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Effects of Molecular Charge on Photoinduced Electron-Transfer Reactions

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Abstract: Fluorescence quenching due to full and partial electron transfer (ET) and back ET within geminate radical pairs are studied (i) in acetonitrile using *N*-methylacridinium ion (MeAc$^+$) as a monocationic fluorescer and aromatic compounds as neutral quenchers and (ii) in methanol using aromatic compounds as neutral fluorescers and methyl and benzyl viologens as dicationic quenchers. By comparison with the results previously obtained for the system of neutral fluorescer and quencher it is demonstrated that the free energy dependence of the rates of fluorescence quenching and back ET is not affected by molecular charge, but the rate of geminate radical separation into free radicals is. In the system of aromatic fluorescer and quencher, in general, fluorescence quenching is induced by a full ET at long distance (i.e., a long-distance ET) when the free energy change ΔG_{fet} in full ET is more negative than −0.5 eV and by a partial ET at contact distance (i.e., an exciplex formation) when ΔG_{fet} is more positive than −0.4 eV. A criterion to determine the ET fluorescence quenching mechanism is given.

1. Introduction

As electron transfer (ET) is one of the most important phenomena, a great interest for a number of chemists is how the ET rate can be controlled. The driving force of ET is the free energy change ΔG_{et} in ET.[1] If the distance between electron donor (D) and acceptor (A) is held constant, Marcus theory[1] predicts that the rate k_{et} of ET shows a bell-shaped dependence on ΔG_{et}. This prediction was confirmed for both intra- and intermolecular ET.[2,3] The theoretical equation of ET involves several kinds of parameters. To determine these parameters by experiments, k_{et} has to be measured in a wide range of ΔG_{et}. To this end recourse has been to photoinduced ET, particularly, to fluorescence quenching due to ET in a highly polar solvent.[3−6] In this case, two kinds of ET take place successively: a forward ET between an excited fluorescer, $^1D^*$ (or $^1A^*$), and a quencher, A (or D), for producing a geminate radical pair (D$^{•+}$/A$^{•−}$) and

a back ET within D$^{•+}$/A$^{•−}$ for reproducing the ground state pair D/A. In liquid solution, D and A are randomly distributed, and hence, they have to approach each other by diffusion up to an encounter distance where ET can take place. Therefore, ET fluorescence quenching followed by back ET may be described as in Schemes 1 and 2.

Scheme 1

$$^1D^* + A \xrightarrow{k_{dif}} {}^1D^*/A \xrightarrow[\Delta G_{fet}]{k_{fet}} D^{•+}/A^{•-} \quad \text{or}$$

$$D + {}^1A^* \xrightarrow{k_{dif}} D/{}^1A^* \xrightarrow[\Delta G_{fet}]{k_{fet}} D^{•+}/A^{•-}$$

Scheme 2

$$D^{•+}/A^{•-} \xrightarrow[\Delta G_{bet}]{k_{bet}} D/A \rightarrow D + A$$
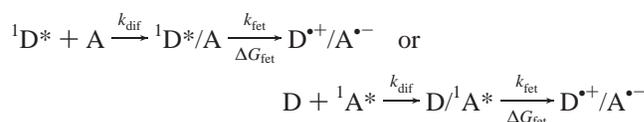
Here, slashes indicate the encounter states of pair species. k_{dif}, k_{fet}, and k_{bet} are the rate constants of diffusion, forward ET, and back ET, respectively. When both D and A are neutral molecules as described in Schemes 1 and 2, the forward and

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back ETs are named as the charge separation (CS) type and the charge recombination (CR) type, respectively.

The free energy changes ΔG_{fet} and ΔG_{bet} in acetonitrile with dielectric constant ϵ are defined for the CS type of forward ET and the CR type of back ET, respectively:[4]

$$\Delta G_{fet} = E_{1/2}{}^{ox} - E_{1/2}{}^{red} - e^2/\epsilon r - E(S_1) \qquad (1)$$

$$\Delta G_{bet} = E_{1/2}{}^{red} - E_{1/2}{}^{ox} + e^2/\epsilon r \qquad (2)$$

Here, $E_{1/2}{}^{ox}$, $E_{1/2}{}^{red}$, $E(S_1)$, and $e^2/\epsilon r$ are the oxidation potential of D, the reduction potential of A, the energy of the fluorescent state, and the Coulomb attraction energy for $D^{\bullet+}/A^{\bullet-}$ at a space r between $D^{\bullet+}$ and $A^{\bullet-}$, respectively.

Chemists cherish a special interest in the reaction efficiency as well as the reaction rate. Free radicals are produced by the dissociation of $D^{\bullet+}/A^{\bullet-}$:

Scheme 3

$$D^{\bullet+}/A^{\bullet-} \xrightarrow{k_{esc}} D^{\bullet+} + A^{\bullet-}$$
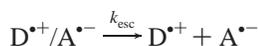
Here, k_{esc} is the rate constant of geminate radical separation into free radicals. According to Scheme 1, the efficiency of geminate radical pair production in the fluorescence quenching due to full ET is unity. Then, the free radical yield Φ_R is given by eq 3. The rate of diffusion depends on the solvent viscosity.

$$\Phi_R = k_{esc}/(k_{esc} + k_{bet}) \qquad (3)$$

For chemists, therefore, the control of photoinduced ET means the control of k_{esc} in addition to k_{fet} and k_{bet}. In this paper it is revealed for various systems of aromatic fluorescer and quencher in polar solvents how these rate parameters are controlled.

In previous work,[6] the detailed mechanism of ET fluorescence quenching has been investigated in acetonitrile and dichloromethane using anthracenecarbonitriles (AC) as $^1A^*$ and several kinds of aromatic compounds as D. It was established that (i) ET fluorescence quenching is induced not only by a full ET at long distance (i.e., a long-distance ET) as shown in Scheme 1, but also by a partial ET at contact distance (i.e., an exciplex formation), and (ii) the switchover of these quenching mechanisms occurs at about $\Delta G_{fet} = -0.45$ eV: A long-distance ET takes place when $\Delta G_{fet} < -0.5$ eV, but an exciplex formation when $\Delta G_{fet} > -0.4$ eV. Moreover, it was found that the primary quenching product is the ground-state geminate radical pairs $D^{\bullet+}/A^{\bullet-}$ when $\Delta G_{fet} = -0.5$ to ~-2.0 eV, but most likely the excited-state geminate radical pairs $D^{\bullet+*}/A^{\bullet-}$ or $D^{\bullet+}/A^{\bullet-*}$ when $\Delta G_{fet} < -2.0$ eV.[6f,g] In the strict sense, therefore, Scheme 1 is valid only for the electron donor and acceptor (EDA) systems with $\Delta G_{fet} = -0.5$ to ~-2.0 eV. In fact, a bell-shaped dependence of k_{bet} on ΔG_{bet} has been confirmed only for such EDA systems.

In the present work, we investigate the effects of molecular charge on the ΔG_{fet} dependence of (i) the quenching mechanism, (ii) the quenching rate constant k_q, (iii) the effective quenching distance r_q, and (iv) Φ_R, and (v) on the ΔG_{bet} dependence of k_{bet}. For this purpose, we compare the ET fluorescence quenching and back ET shown in Schemes 1 and 2 with the following two types of ET fluorescence quenching and back ET:

Scheme 4

$$D + {}^1A^{+*} \rightarrow D/{}^1A^{+*} \rightarrow D^{\bullet+}/A^{\bullet}$$

Scheme 5

$$D^{\bullet+}/A^{\bullet} \rightarrow D/A^+ \rightarrow D + A^+$$

and

Scheme 6

$$^1D^* + A^{2+} \rightarrow {}^1D^*/A^{2+} \rightarrow D^{\bullet+}/A^{\bullet+}$$

Scheme 7

$$D^{\bullet+}/A^{\bullet+} \rightarrow D/A^{2+} \rightarrow D + A^{2+}$$
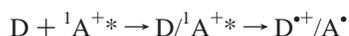
Here, both fluorescer and quencher are aromatic compounds. In that case, the effects of molecular structure and size on ET are minimized and the effect of molecular charge on ET is expected to become distinct.[5]

