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# A comparative study on electron-transfer fluorescence quenching by aliphatic and aromatic amines

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**Abstract**

The electron-transfer (ET) fluorescence quenching of aromatic compounds by aliphatic amines (DABCO, ABCO, and triethylamine) was studied in acetonitrile. The fluorescence quenching rate constant $k_{\rm q}$ suddenly decreases when the free energy change ($\Delta G_{\rm fet}$ ) of full ET in fluorescence quenching increases from $-0.6$ to $-0.4$ eV, indicating that the downhill region shifts by ca. $-0.5$ eV compared with the Rehm–Weller plot, where both fluorescer and quencher are aromatic. The fluorescence quenching distance $r_{\rm q}$ increases with decreasing $\Delta G_{\rm fet}$ and the rate $k_{\rm bet}$ of back ET within geminate radical pairs shows a bell-shaped dependence on the free energy change ($\Delta G_{\rm bet}$) of back ET. Both free energy dependence of $r_{\rm q}$ and $k_{\rm bet}$ are the same as those of aromatic electron donor and acceptor system. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Electron-transfer; Fluorescence quenching; Aliphatic amines

## 1. Introduction

In previous work [1–9], a detailed mechanism of electron-transfer (ET) fluorescence quenching has been investigated in acetonitrile using anthracenecarbonitriles as fluorescers and several kinds of aromatic compounds as quenchers. It was established that, in the case of fluorescence quenching ET between aromatic compounds in polar solvents such as acetonitrile and 1,2-dichloromethane, the switchover of fluorescence quenching mechanism occurs at the free energy change of full ET in fluorescence quenching, $\Delta G_{\rm fet} = -0.5$ eV, i.e. the fluorescence quenching is induced by a partial ET at contact distance of fluorescer and quencher (i.e. by an exciplex formation) when $\Delta G_{\rm fet} > -0.4$ eV and by a full ET at long-distance (i.e. by a long-distance ET) when $\Delta G_{\rm fet} < -0.5$ eV. In the region $\Delta G_{\rm fet} = -0.5 \sim -2.0$ eV, the primary quenching product is the ground-state geminate radical pairs (GRP) and it has been confirmed that the rate $k_{\rm bet}$ of back ET within GRP shows a bell-shaped dependence on the free energy change $\Delta G_{\rm bet}$ of back ET within geminate radical pairs in agreement with the Marcus theory [10,11] for long-distance ET. In the region $\Delta G_{\rm fet} < -2.0$ eV, however, the primary quenching product is considered to be the excited-state geminate radical pairs (GRP*), the counterpart of which is electronically excited [6,7].

$\Delta G_{\rm fet}$ and $\Delta G_{\rm bet}$ are defined as follows [12]

$$\Delta G_{\rm fet} = E_{1/2}^{\rm ox} - E_{1/2}^{\rm red} - \frac{e^2}{\varepsilon r_{\rm q}} - E(S_1) \tag{1}$$

$$\Delta G_{\rm bet} = E_{1/2}^{\rm red} - E_{1/2}^{\rm ox} + \frac{e^2}{\varepsilon r_{\rm bet}} \tag{2}$$

Here, $E_{1/2}^{\rm ox}$, $E_{1/2}^{\rm red}$, and $E(S_1)$ are the oxidation potential of electron donor, the reduction potential of electron acceptor, and the energy of fluorescent state. $e^2/\varepsilon r_{\rm q}$ and $e^2/\varepsilon r_{\rm bet}$ are the Coulomb energies for the oppositely monocharged GRP at distances $r_{\rm q}$ and $r_{\rm bet}$, respectively.

It is well-known that in the case of fluorescence quenching ET between aromatic compounds, the $\Delta G_{\rm fet}$ dependence of quenching rate constant $k_{\rm q}$ follows the Rehm–Weller Plot. Recently, Jacques and co-workers [13–15] have reported that there is a difference in the $\Delta G_{\rm fet}$ dependence of quenching rate constant $k_{\rm q}$ between aromatic quenchers (i.e. π-electron donors) and aliphatic amines (*n*-electron donors).

