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Electron-Transfer (ET) Fluorescence Quenching in Benzonitrile. Evidence of an Intermolecular ET with $\Delta G < -0.5$ eV being a Diffusion-Controlled Process

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The fluorescence quenching electron-transfer (ET) and the back ET within geminate radical ion pairs (GRIP) were studied in benzonitrile (BN) using anthracenecarbonitriles as electron-accepting fluorescers and amino-, methyl- and methoxybenzenes as electron-donating quenchers. A direct evidence that the long-distance ET fluorescence quenching takes place at the diffusion-controlled limit was found for the first time. Furthermore, the present results were compared with the previous ones obtained for the same fluorescer and quencher pairs in acetonitrile (AN) in order to examine whether the photoinduced ET reactions can be affected by the kind of solvent, i.e., aliphatic and aromatic, and particularly to make clear whether there happens to be a π-electron-mediate superexchange ET in BN. The free energy dependence of fluorescence quenching rate constant (k_q), effective quenching distance (r_q), free radical yield (Φ_R), and rate constant (k_{bet}) of back ET within GRIP in BN was the same as that in AN as long as the differences in dielectric constant, diffraction index, and viscosity between BN and AN were taken into account. The fact that there is no particular difference between photoinduced ET reactions in AN and BN evidences the absence of π-electron-mediate superexchange ET in BN.

1. Introduction

It is well-known that the electron-transfer (ET) fluorescence quenching phenomena consists of two kinds of ET: A forward ET between an excited fluorescer $^1D^*$ (or $^1A^*$) and a quencher A (or D) for producing a geminate radical pair ($D^{\bullet+}/A^{\bullet-}$) and a back ET within ($D^{\bullet+}/A^{\bullet-}$) for reproducing the ground state pair (D/A). In a fluid 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, the ET fluorescence quenching followed by back ET may be described as follows:

Scheme 1

$$^1D^* + A \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftharpoons}} (^1D^*/A) \xrightarrow[\Delta G_{fet}]{k_{fet}} (D^{\bullet+}/A^{\bullet-}) \qquad \text{or}$$

$$D + {}^1A^* \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftharpoons}} (D/^1A^*) \xrightarrow[\Delta G_{fet}]{k_{fet}} (D^{\bullet+}/A^{\bullet-})$$

Scheme 2

$$(D^{\bullet+}/A^{\bullet-}) \xrightarrow[\Delta G_{bet}]{k_{bet}} (D/A) \rightarrow D + A$$

Here, parentheses 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. k_{-dif} is the rate constant of diffusive separation of fluorescer and quencher without deactivation after encounter collision. The rate constant k_{dif} (in unit of dm^{-3} mol^{-1} s^{-1}) for diffusion of two spherical particles to an encounter distance is given by[1,2]

$$k_{dif} = 4\pi d_{cc} D N_A \tag{1}$$

Here, d_{cc} (in unit of cm) is the center to center distance of electron donor and acceptor at the encounter distance, D (in unit of cm^2 s^{-1}) is the sum of the diffusion coefficients of two particles in solution, and N_A is Avogadro's number. Equation 1 shows that k_{dif} is linear with respect to not only D but also d_{cc}. In the case of the fluorescence quenching due to the long-distance ET, i.e., the full ET without contact collision of pair species, the effective quenching distance r_q (i.e., the distance between pair species at the instant of fluorescence quenching) depends on the free energy change (ΔG_{fet}) of forward (full) ET: r_q increases with a decrease of ΔG_{fet}.[3,4c,e,f] Therefore, eq 1 may be available to evaluate the rate of fluorescence quenching due to long-distance ET.

When both D and A are neutral molecules, as described in Schemes 1 and 2, the forward and back ET are named as the charge separation (CS) type and the charge recombination (CR) type, respectively.