ET fluorescence quenching and back ET such as in Schemes 4 and 5 are named as the charge shift (CSh) type of ET. This type of ET has been studied by Gould et al.[5a,c] for the first time in order to examine the validity of the Kakitani−Mataga theory.[7] They studied the ΔG_{fet} dependence of Φ_R in the region $-0.30 > \Delta G_{fet} > -0.85$ eV using N-methylacridinium ion (MeAc$^+$) as a monocationic fluorescer, alkylbenzenes as neutral quenchers, and acetonitrile as solvent. On the assumption that k_{esc} does not depend on ΔG_{fet}, they revealed the ΔG_{bet} dependence of k_{bet} in the inverted region, $-2.59 < \Delta G_{bet} < -2.04$ eV. Comparing it with the ΔG_{bet} dependence of k_{bet} for the CR type of back ET, they found a small difference between the CSh and CR types of back ET, but the difference is not as large as predicted by the Kakitani−Mataga theory. It is noted, however, that the above assumption is not valid, because k_{esc} depends on r_q,[8] and r_q depends on ΔG_{fet}.[6h,f,9b]

In the present work, the CSh type of ET fluorescence quenching and back ET are studied in a wide range of ΔG_{fet} using MeAc$^+$ as a monocationic fluorescer and aromatic compounds as neutral quenchers. r_q is determined for every quencher to evaluate k_{esc} correctly. Then, k_{bet} can be found accurately. In this way, the ΔG_{bet} dependence of k_{bet} is exactly studied in a wide range of ΔG_{bet} involving not only the inverted region but also the top and normal regions. Another CSh type of ET fluorescence quenching and back ET such as in Schemes 6 and 7 are studied in methanol using aromatic compounds as neutral fluorescers and methyl and benzyl viologens as dicationic quenchers.

All the results obtained for the three types of ET fluorescence quenching and back ET are compared with one another to make clear the molecular charge effects on these ET reactions. It is shown that the molecular charge effect is significant for k_{esc}, but not for the ΔG_{bet} dependence of k_{bet} and the ΔG_{fet} dependence of the quenching mechanism, k_q, and r_q. As a result, we can easily predict the values of these rate parameters and Φ_R for various systems of aromatic fluorescer and quencher in highly polar solvents such as acetonitrile and methanol, if we can evaluate ΔG_{fet}.

Photochemists cherish another special interest in the mechanism of ET fluorescence quenching, because they take advantage of two types of photosensitized reactions, i.e., electron- and energy-transfer reactions. If fluorescence quenching is induced by a full ET, yielding free radicals, the photosensitized reaction is initiated by ET between the sensitizer and reactant. If fluorescence quenching is induced by a partial

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ET, leading to exciplex formation, in contrast, the photosensitized reaction may be commenced by triplet−triplet energy transfer from the sensitizer to the reactant, because the intersystem crossing of the sensitizer is usually enhanced by exciplex formation. For the above reason, a criterion to determine the ET fluorescence quenching mechanism is summarized.

2. Experimental Section

The methods for synthesis and/or purification of *N*-methylacridinium tetrafluoroborate (AcMe$^+$BF$_4^−$), 2,6,9,10-tetracyanoanthracene (TeCA), aniline (Ani), 4-cyanoaniline (CN-Ani), anisole, *N,N*-dimethylaniline (DMAni), anisidine (AS), 1,4-phenylenediamine (PDA), and *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD) have been reported elsewhere.[6h,10] Toluene (Tol; Aldrich), 4-bromotoluene (Br-Tol; Nakarai), 4-bromoanisole (4-Br-Anisole; Aldrich), 1,2-dimethoxybenzene (1,2-DMB; Aldrich), 1,4-dimethoxybenzene (1,4-DMB; Tokyo Kasei), 1,2,4-trimethoxybenzene (1,2,4-TMB; Aldrich), *o*-xylene (*o*-Xy; Fluka), 1-bromo-2,3-dimethylbenzene (Br-*o*-Xy; Aldrich), *p*-xylene (*p*-Xy; Aldrich), 1,3,5-trimethylbenzene (Mes; Fluka), hexamethylbenzene (HMB; Aldrich), and 4-bromo-*N,N*-dimethylaniline (Br-DMAni; Aldrich) were used as received. Biphenyl (Bp; Wako), 4-bromobiphenyl (Br-Bp; Aldrich), and diphenylamine (DPAmi) were recrystallized from ethanol. Methyl viologen dichloride (MV^{2+}; Aldrich) and benzyl viologen dichloride (BV^{2+}; Aldrich) were recrystallized from methanol. 9-Cyanoanthracene (CA), 9-phenylanthracene (PA), 9,10-dicyanoanthracene (DCA), 9,10-dimethylanthracene (DMA), 9,10-diphenylanthracene (DPA), perylene (Per), and 3,9-dicyanophenanthrene (DCP) were the same as used in previous work.[6c,g,10,11] 9,10-Dimethoxyanthracene (DOMA) was synthesized according to the method described in the literature.[12] 1,2,9,10-Tetracyanoanthracene (TCA) was synthesized by oxidative cyanation of DCA with sodium cyanide and anthraquinone-1-sulfonic acid sodium salt in dry dimethylformamide. Details will be given elsewhere. Acetonitrile (SP grade, Kanto) and methanol (GR grade, Wako) were used as received.

Absorption spectra were recorded on a Hitachi U-3500 spectrophotometer. Fluorescence spectra and fluorescence excitation spectra were measured with a Hitachi F-4500 spectrophotometer. The transient absorption spectra were measured by a conventional flash photolysis. The free radical yield Φ_R and the triplet yield Φ_T in fluorescence quenching were determined by an emission−absorption flash photolysis method.[6,13] This method measures the fluorescence intensity during flash excitation and the initial absorbance of transient absorption simultaneously. The former is used to evaluate the amount of light absorbed by a sample solution, and the latter is used to determine the concentration of transient species produced by a flash excitation. It is noted that this method is available for determining the free radical yield not only in excited singlet quenching but also in triplet quenching. Error limits of this method for determining Φ_R and Φ_T are within 10%.

The oxidation potentials $E_{1/2}^{ox}$ versus SCE were measured in acetonitrile with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte: +0.90 V for Ani, +1.23 V for CN-Ani, +0.71 V for DMAni, +0.58 V for AS, +0.26 V for PDA, +0.10 V for TMPD, +2.12 V for Br-Tol, +1.70 V for anisole, +1.63 V for 4-Br-Anisole, +1.25 V for 1,4-DMB, +2.15 V for Br-*o*-Xy, +1.98 V for Mes, +1.61 V for HMB, +0.86 V for Br-DMAni, +1.84 V for Bp, +1.95 V for Br-Bp, +0.98 V for Per, +1.57 V for CA, +1.89 V for DCA, +2.20 V for TeCA, +2.11 V for TCA, and +2.17 V for DCP. The $E_{1/2}^{ox}$ values for Tol, *o*-Xy, *p*-Xy, 1,2-DMB, 1,2,4-TMB, DMA, DOMA, and DPA have been reported to be +2.28, +1.88, +1.77, +1.45, +1.12, +0.87, +0.98, and +1.22 V, respectively.[14,15] The reduction potentials $E_{1/2}^{red}$ versus SCE for MV^{2+} and BV^{2+} were determined to be −0.36