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In this work, we study the $\Delta G_{\text{fet}}$ dependence of (i) $k_q$, (ii) the effective quenching distance $r_q$, and (iii) the $\Delta G_{\text{bet}}$ dependence of $k_{\text{bet}}$ in acetonitrile, using aromatic compounds as fluorescers and aliphatic amines as quenchers. On the basis of the results, the $\Delta G_{\text{fet}}$ dependence of ET fluorescence quenching mechanism and the $\Delta G_{\text{bet}}$ dependence of $k_{\text{bet}}$ are established for the system of aromatic fluorescer and aliphatic quencher. And then, they are compared with those of the system of aromatic fluorescer and quencher to make clear the difference in photoinduced ET between aromatic and aliphatic quencher.

## 2. Experimental

The methods for synthesis and/or purification of 9-cyanoanthracene (CA), 9-phenylanthracene (PA), 9,10-dicyanoanthracene (DCA), perylene (Per), anthracene (Anth), and pyrene (Py) have been reported elsewhere [3,7,8]. 3-Bromoperylene (Br-Per) was synthesized according to the method described in literature [16]. 1,4-Diazabicyclo[2,2,2]-octane (DABCO, Aldrich), 1-azabicyclo[2,2,2]octane (ABCO, Aldrich) were sublimated in vacuum. Triethylamine (TEA) and acetonitrile (SP grade, Kanto) 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 $\Phi_R$ and the triplet yield $\Phi_T$ in fluorescence quenching were determined by an emission–absorption flash photolysis method [1–9,17]. Almost all the photophysical parameters necessary to determine $\Phi_R$ and $\Phi_T$ have been reported elsewhere [1–9,18]. The molar extinction coefficients for the radical anions of Anth, Per, and Br-Per were determined to be 49 000, 37 000, and 21 000 $M^{-1}\,cm^{-1}$ at 720, 580, and 580 nm, respectively, by use of the photoinduced ET from diphenylamine to these fluorescers. Then, the molar extinction coefficient of 19 000 $M^{-1}\,cm^{-1}$ at 670 nm was used for the diphenylamine radical cation [3]. The molar extinction coefficient of the triplet–triplet absorption for Br-Per was determined to be 19 000 $M^{-1}\,cm^{-1}$ at 500 nm by use of the triplet energy transfer from Anth to Br-Per. Then, the molar extinction coefficient of 73 100 $M^{-1}\,cm^{-1}$ at 420 nm was used for the triplet–triplet absorption of Anth.

The oxidation potentials $E_{1/2}^{\text{ox}}$ versus SCE were measured in acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrolyte, +0.56 V for DABCO, and +0.80 V for ABCO, respectively. The $E_{1/2}^{\text{ox}}$values for TEA has been reported to be 0.98 V [19,20]. The reduction potential $E_{1/2}^{\text{red}}$versus SCE for fluorescers were determined in acetonitrile, −1.58 V for CA, −0.95 V for DCA, −0.45 V for TeCA, −1.96 for An, −2.10 V for Py, −1.65 V for Per and −1.60 V for Br-Per, respectively. All measurements were made at 298 K.

## 3. Results and discussion

### 3.1. ET fluorescence quenching

The rate constants $k_q$ of fluorescence quenching by aliphatic amines were determined from the Stern–Volmer plot for the fluorescence intensity at low quencher concentration (<10 mM), where the plot was linear. The values for $k_q$ and $\Delta G_{\text{fet}}$ are listed in Table 1. The plot of $k_q$ versus $\Delta G_{\text{fet}}$ is shown in Fig. 1 (open circles).

$k_q$ is close to the diffusion-controlled limit, $k_{\text{dif}} \approx 2 \times 10^{10}\,M^{-1}\,s^{-1}$ when $\Delta G_{\text{fet}} < -0.59$ eV, and decreases with increasing $\Delta G_{\text{fet}}$ when $\Delta G_{\text{fet}} > -0.59$ eV. The downhill region shifts by ca. −0.5 eV compared with the Rehm–Weller plot (closed circles), which was obtained for the aromatic electron donor and acceptor (EDA) system [12].

