulted in the most effective cosensitization due to the smallest exothermicity for the electron transfer (ΔG_{et}(1)) among the three cosensitized systems, (DMA–CN, DMA–DCB, and DMA–DCN). Taking the ΔG_{-et} into consideration, it can be expected that although a free-radical ion (CN$^{-\bullet}$) is generated quite effectively, this cannot be expected for DCB and DCN. Furthermore, the subsequent electron transfer from CN$^{-\bullet}$ to the dimers which produces dimer radical cations is most effective among the radical anions of the three cyanoaromatics because the free energy changes (ΔG_{et}(2)) for the



Scheme 1. A plausible reaction pathway for the cycloreversion of stilbazolium dimers; Med: mediator.

Table 4. One-Electron Transfer from Excited Singlet DMA to Mediators and Quantum Yields for Free Radical Ion Formation

Mediators	E^{red}/V vs. SCE	k_q[a)]/$M^{-1}\,s^{-1}$	$\Delta G_{\mathrm{et}}(1)$[b)]/eV	$\Delta G_{-\mathrm{et}}$[c)]/eV	Φ_{sep}[d)]	$\Delta G_{\mathrm{et}}(2)$[e)]/eV
CN	-1.98[f)]	7.28×10^{9}	-0.247	-2.96	0.8	-1.00, -0.66, -0.71
DCB	-1.60[f)]	1.11×10^{10}	-0.629	-2.58	0.1	-0.62, -0.28, -0.33
DCN	-1.28[f)]	1.34×10^{10}	-0.950	-2.26	0.1	-0.30, $+0.04$, -0.01

a) Calculated as τ_s of DMA = 16.9 ns.[22)] b) Calculated according to the Rehm–Weller equation, $\Delta G_{\mathrm{et}}(1) = (E^{\mathrm{ox}} - E^{\mathrm{red}}) - E_s$; the values of E^{ox} and E_s of DMA are 0.98 V[23)] (vs. SCE) and 3.2 eV,[24)] respectively. c) Calculated according to the equation, $\Delta G_{-\mathrm{et}} = E^{\mathrm{red}} - E^{\mathrm{ox}}$. d) Estimated from relevant literature[18)] by using the obtained values of $\Delta G_{-\mathrm{et}}$. e) Calculated according to the equation, $\Delta G_{\mathrm{et}}(2) = E^{\mathrm{red}}(\text{mediator}) - E^{\mathrm{red}}(\text{dimer})$, for *syn*-HH, *syn*-HT, and *anti*-HH, respectively. f) Cited from Ref. 25.

secondary electron transfer are highly exoergonic for $CN^{-\bullet}$. Although the values of $\Delta G_{\mathrm{et}}(2)$ for $DCB^{-\bullet}$ are also exoergonic enough to produce dimer radical cations effectively, the cycloreversion was not effective for the cosensitized system of DMA–DCB because of the low efficiency for the formation of free radical anions.

It should be mentioned here why the efficiencies for the reductive cycloreversion were so disparate, covering a range of about 300-fold variations among those cyclodimers. The one-electron reduction of stilbazolium dimers gives rise to the corresponding dihydropyridyl radical intermediate, which subsequently leads to bond breaking of the cyclobutane ring, as shown in Scheme 1. In the case of reductive cycloreversions, the transferred electron should be populated in the antibonding orbital of the cyclobutane C–C bond.[15)] The population depends on the extent of the overlap of the p orbital at the 4-position of the pyridinium group with the antibonding orbital of the cyclobutane C–C bond.

It has been reported[10c)] that the redox-photosensitized ring cleavage of the indene dimers can be attributed to the through-bond interaction between two π-electron systems. In the case of one-electron oxidative cleavage of the indene dimers, a partial positive charge develops on the cyclobutane C–C bond in the π-complex of a reactive cyclodimer with a radical cation of a sensitizer by means of a through-bond interaction, which facilitates the bond breaking of cyclobutane. The through-bond interaction can be proposed from the fact that the reactive cyclodimers have lower oxidation potentials than the unreactive cyclodimers.

Considering that the reduction potential of *syn*-HH is much lower than those of *syn*-HT and *anti*-HH (Table 3), two pyridinium rings interact with each other through the cyclobutane C–C bond. Thus, the transferred electron in the dihydropyridyl radical intermediate of *syn*-HH can be populated more easily in the antibonding orbital of the cyclobutane C–C bond, which results in the facile breaking of this bond. Although the *anti*-HH dimer also has two vicinal pyridinium rings, there is not so sufficient through-bond interaction as in *syn*-HH. This is because the pyridinium rings in the *anti*-HH cyclodimer can rotate rather freely due to the less hindered *trans* configuration of the two vicinal pyridinium rings, resulting in a smaller overlap between the two orbitals. It is thus reasonable to conclude that the reductive cleavage of *syn*-HH is much more effective than those of *syn*-HT and *anti*-HH.