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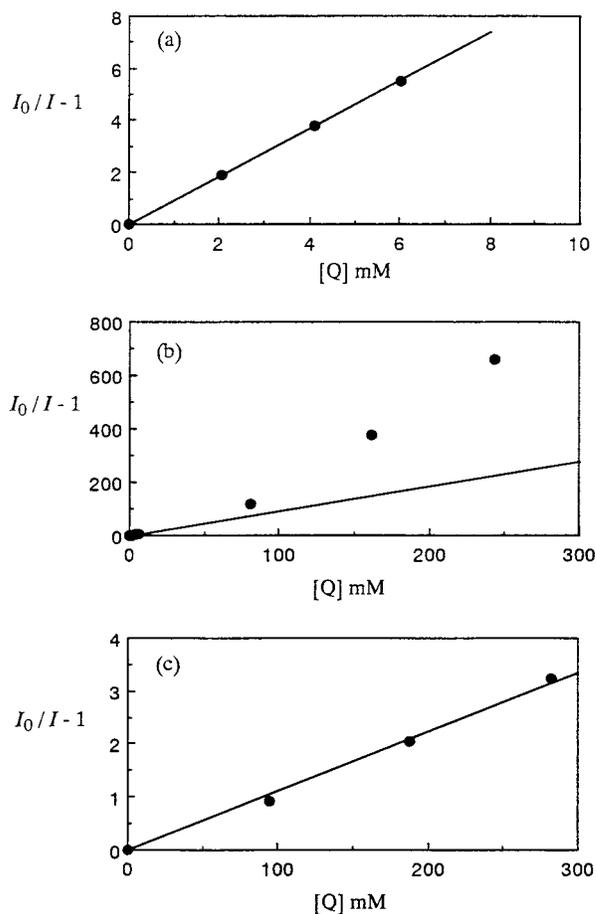
Figure 1. Stern−Volmer plots for fluorescence intensity in acetonitrile: (a, b) the *N*-methylacridinium ion−*N,N*-dimethylaniline pair, (c) the *N*-methylacridinium ion−toluene pair.

and −0.46 V in acetonitrile, respectively. $E_{1/2}^{red}$, $E(S_1)$, and the fluorescence lifetime τ_f for MeAc$^+$ in acetonitrile were determined to be −0.48 V, +2.75 eV, and 33 ns, respectively.[10] The values of $E(S_1)$ for DMA, DOMA, Per, DPA, CA, DCP, DCA, TeCA, and TCA were determined to be 3.14, 3.05, 2.83, 3.16, 3.04, 3.56, 2.89, 2.89, and 2.67 eV in methanol, respectively. The values of τ_f for DMA, DOMA, Per, DPA, CA, DCP, and DCA in deaerated methanol were determined to be 19.$_0$, 12.$_2$, 5.6, 9.2, 16.$_2$, 19.$_3$, and 13.$_6$, respectively. The values of τ_f for TeCA and TCA in aerated methanol were determined to be 14.$_7$ and 15.$_9$ ns, respectively.

In the case of fluorescence quenching of MeAc$^+$ by aromatic compounds in acetonitrile, the aerated solution was used to determine k_q, r_q, and Φ_R, but the sample solution for determining Φ_T was deaerated by repeating freeze−pump−thaw cycles. In the case of fluorescence quenching of aromatic compounds by MV^{2+} and BV^{2+} in methanol, the sample solutions except for TeCA and TCA were used after being bubbled through nitrogen gas. k_q values for TeCA and TCA were measured in the aerated solutions. All measurements were made at 298 K.

3. Results and Discussion

3.1. Fluorescence Quenching of Monocationic Dye by Aromatic Compounds in Acetonitrile: A^{+*} + D → A$^{\bullet}$ + D$^{\bullet+}$. The k_q values were determined from the Stern−Volmer (SV) plots for the fluorescence intensity at low quencher concentration, where the plots were linear as illustrated in Figure 1a,c. The r_q values were evaluated by use of the modified

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Table 1. Free Energy Changes of ET Fluorescence Quenching of MeAc$^+$ in Acetonitrile (ΔG_{fet}) and of Back ET within D$^{\bullet+}$/A$^{\bullet}$ (ΔG_{bet}), Fluorescence Quenching Rate Constants (k_{q}), Effective Quenching Distances (r_{q}), Free Radical Yields (Φ_{R}), and Rate Constants of D$^{\bullet+}$/A$^{\bullet}$ Separation into Free Radicals (k_{esc}) and Back ET within D$^{\bullet+}$/A$^{\bullet}$ (k_{bet})

quencher	ΔG_{fet}, eV	k_{q}, 10^{10} M^{-1} s^{-1}	r_{q}, Å	Φ_{R}	k_{esc}, 10^{10} s^{-1}	k_{bet}, 10^{10} s^{-1}	ΔG_{bet}, eV
Tol	0.01	0.036					−2.76
Mes	−0.29	1.3	3.1	0.19			−2.46
o-Xy	−0.39	1.4	3.4	0.27			−2.36
Bp	−0.42	1.5	4.0	0.10			−2.33
p-Xy	−0.50	1.4	3.8	0.094			−2.25
anisole	−0.57	1.6	5.0	0.035	1.4	38.6	−2.18
HMB	−0.74	1.8	(6.6)	0.021	0.80	37.3	−2.01
1,2-DMB	−0.82	2.0	6.6	0.0062	0.80	130	−1.93
1,4-DMB	−1.02	2.3	6.7	0.0096	0.78	81	−1.73
CN-Ani	−1.04	2.0	7.8	0.010	0.58	55	−1.71
1,2,4-TMB	−1.15	2.3	7.2	0.013	0.68	52	−1.60
aniline	−1.34	2.9	7.5	0.013	0.62	46	−1.41
DPAmi	−1.44	2.8	8.2	0.058	0.54	8.5	−1.31
DMAni	−1.56	2.8	11	0.038	0.30	7.6	−1.19
AS	−1.69	2.7	12	0.065	0.24	3.9	−1.06
PDA	−1.93	2.8	(12)	0.45	0.24	0.29	−0.82
TMPD	−2.17	2.9	(12)	0.24	0.24	0.76	−0.58
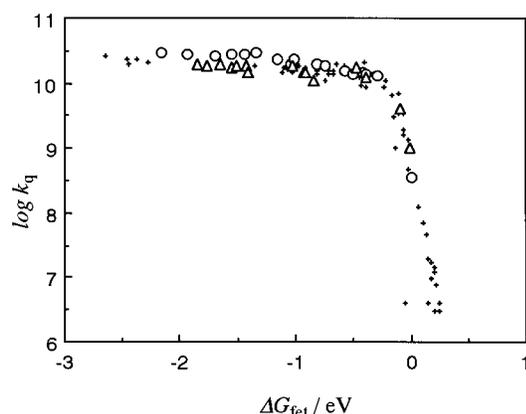
Figure 2. k_{q} versus ΔG_{fet} for the *N*-methylacridinium ion−aromatic molecule pairs (circles), the aromatic molecule−viologen pairs (triangles), and the Rehm−Weller plot (crosses).

Stern−Volmer equation[16] at such high quencher concentrations as 0.1−0.3 M, where the SV plots deviate upward from the straight line as illustrated in Figure 1b.

The values for k_{q}, r_{q}, and ΔG_{fet} are listed in Table 1. For the CSh type of ET fluorescence quenching and back ET in acetonitrile such as in Schemes 4 and 5, ΔG_{fet} and ΔG_{bet} are given by[4]

$$\Delta G_{\text{fet}} = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} - E(\text{S}_1) \qquad (4)$$

$$\Delta G_{\text{bet}} = E_{1/2}^{\text{red}} - E_{1/2}^{\text{ox}} \qquad (5)$$

The plot of k_{q} versus ΔG_{fet} is shown in Figure 2 (circles). This plot agrees with the Rehm−Weller plot (crosses)[4] obtained for the system of neutral fluorescer and quencher. It can be concluded that the ΔG_{fet} dependence of k_{q} is not affected by a positive charge of fluorescer.