The effective quenching distance $r_q$ was determined by use of the modified Stern–Volmer equation [21,22] at such high quencher concentrations as 0.1–0.2 M. Even at such high quencher concentration, the fluorescence spectrum has not been changed. The values for $r_q$ are listed in Table 1. The plot of $r_q$ versus $\Delta G_{\text{fet}}$ is shown in Fig. 2 (open circles). This plot is quite similar to that obtained for the aromatic EDA system (triangles) [6,8], indicating that the electronic interaction for inducing ET between aliphatic and aromatic molecule is almost the same in strength as that between aromatic molecules.

In the region $\Delta G_{\text{fet}} \geq -0.5$ eV, $r_q$ is in the range 4–5 Å which is close to the inter-planar separation of 3 Å in an exciplex consisting of two aromatic molecules [21–23] and the energy gap $|\Delta G_{\text{fet}}|$ between the locally excited singlet-state and the contact radical pair state is small. Therefore, it may be supposed that the fluorescence quenching is induced by exciplex formation in a similar way to the aromatic EDA system.

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.

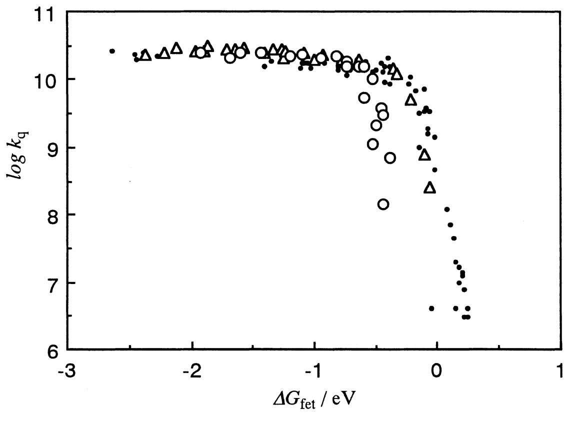

Fig. 1. Plots of $k_q$ vs. $\Delta G_{\text{fet}}$. Quencher, aliphatic amines (open circles), aromatic amines (open triangles), and the Rehm–Weller plot (closed circles).

Table 1
Free energy changes of ET fluorescence quenching parameter[a]

| Fluorescer | Quencher | $\Delta G_{\mathrm{fet}}$/eV | $k_q/10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ | $r_q$/Å | $\Delta G_{\mathrm{bet}}$/eV | $\Phi_R$ | $k_{\mathrm{esc}}/10^{10}\,\mathrm{s}^{-1}$ | $k_{\mathrm{bet}}/10^{10}\,\mathrm{s}^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Phen | TEA | −0.39 | 0.07 | – | −3.20 | – | – | – |
| Phen | ABCO | −0.44 | 0.014 | 4.3 | −3.15 | – | – | – |
| Per | TEA | −0.44 | 0.30 | – | −2.41 | – | – | – |
| Per | ABCO | −0.49 | 0.21 | 4.5 | −2.36 | 0.080 | – | – |
| An | TEA | −0.52 | 1.0 | 4.2 | −2.76 | – | – | – |
| An | ABCO | −0.59 | 0.53 | 5.5 | −2.69 | 0.056 | 0.238 | 4.01 |
| CA | TEA | −0.64 | 1.6 | 5.4 | −2.40 | 0.016 | 0.239 | 14.7 |
| Per | DABCO | −0.71 | 1.6 | 5.7 | −2.14 | 0.003 | 0.236 | 78.4 |
| CA | ABCO | −0.73 | 1.5 | 5.9 | −2.31 | 0.006 | 0.230 | 38.1 |
| Py | DABCO | −0.74 | 1.8 | 6.0 | −2.59 | 0.040 | 0.233 | 5.58 |
| An | DABCO | −0.82 | 2.2 | 6.6 | −2.46 | 0.012 | 0.223 | 18.4 |
| CA | DABCO | −0.95 | 2.1 | 7.4 | −2.09 | 0.005 | 0.207 | 41.2 |
| DCA | TEA | −1.10 | 2.3 | 8.0 | −1.79 | 0.005 | 0.194 | 38.6 |
| DCA | ABCO | −1.19 | 2.2 | 7.8 | −1.70 | 0.007 | 0.199 | 28.2 |
| DCA | DABCO | −1.43 | 2.4 | 8.5 | −1.46 | 0.021 | 0.185 | 8.62 |
| TeCA | TEA | −1.60 | 2.5 | 8.5 | −1.29 | 0.030 | 0.185 | 5.98 |
| TeCA | ABCO | −1.69 | 2.1 | 8.5 | −1.20 | 0.042 | 0.185 | 4.21 |
| TeCA | DABCO | −1.92 | 2.4 | 10.2 | −0.97 | 0.164 | 0.153 | 0.78 |