The free energy changes ΔG_{fet} of forward ET and ΔG_{bet} of back ET in acetonitrile with dielectric constant ϵ are defined

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for the CS type of forward ET and the CR type of back ET, respectively:[5]

$$\Delta G_{\mathrm{fet}} = E_{1/2}{}^{\mathrm{ox}} - E_{1/2}{}^{\mathrm{red}} - e^2/\epsilon r_{\mathrm{fet}} - E(\mathrm{S}_1) \qquad (2)$$

$$\Delta G_{\mathrm{bet}} = E_{1/2}{}^{\mathrm{red}} - E_{1/2}{}^{\mathrm{ox}} + e^2/\epsilon r_{\mathrm{bet}} \qquad (3)$$

Here, $E_{1/2}{}^{\mathrm{ox}}$, $E_{1/2}{}^{\mathrm{red}}$, and $E(\mathrm{S}_1)$ are the oxidation potential of D, the reduction potential of A, and the energy of fluorescent state. $e^2/\epsilon r_{\mathrm{fet}}$ and $e^2/\epsilon r_{\mathrm{bet}}$ are the Coulomb attraction energies for the geminate radical pairs at distances r_{fet} and r_{bet} where forward ET and back ET take place, respectively. It is noted that the value for r_{fet} is not necessarily the same as the value for r_{bet}, because both of the geminate radical pair species may diffuse at random within a solvent cage before proceeding to the back ET. In the case of the fluorescence quenching due to long-distance ET, r_{fet} corresponds to r_{q}. Therefore, the back ET may take place not only at the distance r_{q} but also at the other distances.

The back ET competes with the dissociation of $(\mathrm{D}^{\bullet+}/\mathrm{A}^{\bullet-})$ into free radical ion pairs:

Scheme 3

$$(\mathrm{D}^{\bullet+}/\mathrm{A}^{\bullet-}) \xrightarrow{k_{\mathrm{esc}}} \mathrm{D}^{\bullet+} + \mathrm{A}^{\bullet-}$$

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

$$\Phi_{\mathrm{R}} = k_{\mathrm{esc}}/(k_{\mathrm{esc}} + k_{\mathrm{bet}}) \qquad (4)$$

In previous work[4] a detailed mechanism of ET fluorescence quenching between aromatic compounds has been investigated in polar solvents such as acetonitrile (AN), 1,4-dichloromethane, and methanol. It was established that the fluorescence quenching mechanism depends on the effective quenching distance r_{q} and ΔG_{fet} and that the switchover of fluorescence quenching mechanism occurs at $\Delta G_{\mathrm{fet}} \approx -0.5$ eV. When $\Delta G_{\mathrm{fet}} > -0.5$ eV, the fluorescence quenching is induced by a partial ET at contact distance ($r_{\mathrm{q}} \leq 5$ Å) of fluorescer and quencher (i.e., by an exciplex formation) and the fluorescence quenching rate constant (k_{q}) decreases with increasing ΔG_{fet}. When $\Delta G_{\mathrm{fet}} < -0.5$ eV, the fluorescence quenching is induced by a long-distance ET ($r_{\mathrm{q}} > 5$ Å), k_{q} is close to the diffusion-controlled limit, and r_{q} increases with decreasing ΔG_{fet}. As long as the quenching products are the ground-state geminate radical pairs (GRIP), the rate constant (k_{bet}) of back ET within GRIP obtained by use of eq 4 shows the bell-shaped free energy dependence in agreement with the semiclassical theory of long-distance ET.[4]

In this work, we study the ΔG_{fet} dependence of fluorescence quenching mechanism and the ΔG_{bet} dependence of k_{bet} using anthracenecarbonitriles as electron-accepting fluorescers, amino-, methyl- and methoxybenzenes as electron-donating quenchers, and benzonitrile (BN) as solvent. All the results are compared with the results obtained for the same fluorescer-quencher pairs in AN to examine whether the π-electrons of solvent molecules affect the photoinduced ET and to make clear whether a long-distance ET can be mediated by the π-electrons of solvent molecules. Furthermore, a new evidence for the rate constant of fluorescence quenching ET between aromatic molecules in a highly polar solvent being a diffusion-controlled limit is given for the first time.

2. Experimental Section

The methods for syntheses and/or purifications of 9-cyanoanthracence (CA), 9,10-dicyanoanthracene (DCA), 2,6,9,10-tetracyanoanthracene (TeCA), 4-cyanoaniline (CN-Ani), aniline (Ani), anisole, *N*,*N*-dimethylaniline (DMAni), anisidine (AS), 4-phenylenediamine (PDA) have been reported elsewhere.[4b,c,e] 1,2-Dimethoxybenzene (*o*-DMB, Aldrich), 1,4-dimethoxybenzene (*p*-DMB; Tokyo Kasei), 4-bromo-*N*,*N*-dimethylaniline (Br-DMAni; Aldrich), 4-bromoanisole (Br-Anisole; Aldrich), and BN (HPLC grade, Aldrich) were used as received.