In Figure 3 is shown the plot of r_{q} versus ΔG_{fet} (circles). In the region $-0.3 > \Delta G_{\text{fet}} > -2.0$ eV, r_{q} increases linearly with a decrease in ΔG_{fet}. This plot is compared with the plot obtained for the CS type of ET fluorescence quenching (squares). It is
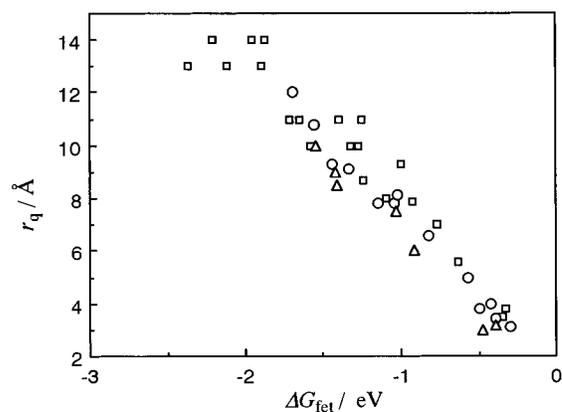
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Figure 3. r_{q} versus ΔG_{fet} for the *N*-methylacridinium ion−aromatic molecule pairs (circles), the anthracenecarbonitrile−aromatic molecule pairs (squares), and the aromatic molecule−viologen pairs (triangles).

obvious that the ΔG_{fet} dependence of r_{q} is not affected by a positive charge of fluorescer. Unfortunately, the r_{q} values for PDA, TMPD, and HMB cannot be determined, because MeAc$^+$ is bleached in the dark by addition of these amines and HMB is slightly soluble in acetonitrile. From the plots shown in Figure 3, the r_{q} values for PDA, TMPD, and HMB were estimated to be 12, 12, and 6.6 Å, respectively. It is noted that the ΔG_{fet} dependence of r_{q} for the CS type of fluorescence quenching shown in Figure 3 was confirmed by Murata et al.[9b]

In the region $\Delta G_{\text{fet}} \geq -0.5$ eV, r_{q} is in the range 3−4 Å, which is close to the interplanar separation in the excimer and exciplex,[17] and moreover, the energy gap between the locally excited singlet state and the contact radical pair state is small (≤ 0.5 eV). Therefore, the fluorescence quenching in this region of ΔG_{fet} is considered to be induced by exciplex formation in a manner similar to that of the system of neutral fluorescer and quencher, although exciplex fluorescence has not been observed at all for any system listed in Table 1. In the region $\Delta G_{\text{fet}} < -0.5$ eV, r_{q} is greater than 5 Å, indicating that fluorescence quenching is induced by long-distance ET.

Flashing of the solution containing MeAc$^+$ alone gives no transient absorption, because the fluorescence yield (Φ_{F}) of MeAc$^+$ is close to unity in acetonitrile.[10a] Flashing of the solution containing MeAc$^+$ and a quencher other than Bp gave the transient absorption due to fluorescer neutral radical (MeAc$^{\bullet}$) and quencher radical cation (D$^{\bullet+}$). When Bp was used as a quencher, the triplet−triplet (T−T) absorption of MeAc$^+$ was observed in addition to the transient absorption due to MeAc$^{\bullet}$ and D$^{\bullet+}$. Figure 4 exemplifies the transient absorption spectrum for the deaerated solution containing 20 μM MeAc$^+$ and 2.7 mM DPAmi. The broad band at about 20 000 cm^{-1} and the sharp band at about 15 000 cm^{-1} are attributed to MeAc$^{\bullet}$ and the radical cation (DPAmi$^{\bullet+}$) of DPAmi, respectively. The molar extinction coefficient for DPAmi$^{\bullet+}$ has been determined to be 19 000 M^{-1} cm^{-1} at 670 nm.[6c] The molar extinction coefficient for MeAc$^{\bullet}$ was determined to be 1520 M^{-1} cm^{-1} at 520 nm assuming that equal amounts of MeAc$^{\bullet}$ and DPAmi$^{\bullet+}$ were produced by flash photolysis. The molar extinction coefficient for ^{3}MeAc$^+$ was determined to be 3570 M^{-1} cm^{-1} at 860 nm by the triplet energy transfer from cyanophenanthrene to MeAc$^+$. The molar extinction coefficient for the cyanophenanthrene triplet has been determined to be 6800 M^{-1} cm^{-1} at 488 nm.[11] The Φ_{R} values were determined for various quenchers as listed

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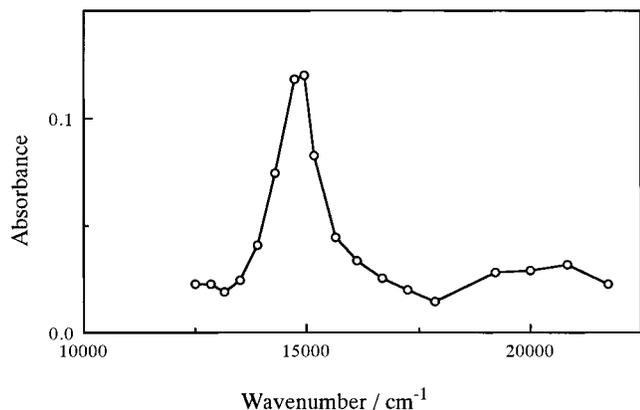
Figure 4. Transient absorption spectrum for the *N*-methylacridinium ion−diphenylamine pair (100 μs after flashing).

Table 2. Free Energy Changes of ET Fluorescence Quenching of MeAc$^+$ in Acetonitrile (ΔG_{fet}), Fluorescence Quenching Rate Constants (k_q), Effective Quenching Distances (r_q), Free Radical Yields (Φ_R), and Triplet Yields (Φ_T)

quencher	ΔG_{fet}, eV	k_q, $10^{10}\,M^{-1}\,s^{-1}$	r_q, Å	Φ_R	Φ_T
4-Br-Tol	−0.15	0.83	3.5	0.22	0.12
Br-o-Xy	−0.12	1.3	3.2	0.19	0.55
Br−Bp	−0.32	1.4	3.4	0.20	0.11
4-Br-Anisole	−0.64	1.6	5.1	0.035	
4-Br-DMAni	−1.41	2.8	8.0	0.070	

in Table 1. The triplet yields Φ_T in fluorescence quenching were null except that for Bp. The Φ_T for Bp was determined to be 0.036.

In the region $\Delta G_{fet} \geq -0.5$ eV (or $\Delta G_{bet} \leq -2.25$ eV), the triplet energy $E(T_1)$ (= 1.79−2.01 eV[10]) of MeAc$^+$ is lower than the energy $|\Delta G_{bet}|$ of the geminate radical pair D$^{\bullet+}$/A$^\bullet$. Therefore, the triplet state (^{3}MeAc$^+$) of MeAc$^+$ is not expected to be quenched by ET from the quencher to ^{3}MeAc$^+$. Indeed, the T−T absorption was observed, when Bp with $\Delta G_{fet} = -0.42$ eV was used as a quencher.

When MeAc$^+$ is used as fluorescer, ^{3}MeAc$^+$ may be produced in fluorescence quenching through either exciplex formation followed by intersystem crossing or long-distance ET followed by a spin-forbidden back ET within the geminate radical pair. It is noted that the latter can take place only when $E(T_1) < |\Delta G_{bet}|$. The formation of ^{3}MeAc$^+$ is expected to be significantly enhanced by exciplex formation, but not as much by long-distance ET followed by a spin-forbidden back ET. Certainly, such expectation has been confirmed using CA and DCA with $\Phi_F \approx 1$ as fluorescers.[6c,h]

If fluorescence quenching is induced by exciplex formation, it is possible for Φ_T to become larger than 0.1 by a heavy atom substitution on the quencher,[6c] because the intersystem crossing within the exciplex is strongly enhanced by the presence of a heavy atom. If fluorescence quenching is induced by long-distance ET, in contrast, it is difficult for Φ_T to exceed 0.1,[6c] even though the spin-forbidden back ET is enhanced by the presence of a heavy atom as substantiated theoretically by Salem and Roeland.[18] It has been confirmed in previous work[6i] on triplet quenching ET that the heavy atom effect on the spin-forbidden back ET of the free radical pairs as well as the geminate radical pairs is well interpreted in terms of their theory. When $E(T_1) < |\Delta G_{bet}|$, therefore, the study of the heavy atom effect on Φ_T is useful in determining the fluorescence quenching mechanism.

On the basis of the above strategy, the ET fluorescence quenching mechanism in the region -1.41 eV $\leq \Delta G_{fet} \leq -0.12$ eV was studied using bromine-substituted quenchers such as 4-Br-Tol, Br−Bp, Br-o-Xy, 4-Br-Anisole, and 4-Br-DMAni. The values of Φ_R and Φ_T for these bromine-substituted quenchers were determined as listed in Table 2.