[a] ($\Delta G_{\mathrm{fet}}$) — free energy change of ET fluorescence quenching; ($\Delta G_{\mathrm{bet}}$) — free energy changes of back ET within GRP; ($k_q$) — fluorescence quenching rate constants; ($r_q$) — effective quenching distances; ($\Phi_R$) — free radical yields; ($k_{\mathrm{esc}}$) — rate constants of GRP separation into free radicals; ($k_{\mathrm{bet}}$) — rate constants of back ET within GRP.

As shown in Table 1, the free radical yield $\Phi_R$ in fluorescence quenching decreases with decreasing $\Delta G_{\mathrm{fet}}$, passes through a minimum at $\Delta G_{\mathrm{fet}} \approx -1.0$ eV, and then increases. This result is almost the same as that obtained for the aromatic EDA system [1,5].

If fluorescence quenching is induced by exciplex formation, the triplet yield $\Phi_T$ in fluorescence quenching is expected to be strongly enhanced by a heavy atom substitution on fluorescer and/or quencher, because the intersystem crossing within exciplex can be efficiently enhanced by a heavy atom involved in fluorescer and/or quencher [3]. If fluorescence quenching is induced by long-distance ET, in contrast, $\Phi_T$ is not enhanced by the heavy atom substitution at all, when the energy $E(T_1)$ of lowest excited triplet-state is higher than the energy $|\Delta G_{\mathrm{bet}}|$ of GRP. Even when $E(T_1) < |\Delta G_{\mathrm{bet}}|$, $\Phi_T$ is not so enhanced by the heavy atom substitution, because the spin-orbit interaction within GRP is weak. Therefore, the heavy atom effect on $\Phi_T$ is a measure for determining the quenching mechanism.

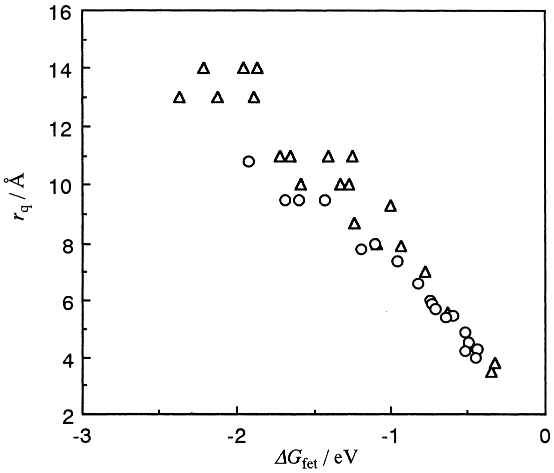

Fig. 2. Plots of $r_q$ vs. $\Delta G_{\mathrm{fet}}$. Quencher, aliphatic amines (circles), aromatic amines (triangles).