Experimental

General. Photoirradiation was carried out by Hitachi 650-10S fluorescence spectrophotometer with a 150 W Xe lamp and a monochrometer. The HPLC was recorded on a Shimadzu LC-10A chromatograph using a Shiseido CAPCELL PAK C18 UG120 S-3 μm. The UV spectra were recorded on a Shimadzu UV-265 spectrophotometer. The fluorescence spectra were recorded on a Hitachi 650-10S fluorescence spectrophotometer with a 150 W Xe lamp and a monochrometer. Cyclic voltammograms were recorded on a BAS CV-50W.

Materials. 1-Methyl-4-(2-phenylethenyl)pyridinium ion and its cyclodimers, *syn*-HH, *syn*-HT, and *anti*-HH, were synthesized in accordance with previous literature.[19)] 9,10-Dimethoxyanthracene was synthesized according to previous literature.[20)] 1-Cyanonaphthalene was purchased from Tokyo Kasei Co., Ltd. and purified by distillation under vacuo. 1,4-Dicyanobenzene was purchased from Tokyo Kasei Co., Ltd. and was recrystallized from ethyl alcohol.

1,4-Dicyanonaphthalene was synthesized in accordance with previous literature.[21] Acetonitrile was dried by refluxing over calcium hydride and was purified by distillation.

Photocycloreversion of Stilbazolium Cyclodimers. Acetonitrile solutions of stilbazolium dimer iodide or methyl sulfate salts (2.0 or 1.0×10^{-3} mol dm^{-3}) were irradiated at 355±5 and 255±5 nm (Hitachi 650-10S) for CT and $\pi\pi^*$ excitation under Ar. For a photosensitized one-electron-reductive reaction, the acetonitrile solutions of 9,10-dimethoxyanthracene (DMA) (3.0×10^{-4} mol dm^{-3}) with *syn*-HH, *syn*-HT, or *anti*-HH (1.0×10^{-3} mol dm^{-3}, methyl sulfate salts) were irradiated at 400±5 nm under Ar. For the cosensitized cycloreversion, the cyanoaromatics, i.e., 1-cyanonaphthalene (CN), 1,4-dicyanonaphthalene (DCN), and 1,4-dicyanobenzene (DCB), were added as electron mediators (5.0×10^{-2} or 2.5×10^{-2} mol dm^{-3}). The irradiated solutions were analyzed by HPLC using 0.1 mol dm^{-3} of a sodium chloride aqueous solution and methyl alcohol at a ratio of 7 : 3 as the eluent.

Quantum Yield Determination. Potassium ferrioxalate actinometry was used to measure the light quanta at 255, 355, and 400±5 nm through a monochromator with a 150 W Xe lamp (Hitachi 650-10S). The quantum yield of cycloreversion refers to the number of dimer splittings per absorbed photon. In all of the measurements, the photoreaction yield was limited to less than 1%, so that the absorption of the photon by the products could be ignored, especially in the case of CT excitation. The quantum yields obtained with irradiation at 355±5 nm were corrected for differences in the absorption intensities of the CT bands between the three dimers. For cosensitized cycloreversion, no corrections were needed because each cyanoaromatic was added to quench the excited singlet DMA equally.

Fluorescence Quenching of the Excited Singlet 9,10-Dimethoxyanthracene. The fluorescence spectra of DMA in acetonitrile having a $\lambda_{\max} = 440$ nm were measured in various amounts of stilbazolium dimers (up to 2×10^{-3} mol dm^{-3}) under Ar. All of the dimers quenched the fluorescence of DMA, and the Stern–Volmer plots were determined to give the values of $k_q\tau$ as the slopes of these lines. The quenching rate constants (k_q) were then calculated from the fluorescence lifetime of DMA, $\tau_s = 16.9$ ns.[22]

Cyclic Voltammetry Measurement. The reduction potentials were measured by cyclic voltammetry (BAS CV-50W) in Ar-saturated acetonitrile solutions (1×10^{-3} mol dm^{-3}) vs. Ag/Ag$^+$ reference electrode, using ferrocene as the internal standard. Tetrabutylammonium perchlorate (0.1 mol dm^{-3}) was used as a supporting electrolyte and the scan speed was 0.1 V s^{-1}. The cyclic voltammograms of the stilbazolium cyclodimers were irreversible, and therefore the values given are the half-wave potentials, converted to V vs. SCE. The half-wave potentials were obtained by adding 0.0285 V to the cathodic peak potentials, assuming that a one-electron reduction takes place. The free energy changes (ΔG_{et}) for the one-electron transfer were calculated from the Rehm–Weller equation using the oxidation potential and excited singlet energy of 9,10-dimethoxyanthracene, $E^{ox} = 0.98$ V[23] (vs. SCE) and $E_s = 3.2$ eV,[24] respectively.

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