When $\Delta G_{fet} > -0.5$ eV, Φ_T is significantly increased by a bromine atom substitution on the quencher. This means that fluorescence quenching is induced by exciplex formation in the region $\Delta G_{fet} > -0.5$ eV. In the region $\Delta G_{fet} < -0.5$ eV, in

contrast, the T−T absorption was not observed, even when a bromine-substituted quencher was used. When 4-Br-Anisole is used as a quencher, ^{3}MeAc$^+$ is not considered to be quenched by rapid ET from 4-Br-Anisole to ^{3}MeAc$^+$, because $|\Delta G_{bet}|$ (= 2.11 eV) > $E(T_1)$. No observation of the T−T absorption in the region $\Delta G_{fet} < -0.5$ eV is evidence for fluorescence quenching due to long-distance ET.[6b−e,g,h] Therefore, it will be valid even for the CSh type of fluorescence quenching that the switchover ΔG_{fet} of the fluorescence quenching mechanism takes place at $\Delta G_{fet} = -0.4$ to -0.5 eV.

As shown in Table 1, Φ_R decreases with a decrease in ΔG_{fet}, passes through a minimum at $\Delta G_{fet} = -0.82$ eV, increases, and again decreases. Such ΔG_{fet} dependence of Φ_R in the region $\Delta G_{fet} < -0.5$ eV has already been observed for the system of neutral fluorescer and quencher, where $E(S_1)$ has been held nearly constant, 2.89−3.04 eV.[6d,f,h] When fluorescence quenching is induced by long-distance ET for producing D$^{\bullet+}$/A$^\bullet$, Φ_R may be given by eq 3.

As there is no Coulomb interaction between D$^{\bullet+}$ and A$^\bullet$, k_{esc} can be calculated by eq 6.[8] Assuming that the sum (D) of the

$$k_{esc} = D/r_q^2 \tag{6}$$

diffusion coefficients of electron donor and acceptor is 3.5×10^{-5} cm^2 s^{-1} in acetonitrile,[16a] the k_{esc} values are calculated from r_q by use of eq 6. k_{esc} tends to decrease with an increase in r_q or with a decrease in ΔG_{fet}. Using eq 3, we can calculate the k_{bet} values from the Φ_R values and the k_{esc} values (Table 1). In Figure 5, the k_{bet} values are plotted with respect to ΔG_{bet} (circles).

If the back ET within D$^{\bullet+}$/A$^\bullet$ takes place at a space r_{bet} between D$^{\bullet+}$ and A$^\bullet$, the rate of back ET may be given by the following semiclassical equation for long-distance ET:[2,19,20]

$$k_{et} = (4\pi^3/h^2\lambda_S k_B T)^{1/2}|V|^2\sum(e^{-S}S^w/w!)\exp[-(\Delta G_{et} + \lambda_S + wh\nu)^2/4\lambda_S k_B T] \tag{7}$$

Here

$$S = \lambda_v/h\nu$$

$$\lambda_S = (e^2/2)(1/r_A + 1/r_D - 2/r_{bet})(1/n^2 - 1/\epsilon) \tag{8}$$

$$|V|^2 = |V_0|^2\exp[-\beta\{r_{bet} - (r_A + r_D)\}] \tag{9}$$

k_B is the Boltzmann constant.

The back ET within D$^{\bullet+}$/A$^\bullet$ begins just after fluorescence quenching. Therefore, we first assume $r_{bet} = r_q$ to calculate k_{bet}. Then, the solvent reorganization energies λ_S were calculated by use of eq 8. λ_S ranges from 1.02 eV for $r_q = 5.0$ Å to 1.90 eV for $r_q = 12$ Å. The values for $|V|^2$ were calculated by use of eq 9.[9a,21] $|V|$ ranges from 247 cm^{-1} for $r_q = 5.0$ Å to 7.5

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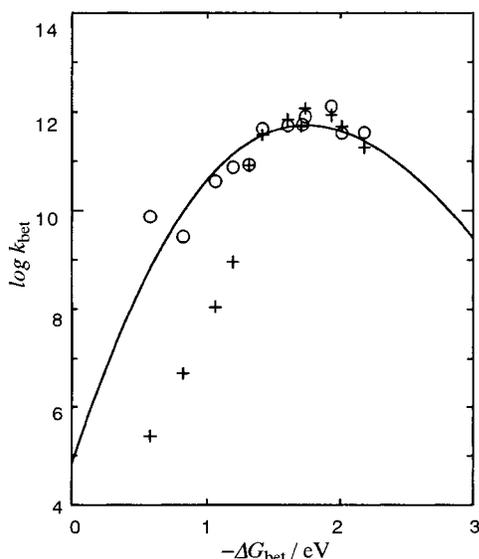
Figure 5. k_{bet} versus ΔG_{bet} for the N-methylacridinium ion−aromatic molecule pairs: circles, calculated by eqs 3 and 6; crosses, calculated by eqs 7−9 with fitting parameters $|V_0| = 120$ cm^{-1}, $\beta = 1$ Å^{-1}, $\lambda_v = 0.25$ eV, $r_A = r_D = 3$ Å, and $r_{bet} = r_q$; solid curve, calculated by eqs 7−9 with fitting parameters $|V_0| = 120$ cm^{-1}, $\beta = 1$ Å^{-1}, $r_D = r_A = 3$ Å, $\lambda_v = 0.25$ eV, $h\nu = 1500$ cm^{-1}, $r_{bet} = 7.5$ Å, and $\lambda_S = 1.52$ eV.

cm^{-1} for $r_q = 12$ Å. To fit the theory and experiment as best we can, the other parameters were assumed as follows: the electron exchange matrix element at the contact distance of electron donor and acceptor $|V_0| = 120$ cm^{-1};[9a] the attenuation parameter $\beta = 1$ Å^{-1};[9a] the reactant vibrational reorganization energy $\lambda_v = 0.25$ eV;[5,6] the average energy of the active vibrational mode $h\nu = 1500$ cm^{-1};[5,6] the radii of the electron donor and acceptor $r_D = r_A = 3$ Å.[9a] As shown in Figure 5, the theoretical plot (crosses) calculated by setting $r_{bet} = r_q$ fits in with the experimental plot only in a narrow region, $-2.2 < \Delta G_{bet} < -1.3$ eV (or $-1.4 < \Delta G_{fet} < -0.5$ eV). In previous work,[6a,d−f,h] it was found that the plot of k_{bet} versus ΔG_{bet} for the system of neutral fluorescer and quencher is well reproduced by eq 7 in a wide range of ΔG_{bet}, i.e., $-2.7 < \Delta G_{bet} < -1.0$ eV, when $|V|$ and λ_S are fixed at 39 cm^{-1} and 1.45 eV, respectively.[6h] Since both of the geminate radical pair species may diffuse at random within a solvent cage before proceeding to the back ET, the back ET may take place not only at r_q but also at various distances. As a result, the back ET is likely to take place approximately at a fixed distance. It is noted, moreover, that both λ_S and V have been determined independent of r_{bet} so far.[5,6] For more rigorous discussion, λ_S and $|V|$ have to be related to r_{bet} by use of eqs 8 and 9.