To confirm the quenching mechanism in the region $\Delta G_{\mathrm{fet}} \geq -0.5$ eV, $\Phi_T$ and $\Phi_R$ were measured using Br-Per as fluorescer and ABCO and DABCO as quenchers. In the system of Br-Per and ABCO with $\Delta G_{\mathrm{fet}} = -0.44$ eV, $\Phi_T$ and $\Phi_R$ were determined to be 0.19 and 0.025, respectively. By comparison with the system of Per and ABCO with $\Delta G_{\mathrm{fet}} = -0.49$ eV, $\Phi_T$ extremely increases and $\Phi_R$ significantly decreases. In the system of Br-Per and DABCO with $\Delta G_{\mathrm{fet}} = -0.75$ eV, $\Phi_T$ and $\Phi_R$ were determined to be null and 0.003, respectively. These results indicate that fluorescence quenching is induced by exciplex formation in the region $\Delta G_{\mathrm{fet}} \geq -0.5$ eV, but by long-distance ET in the region $\Delta G_{\mathrm{fet}} < -0.5$ eV. Therefore, the switchover of ET fluorescence quenching mechanism takes place at $\Delta G_{\mathrm{fet}} \approx -0.5$ eV in agreement with the aromatic EDA system.

### 3.2. Back electron transfer within GRP

When fluorescence quenching is induced by long-distance ET for producing GRP, the efficiency of GRP is unity. Then, $\Phi_R$ is given by Eq. (3)

$$\Phi_R = \frac{k_{\mathrm{esc}}}{(k_{\mathrm{esc}} + k_{\mathrm{bet}})} \tag{3}$$

Here, $k_{\mathrm{esc}}$ is the rate constant for GRP separation into free radicals. According to the Tachiya theory [24], $k_{\mathrm{esc}}$ for an oppositely monocharged GRP is given by Eq. (4)

$$k_{\mathrm{esc}} = \frac{D r_c}{[r_q^3\{\exp(r_c/r_q) - 1\}]} \tag{4}$$

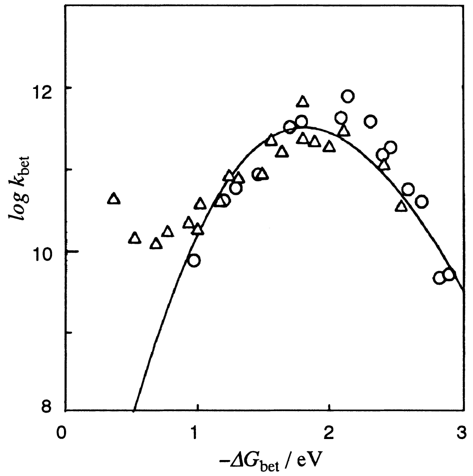

Fig. 3. Plots for $k_{\rm bet}$ vs. $\Delta G_{\rm bet}$. Quencher, aliphatic amines (circles), aromatic amines (triangles). The solid curve was calculated by use of Eqs. (6–8) with fitting parameters $|V_0| = 120\,{\rm cm}^{-1}$, $\beta = 1.0\,Å^{-1}$, $\lambda_{\rm v} = 0.25\,{\rm eV}$, $r_{\rm A} = r_{\rm D} = 3\,Å$, $h\nu = 1500\,{\rm cm}^{-1}$, $r_{\rm bet} = 8.0\,Å$, and $\lambda_{\rm S} = 1.59\,{\rm eV}$.

Here $r_{\rm c}$ is the Onsager distance

$$r_{\rm c} = \frac{e^2}{\varepsilon k_{\rm B}T} \tag{5}$$

As the sum (D) of the diffusion-coefficients for EDA is $3.5\times10^{-5}\,{\rm cm}^2\,{\rm s}^{-1}$ in acetonitrile [21], $k_{\rm esc}$'s are calculated by use of Eq. (4) and the $r_{\rm q}$'s listed in Table 1. Thus, $k_{\rm bet}$'s are calculated from Eq. (3) and the $\Phi_{\rm R}$'s listed in Table 1. The values for $\Delta G_{\rm bet}$, $k_{\rm esc}$, and $k_{\rm bet}$ are summarized in Table 1. In Fig. 3, $k_{\rm bet}$'s are plotted with respect to $\Delta G_{\rm bet}$ (circles). The plot of $k_{\rm bet}$ versus $\Delta G_{\rm bet}$ for the aromatic EDA system is also depicted in this figure (triangles). Both $\Delta G_{\rm bet}$ dependence of $k_{\rm bet}$ is quite similar to each other in the region $-1.0 < \Delta G_{\rm bet} < -2.7\,{\rm eV}$.

When the back ET within GRP takes place at the distance $r_{\rm bet}$, the rate of back ET may be given by the following semiclassical equation for long-distance ET [25–29]

$$k_{\rm bet} = \left(\frac{4\pi}{h^2\lambda_{\rm S}k_{\rm B}T}\right)^{1/2}|V|^2\sum\left(\frac{{\rm e}^{-S}S^w}{w!}\right)\times\exp\left[-\frac{\Delta G_{\rm bet}+\lambda_{\rm S}+wh\nu}{4\lambda_{\rm S}k_{\rm B}T}\right] \tag{6}$$

Here

$$S = \frac{\lambda_{\rm v}}{h\nu}$$

$$\lambda_{\rm S} = \frac{{\rm e}^2}{8\pi\varepsilon_0}\left(\frac{1}{r_{\rm A}}+\frac{1}{r_{\rm D}}-\frac{2}{r_{\rm bet}}\right)\left(\frac{1}{n^2}-\frac{1}{\varepsilon}\right) \tag{7}$$

$$|V|^2 = |V_0|^2\exp[-\beta\{r_{\rm bet}-(r_{\rm A}+r_{\rm D})\}] \tag{8}$$

$k_{\rm B}$ is the Boltzman constant, $r_{\rm D}$ and $r_{\rm A}$ are the radii of electron donor and acceptor.

As demonstrated in previous work [9], $r_{\rm bet}$ is not necessarily the same as $r_{\rm q}$. $r_{\rm q}$ is the most contributory distance for ET fluorescence quenching, but not always that for back ET. $r_{\rm q}$ depends on $\Delta G_{\rm fet}$ as shown in Fig. 2. Similarly, the most contributory distance for back ET is considered to depend on $\Delta G_{\rm bet}$. The GRP species may diffuse at random within a solvent cage before proceeding to back ET. Therefore, it is expected that back ET takes place at a distance between $r_{\rm q}$ and the most contributory distance for back ET, which may be evaluated from Fig. 2 by replacing $\Delta G_{\rm fet}$ with $\Delta G_{\rm bet}$. To fit the theory and experiment as best we can, the parameters other than $r_{\rm bet}$ were assumed to be the same as used in previous work on the aromatic EDA system, the reactant vibrational reorganization energy, $\lambda_{\rm v} = 0.25\,{\rm eV}$, the average energy of active vibrational mode, $h\nu = 1500\,{\rm cm}^{-1}$; the radii of electron donor and acceptor, $r_{\rm D} = r_{\rm A} = 3\,Å$, the attenuation parameter, $\beta = 1\,Å^{-1}$, the electron exchange matrix element at contact distance of EDA, $|V_0| = 120\,{\rm cm}^{-1}$. As shown in Fig. 3, the theoretical curve calculated by setting $r = 8.0\,Å$ (and $\lambda_{\rm S} = 1.59\,{\rm eV}$) fits in with the experimental plot. So the back ET within GRP is considered to occur at the electron donor and acceptor separation of 8.0 Å on average, although $r_{\rm q}$ ranges from 6.0 to 12 Å.

## 4. Summary and concluding remarks

All the results obtained in this work are compared with the previous ones obtained for the aromatic EDA system.