The maximum value of k_{bet} for the CSh type of back ET is 1.3×10^{12} s^{-1} as shown in Table 1. This is close to that for the CR type of back ET, i.e., 0.63×10^{12} s^{-1}.[6h] Therefore, it may be assumed for the systems of aromatic fluorescer and quencher that $|V_0|$ is held a constant regardless of the type of back ET. Thus, the experimental plots are fitted with theory using an apparent distance r_{bet} for back ET as a fitting parameter and assuming $|V_0| = 120$ cm^{-1}, $\beta = 1$ Å^{-1}, $r_D = r_A = 3$ Å, $\lambda_v = 0.25$ eV, and $h\nu = 1500$ cm^{-1}. The best fitting curve depicted in Figure 5 was obtained for $r_{bet} = 7.5$ Å and $\lambda_S = 1.52$ eV. This theoretical curve fits in with all the experimental plots except for TMPD with $\Delta G_{bet} = -0.58$ eV (or $\Delta G_{fet} = -2.17$ eV). Therefore, it may be concluded that (i) the quenching mechanism in the region $-1.93 \leq \Delta G_{fet} \leq -0.57$ eV (or -0.82

$\geq \Delta G_{bet} \geq -2.18$ eV) is a long-distance ET for producing D$^{\bullet +}$/A$^{\bullet}$ and (ii) the back ET within D$^{\bullet +}$/A$^{\bullet}$ occurs at $r_{bet} = 7.5$ Å on average. The latter conclusion is consistent with the theoretical study on the ΔG_{et} dependence of the most contributory ET distance:[9a] It is shorter than 6 Å when $\Delta G_{et} > -1.0$ eV, 7.5 Å when $\Delta G_{et} \approx -2.0$ eV, and longer than 11 Å when $\Delta G_{et} < -3.0$ eV. Here, we refer to two extreme cases involved in Table 1: (i) When $\Delta G_{bet} = -2.18$ eV (or $\Delta G_{fet} = -0.57$ eV), the most contributory distance for back ET is close to 7.5 Å. Therefore, the back ET with $\Delta G_{bet} = -2.18$ eV occurs mostly at r_{bet} longer than $r_q = 5.0$ Å. (ii) When $\Delta G_{bet} = -0.82$ eV (or $\Delta G_{fet} = -1.93$ eV), in contrast, the most contributory distance for back ET is shorter than 6 Å. Therefore, the back ET with $\Delta G_{bet} = -0.82$ eV occurs mostly at r_{bet} shorter than $r_q = 12$ Å. In both cases, the most contributory distance for back ET is intermediate between 5 and 12 Å. This is the reason r_{bet} can be assumed to be $\sim$7.5 Å in the region $-2.18 < \Delta G_{bet} < -0.82$ eV. Other evidence for the back ET taking place at an approximately fixed distance is the nearly single-exponential decay of the geminate radical pairs D$^{\bullet +}$/A$^{\bullet -}$.[3] If the back ET occurs at various distances, the decay of D$^{\bullet +}$/A$^{\bullet -}$ has to be multiexponential.

In the region $\Delta G_{fet} < -2.0$ eV, the production of D$^{\bullet +}$*/A$^{\bullet -}$ or D$^{\bullet +}$/A$^{\bullet -}$* has been pointed out.[6f,g] Therefore, the disagreement between the theoretical curve and the experimental plot for TMPD with $\Delta G_{fet} = -2.17$ eV may be interpreted by taking into account the production of D$^{\bullet +}$*/A$^{\bullet}$ or D$^{\bullet +}$/A$^{\bullet}$*. In fact, the aromatic radical ions have their absorption in the near-infrared region,[22] indicating that the excitation energies of the radical ions are as small as <1.60 eV. Then, the free energy change (ΔG_{fet}*) of full ET for producing D$^{\bullet +}$*/A$^{\bullet}$ or D$^{\bullet +}$/A$^{\bullet}$* is estimated to be $-2.17 < \Delta G_{fet}$* < -0.57 eV for the pair of MeAc$^+$ and TMPD. The value $-2.17 < \Delta G_{fet}$* < -0.57 eV ensures the diffusion-controlled fluorescence quenching by long-distance ET for producing D$^{\bullet +}$/A$^{\bullet}$*. The ΔG_{bet} for back ET within D$^{\bullet +}$/A$^{\bullet}$ is -0.58 eV, and the free energy change (ΔG_{bet}*) for back ET within D$^{\bullet +}$*/A$^{\bullet}$ or D$^{\bullet +}$/A$^{\bullet}$* is estimated to be $-2.18 < \Delta G_{bet}$* < -0.58 eV. As $\lambda_S = 1.52$ eV, the back ET with $-2.18 < \Delta G_{bet}$* < -0.58 eV is much faster than the back ET with $\Delta G_{bet} = -0.58$ eV. Therefore, the free radical yield for D$^{\bullet +}$*/A$^{\bullet}$ or D$^{\bullet +}$/A$^{\bullet}$* is expected to be significantly lower than that for D$^{\bullet +}$/A$^{\bullet}$. In this case, the calculation of k_{bet} from Φ_R by use of eq 3 gives a higher value compared with the real one. The upward deviation of the experimental plots from the theoretical curve for k_{bet} in the region $\Delta G_{fet} < -2.0$ eV is evidence for the generation of D$^{\bullet +}$*/A$^{\bullet}$ and/or D$^{\bullet +}$/A$^{\bullet}$* as the primary quenching product.

To investigate the charge effect on back ET within the geminate radical pairs, the ΔG_{bet} dependence of k_{bet} for D$^{\bullet +}$/A$^{\bullet}$ (Figure 5, circles) is compared with that for D$^{\bullet +}$/A$^{\bullet -}$ (Figure 6, squares).[6h] Both ΔG_{bet} dependencies of k_{bet} are quite similar to each other in the region $-2.2 < \Delta G_{bet} < -0.8$ eV. Therefore, it is concluded that the ΔG_{bet} dependence of k_{bet} does not depend on the types of ET such as the CSh type and the CR type.

It is noteworthy that the molecular charge effect on Φ_R arises through the molecular charge effect on k_{esc}. According to the Tachiya theory,[8] k_{esc} for D$^{\bullet +}$/A$^{\bullet -}$ is given by eq 10.[6h] Here r_c is

$$k_{esc} = Dr_c/[r_q^3\{\exp(r_c/r_q) - 1\}] \qquad (10)$$

the Onsager distance:

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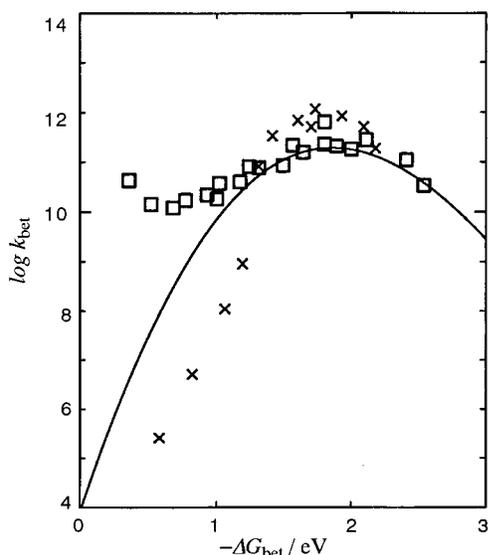
Figure 6. k_{bet} versus ΔG_{bet} for the anthracenecarbonitrile–aromatic molecule pairs: squares, calculated by eqs 3 and 10; crosses, calculated by eqs 7–9 with fitting parameters $|V_0| = 120$ cm^{-1}, $\beta = 1$ Å^{-1}, $\lambda_v = 0.25$ eV, $r_A = r_D = 3$ Å, and $r_{bet} = r_q$; solid curve, calculated by eqs 7–9 with fitting parameters $|V_0| = 120$ cm^{-1}, $\beta = 1$ Å^{-1}, $r_D = r_A = 3$ Å, $\lambda_v = 0.25$ eV, $h\nu = 1500$ cm^{-1}, $r_{bet} = 7.5$ Å, and $\lambda_S = 1.52$ eV.

$$r_c = e^2/\epsilon k_B T \qquad (11)$$

In acetonitrile, r_c is calculated to be 14.4 Å. k_{esc} for $D^{\bullet+}/A^{\bullet-}$ is smaller than that for $D^{\bullet+}/A^{\bullet}$ as a result of Coulomb attraction. The difference in k_{esc} between $D^{\bullet+}/A^{\bullet}$ and $D^{\bullet+}/A^{\bullet-}$ increases with a decrease in the dielectric constant ϵ. Therefore, Φ_R may be controlled by changing the solvent polarity.

3.2. Fluorescence Quenching of Aromatic Compounds by Dicationic Ions in Methanol. $D^* + A^{2+} \rightarrow D^{\bullet+} + A^{\bullet+}$. The fluorescence quenching by MB^{2+} and BV^{2+} was studied in methanol, because the solubility of these viologens in acetonitrile is not high enough to quench fluorescence effectively. When these viologens are used as quenchers, the exciplex fluorescence is not detected. The values for k_q and r_q were determined as listed in Table 3. ΔG_{fet} and ΔG_{bet} in methanol were evaluated by eqs 12 and 13, respectively.[23] Here, ϵ and ϵ' are the dielectric constants of acetonitrile and methanol, respectively.

$$\Delta G_{fet} = E_{1/2}^{ox} - E_{1/2}^{red} + e^2/\epsilon' r_q + (e^2/2)(1/r_A + 1/r_D)$$
$$(1/\epsilon' - 1/\epsilon) - E(S_1) \quad (12)$$

$$\Delta G_{bet} = E_{1/2}^{red} - E_{1/2}^{ox} - e^2/\epsilon' r_q - (e^2/2)(1/r_A + 1/r_D)$$
$$(1/\epsilon' - 1/\epsilon) \quad (13)$$

Figure 2 shows that the ΔG_{fet} dependence of k_q (triangles) is the same as the Rehm–Weller plot (crosses). As shown in Figure 3, the ΔG_{fet} dependence of r_q (triangles) is the same as that obtained for the system of neutral fluorescer and quencher (squares). Therefore, the ΔG_{fet} dependence of k_q and r_q is not affected by the positive charges of the quencher. It is noted that the r_q values cannot be determined for DCP and DMA with MV^{2+} and for DCP, DPA, DOMA, and DMA with BV^{2+}, because the absorption spectrum of the quencher overlaps with that of the fluorescer at a high quencher concentration. The r_q values for these fluorescers were estimated from the plots shown in Figure 3.

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Judging from the ΔG_{fet} dependence of k_q and r_q, the quenching mechanism is supposed to be exciplex formation in the region $\Delta G_{fet} > -0.4$ eV. However, exciplex fluorescence has not been observed even for the systems with $\Delta G_{fet} > -0.4$ eV such as DCA-MV^{2+} ($\Delta G_{fet} = -0.39$ eV) and DCA-BV^{2+} ($\Delta G_{fet} = -0.47$ eV). Evidence of exciplex formation for these EDA systems is given below. In the region $\Delta G_{fet} < -0.5$ eV, $r_q > 5$ Å, and hence, fluorescence quenching is induced by long-distance ET.

Flashing of the solution containing D and A^{2+} gives the transient absorption due to $D^{\bullet+}$ and $A^{\bullet+}$, the decay rate of which is too low to determine. The molar extinction coefficient for the positively charged radical cation (MV$^{\bullet+}$) of MV^{2+} has been reported to be 13 800 M^{-1} cm^{-1} at 609 nm in methanol.[24] The molar extinction coefficient for the positively charged radical cation (BV$^{\bullet+}$) of BV^{2+} was determined to be 18 800 M^{-1} cm^{-1} at 606 nm in methanol. The values for Φ_R were determined as listed in Table 3.

In Table 3, we cannot find any regular correlation between Φ_R and ΔG_{fet}. This is due to the fact that $E(S_1)$ changes from fluorescer to fluorescer. It should be noted that Φ_R depends on ΔG_{bet}, but not necessarily on ΔG_{fet}.

If the fluorescence quenching by MV^{2+} and BV^{2+} is induced by a long-distance ET, Φ_R is given by eq 3. k_{esc} for $D^{\bullet+}/A^{\bullet+}$ can be calculated by eq 14 derived according to the Tachiya

$$k_{esc} = Dr_c/[r_q^3\{1 - \exp(-r_c/r_q)\}] \qquad (14)$$

theory.[8] D is expressed as $D = k_B T/6\pi\eta$.[17] The viscosity coefficient η is 1.6 times greater in methanol than in acetonitrile: 0.547 cP at 298 K for methanol and 0.325 cP at 303 K and 0.375 cP at 288 K for acetonitrile.[25] In the calculation of k_{esc} in methanol, therefore, $D = 2.2 \times 10^{-5}$ cm^2 s^{-1} was used. r_c is calculated to be 16.6 Å in methanol. The k_{bet} values were calculated from the Φ_R values by use of eqs 3 and 14. The values for ΔG_{bet}, k_{esc}, and k_{bet} are summarized in Table 3. It is noted that k_{esc} for $D^{\bullet+}/A^{\bullet+}$ is greater than those for $D^{\bullet+}/A^{\bullet-}$ and $D^{\bullet+}/A^{\bullet}$ as the result of Coulomb repulsion.

In Figure 7, the k_{bet} values are plotted with respect to ΔG_{bet} (triangles). The crosses in Figure 7 were obtained by use of eqs 7–9 and the following fitting parameters: $|V_0| = 120$ cm^{-1}, $\beta = 1$ Å^{-1}, $r_D = r_A = 3$ Å, $\lambda_v = 0.25$ eV, $h\nu = 1500$ cm^{-1}, and $r_{bet} = r_q$. Then, λ_S changes from 1.29 eV for $r_q = 6$ Å to 1.93 eV for $r_q = 12$ Å. The theoretical curve shown in Figure 7 was obtained by use of eqs 7–9 and the following fitting parameters: $|V_0| = 120$ cm^{-1}, $\beta = 1$ Å^{-1}, $r_D = r_A = 3$ Å, $\lambda_v = 0.25$ eV, $h\nu = 1500$ cm^{-1}, $r_{bet} = 9.0$ Å, and $\lambda_S = 1.72$ eV.

The theoretical plot (crosses) calculated by setting $r_{bet} = r_q$ fits in with the experimental plot (triangles) in the region $-1.4 < \Delta G_{bet} < -2.8$ eV, but deviates downward from the experimental plot in the region $\Delta G_{bet} \geq -1.4$ eV. In contrast, the theoretical curve calculated by setting $r_{bet} = 9.0$ Å fits in with the experimental plot in the whole region studied. Therefore, it is concluded that (i) the quenching mechanism in the region $-0.5 > \Delta G_{fet} \geq -1.85$ eV is a long-distance ET for producing $D^{\bullet+}/A^{\bullet+}$ and (ii) a back ET within $D^{\bullet+}/A^{\bullet+}$ occurs at the electron donor and acceptor separation of 9.0 Å on average although r_q spans from 6.0 to 12 Å.

If the fluorescence quenching of the systems of DCA-MV^{2+} ($\Delta G_{bet} = -2.50$ eV) and DCA-BV^{2+} ($\Delta G_{bet} = -2.42$ eV) is induced by long-distance ET, k_{bet} is calculated from r_q and Φ_R by use of eqs 3 and 14: 1.3×10^{12} s^{-1} for the former system

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Table 3. Free Energy Changes of ET Fluorescence Quenching in Methanol (ΔG_{fet}) and Back ET within $D^{\bullet+}/A^{\bullet+}$ (ΔG_{bet}), Fluorescence Quenching Rate Constants (k_q), Effective Quenching Distances (r_q), Free Radical Yields (Φ_R), and Rate Constants of $D^{\bullet+}/A^{\bullet+}$ Separation into Free Radicals (k_{esc}) and Back ET within $D^{\bullet+}/A^{\bullet+}$ (k_{bet})