1. The switchover $\Delta G_{\rm fet} \approx -0.5\,{\rm eV}$ of quenching mechanism between exciplex formation and long-distance ET does not depend on whether quencher is aromatic or aliphatic. The quenching is induced by exciplex formation in the region $\Delta G_{\rm fet} > -0.5\,{\rm eV}$ and by long-distance ET in the region $\Delta G_{\rm fet} < -0.5\,{\rm eV}$.
2. The $\Delta G_{\rm fet}$ dependence of $k_{\rm q}$ for aliphatic quencher is different from that for aromatic quencher as shown in Fig. 1. The downhill region shifts from $\Delta G_{\rm fet} \approx -0.0$ to $-0.5\,{\rm eV}$ by changing the quencher from aromatic to aliphatic.
3. The $\Delta G_{\rm fet}$ dependence of $r_{\rm q}$ for aliphatic quencher is the same as that for aromatic quencher. As shown in Fig. 2, $r_{\rm q}$ increases almost linearly with a decrease in $\Delta G_{\rm fet}$ in the region $-2.0 < \Delta G_{\rm fet} < -0.3\,{\rm eV}$.
4. The $\Delta G_{\rm bet}$ dependence of $k_{\rm bet}$ does not depend on whether the quencher is aromatic or aliphatic. As shown in Fig. 3, $k_{\rm bet}$ is given by a theoretical calculation with the following fitting parameters, which are the same for both aromatic and aliphatic quenchers, $|V_0| = 120\,{\rm cm}^{-1}$, $r_{\rm D} = r_{\rm A} = 3\,Å$, $\lambda_{\rm v} = 0.25\,{\rm eV}$, $h\nu = 1500\,{\rm cm}^{-1}$, $\lambda_{\rm S} = 1.59\,{\rm eV}$.

Since the strength of electronic interaction for inducing ET is the same for both aromatic and aliphatic quenchers, the difference in $k_{\rm q}$ in the region $\Delta G_{\rm fet} > -0.5\,{\rm eV}$, where fluorescence quenching is due to exciplex formation, may be attributed to the difference in the stabilization energy of exciplex between aromatic and aliphatic quenchers. In the system of aromatic fluorescer and quencher, the exciplex can be especially stabilized by optimizing a face-to-face mutual orientation of two aromatic molecules. In the system of aromatic fluorescer and aliphatic quencher, in contrast, such a special stabilization cannot be expected. When aliphatic compound is used as quencher, therefore, the exciplex may readily dissociate to reproduce the parent species without electronic deactivation. If the exciplex dissociation occurs before the deactivation of exciplex, fluorescence quenching does not take place. If the deactivation of exciplex occurs rapidly before the exciplex dissociation, in contrast, $k_q$ is close to $k_{dif}$. If the exciplex dissociation competes well with the deactivation of exciplex, $k_q$ is smaller than $k_{dif}$. The sudden decrease in $k_q$ with increasing $\Delta G_{fet}$ in the region $\Delta G_{fet} > -0.5\,eV$ indicates that the face-to-face mutual orientation of two aromatic molecules is quite important for an exciplex formation.

If fluorescence quenching is induced by long-distance ET, $k_q$ is given by Eq. (9) [30]

$$\frac{1}{k_q} = \frac{1}{k_{dif}} + \frac{1}{k_{fet}} \tag{9}$$

where, $k_{fet}$ is the rate constant of long-distance ET at $r_q$. In the region $\Delta G_{fet} < -0.8\,eV$ where $r_q > r_D + r_A = 6\,Å$, $k_{fet}$ can be calculated by use of Eq. (6) together with the above fitting parameters and by replacing $r_{bet}$ with $r_q$ shown in Fig. 2. All the calculated values are close to $k_{dif}$ in agreement with the experimental results. In the region $\Delta G_{fet} > -0.5eV$, $k_{fet}$ cannot be calculated by use of Eq. (6) as long as $r_D = r_A = 3\,Å$ is assumed, because $r_q < r_D + r_A$. However the sudden decrease in $k_q$ with increasing $\Delta G_{fet}$ in the region $\Delta G_{fet} > -0.5\,eV$ evidences that the full ET in this region is not so fast as to bring about the diffusion-controlled fluorescence quenching.

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