fluorescer	quencher	ΔG_{fet}, eV	k_q, 10^{10} M^{-1} s^{-1}	r_q, Å	Φ_R	k_{esc}, 10^{10} s^{-1}	k_{bet}, 10^{10} s^{-1}	ΔG_{bet}, eV
TCA	MV^{2+}	−0.01	0.11					−2.66
TeCA	MV^{2+}	−0.09	0.42					−2.81
DCA	MV^{2+}	−0.39	1.22	3.2	0.079			−2.50
DCA	BV^{2+}	−0.47	1.70	3.0	0.071			−2.42
DCP	MV^{2+}	−0.84	1.12	(6.0)	0.320	1.78	3.78	−2.72
CA	MV^{2+}	−0.92	1.47	6.0	0.071	1.78	23.3	−2.12
DCP	BV^{2+}	−0.93	1.50	(6.0)	0.500	1.78	1.78	−2.63
CA	BV^{2+}	−1.03	1.82	7.5	0.042	0.70	15.9	−2.01
DPA	MV^{2+}	−1.41	1.45	8.5	0.140	0.68	4.20	−1.75
Per	BV^{2+}	−1.42	1.88	9.0	0.12	0.59	4.29	−1.41
DPA	BV^{2+}	−1.51	1.87	(9.0)	0.060	0.59	9.17	−1.65
DOMA	MV^{2+}	−1.55	1.76	10.0	0.280	0.45	1.16	−1.50
DOMA	BV^{2+}	−1.65	1.99	(11.0)	0.160	0.35	1.84	−1.40
DMA	MV^{2+}	−1.76	1.82	(12.0)	0.220	0.28	0.99	−1.38
DMA	BV^{2+}	−1.85	1.92	(12.0)	0.096	0.28	2.62	−1.29
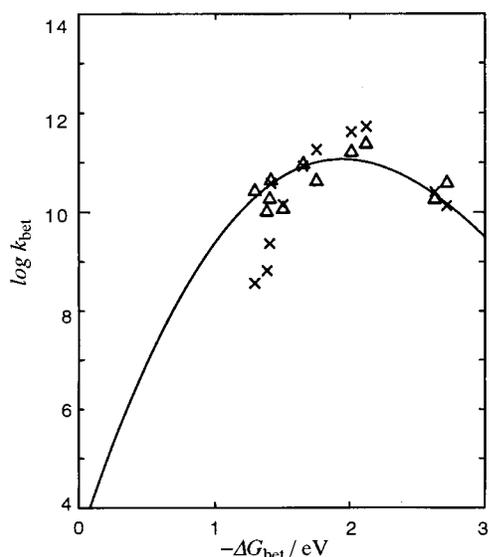
Figure 7. k_{bet} versus ΔG_{bet} for the aromatic molecule−aromatic dication pairs: triangles, calculated by eqs 3 and 14; crosses, calculated by eqs 7−9 with fitting parameters $|V_0| = 120$ cm^{-1}, $\beta = 1$ Å^{-1}, $\lambda_v = 0.25$ eV, $r_A = r_D = 3$ Å, and $r_{bet} = r_q$; solid curve, calculated by eqs 7−9 with fitting parameters $|V_0| = 120$ cm^{-1}, $\beta = 1$ Å^{-1}, $r_D = r_A = 3$ Å, $\lambda_v = 0.25$ eV, $h\nu = 1500$ cm^{-1}, $r_{bet} = 9.0$ Å, and $\lambda_S = 1.72$ eV.

and 1.8×10^{12} s^{-1} for the latter system. These values are 1 order of magnitude greater than the theoretical values for k_{bet} at $\Delta G_{bet} = -2.50$ and -2.42 eV. Such a great upward deviation of the experimental plot from the theoretical curve in the region $\Delta G_{fet} > -0.5$ eV is evidence for fluorescence quenching due to exciplex formation. Consequently, the switchover of the ET quenching mechanism takes place at $\Delta G_{fet} \approx -0.5$ eV in agreement with the system of neutral fluorescer and quencher. The lifetime of the exciplex consisting of neutral fluorescer and dicationic quencher is supposed to be very short, because the contact radical ion pair state is destabilized by the Coulomb repulsion.

4. Summary and Conclusions

All the results obtained for the three types of ET fluorescence quenching and back ET within three types of geminate radical pairs are compared with one another to understand the general features of photoinduced ET in polar solvents.

(1) The switchover ΔG_{fet} of the quenching mechanism between exciplex formation and long-distance ET is the same

among the three types of quenching reactions and is −0.4 to −0.5 eV: The quenching is induced by exciplex formation in the region $\Delta G_{fet} > -0.4$ eV, and by long-distance ET in the region $\Delta G_{fet} < -0.5$ eV.

(2) The ΔG_{fet} dependence of k_q is the same among the three types of quenching reactions and is represented by the Rehm−Weller plot as shown in Figure 2.

(3) The ΔG_{fet} dependence of r_q is the same among the three types of quenching reactions: As shown in Figure 3, r_q increases almost linearly with a decrease in ΔG_{fet} in the region $-2.0 < \Delta G_{fet} < -0.3$ eV.

(4) The ΔG_{fet} dependence of Φ_R is not necessarily the same among the three types of quenching reactions: Φ_R depends on ΔG_{bet} rather than ΔG_{fet}.

(5) The quenching mechanism in the region $-2.0 < \Delta G_{fet} < -0.5$ eV is the same among the three types of quenching reactions: the long-distance ET for producing the ground-state geminate radical pairs.

(6) The ΔG_{bet} dependence of k_{bet} is almost the same among the three types of quenching reactions as shown in Figures 5−7: It is well reproduced with a semiclassical theory for long-distance ET, i.e., by eqs 7−9 with the fitting parameters $|V_0| = 120$ cm^{-1}, $\beta = 1$ Å^{-1}, $r_D = r_A = 3$ Å, $\lambda_v = 0.25$ eV, and $h\nu = 1500$ cm^{-1}.

(7) The average distance r_{bet} between the electron donor and acceptor for inducing the back ET within the geminate radical pair is almost the same among the three types of quenching reactions: $r = 7.5-9.0$ Å.

(8) λ_S is almost the same among the three types of quenching reactions: $\lambda_S = 1.52-1.72$ eV.

(9) When $\Delta G_{fet} < -2.0$ eV, the disagreement in k_{bet} between the experimental one determined from Φ_R and the theoretical one is evidence for the production of excited-state geminate pairs.

(10) Φ_R is significantly affected by the molecular charge on the fluorescer and/or quencher through the molecular charge effect on k_{esc} according to eqs 6, 10, and 14.[8] The effect is enhanced with a decrease in solvent polarity.

(11) The molecular charge affects the stability of the exciplex: the observation of exciplex fluorescence may be expected for $^1D^*/A$ and $D/^1A^*$, but not for $^1A^{+*}/D$ and $^1D^*/A^{2+}$.

Consequently, the long-distance ET itself, i.e., both the ET fluorescence quenching in the region $\Delta G_{fet} < -0.5$ eV and the back ET within the geminate radical pairs, is not significantly affected by the molecular charge on the fluorescer and quencher.

This confirms the validity of the theoretical consideration by Tachiya[26] that the molecular charge does not affect the rate of long-distance ET in highly polar solvents.

In agreement with this conclusion, it has been confirmed that the ΔG_{fet} dependence of k_q, i.e., $k_q = k_{dif}$ in the region $-2.0 < \Delta G_{fet} < -0.5$ eV, is well reproduced by use of eq 15.[9,27] In this case, k_{fet} is calculated by use of eq 7 together with the above fitting parameters and r_q.

$$1/k_q = 1/k_{dif} + 1/k_{fet} \qquad (15)$$

5. Criteria for Determining the ET Fluorescence Quenching Mechanism When Both Electron Donor and Acceptor Are Aromatic Molecules

Exciplex formation: (1) exciplex fluorescence; (2) $r_q < 5$ Å; (3) $\Delta G_{fet} > -0.4$ eV; (4) significant enhancement of Φ_T by a heavy-atom substitution on the quencher; (5) upward deviation of the k_{bet} determined with Φ_R from the theoretical curve.

Long-distance ET for producing the ground-state geminate radical pair: (1) $r_q > 5$ Å; (2) $-2.0 < \Delta G_{fet} < -0.5$ eV; (3) agreement of the k_{bet} determined from Φ_R with the theoretical curve; (4) no enhancement of Φ_T by a heavy-atom substitution on the quencher; (5) $\Phi_R \gg \Phi_T$.

Long-distance ET for producing the excited-state geminate radical pair: (1) $r_q > 10$ Å; (2) $\Delta G_{fet} < -2.0$ eV; (3) upward deviation of the k_{bet} determined with Φ_R from the theoretical curve; (4) absorption bands of the radicals in the near-infrared region.

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