The absorption spectra were recorded on a Hitachi U-3500 spectrophotometer. The fluorescence and its excitation spectra were measured by a Hitachi F-4500 spectrophotometer. The fluorescence lifetimes τ_{f} were measured by a Horiba NAES-700 spectrophotometer.

The values of $E(\mathrm{S}_1)$ for CA, DCA, and TeCA were determined to be 2.99, 2.86, and 2.82 eV in BN, respectively. The values of τ_{f} for CA, DCA, and TeCA were determined to be 12.2, 12.0, and 12.6 ns in BN, respectively. The transient absorption spectra were measured by a conventional microsecond 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]

The molar extinction coefficient ϵ_{R} (λ_{max}) of the radical cation for diphenylamine (DPA) was determined to be 21 000 M^{-1} cm^{-1} at 680 nm by means of the triplet state ET from DPA to triplet acriflavine (ϵ_{T} (λ_{max}) = 8200 M^{-1} cm^{-1} at 660 nm). The molar extinction coefficient of acriflavine radical was also determined to be 16 400 M^{-1} cm^{-1} at 380 nm. ϵ_{R} (λ_{max}) for DCA and TeCA were determined to be 8400 M^{-1} cm^{-1} at 710 nm and 11 000 M^{-1} cm^{-1} at 600 nm, respectively, by means of the fluorescence quenching ET from DPA to these compounds.

The values for ΔG_{fet} and ΔG_{bet} in BN were calculated from those in AN[4c,e,f] by use of the Born equation.[7] The validity of these calculated values was confirmed by comparing them with the experimental values that were obtained from the measured values of $E_{1/2}{}^{\mathrm{red}}$ for DCA and $E_{1/2}{}^{\mathrm{ox}}$ for anisole, *p*-DMB, Ani, DMAni, AS, and PDA in BN with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte: $E_{1/2}{}^{\mathrm{red}} = -0.95$ V and $E_{1/2}{}^{\mathrm{ox}} = +1.93$, $+1.42$, $+0.95$, $+0.80$, $+0.65$, and, $+0.27$ V, respectively. One can easily confirm a good agreement between the calculated and measured values.

All measurements were made at 298 K.

3. Results and Discussion

3.1. ET Fluorescence Quenching. The rate constant k_{q} of fluorescence quenching in BN was 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} are listed in Table 1 together with ΔG_{fet}. The plot of k_{q} versus ΔG_{fet} in BN is shown in Figure 1 (○), which is similar to that obtained for the same fluorescer−quencher pairs in AN[4e,f] (△) and also to the Rehm−Weller plot[5] (small dots). Here, we compare the plot shown by ○ with that shown by △, because both plots were obtained for the same fluorescer−quencher pairs. The values for k_{q} in BN are 2 times or more lower than those in AN in the region $\Delta G_{\mathrm{fet}} < -0.5$ eV. This result may be attributed to the difference in solvent viscosity η: $\eta = 1.237$ cP at 298 K for BN and 0.341 cP at 298 K for AN.[8] Therefore, the ΔG_{fet} dependence of k_{q} does not depend on whether the solvent is aliphatic or aromatic as long as the difference in the rate of diffusion is taken into account.

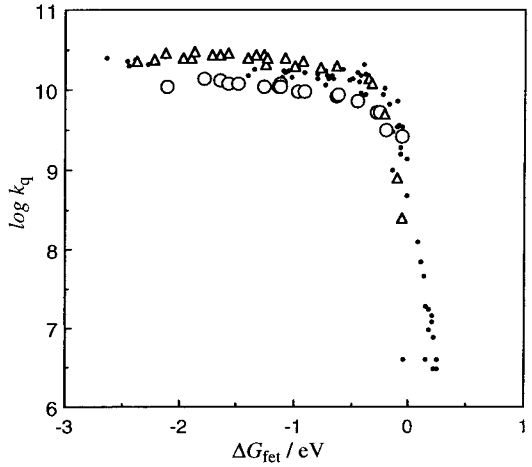

Figure 1. Plots of k_q versus ΔG_{fet}. Solvent: BN (○) and AN (△); the Rehm−Weller plot (small dots).

TABLE 1: Free Energy Changes of ET Fluorescence Quenching (ΔG_{fet}) and of the Back ET within GRIP (ΔG_{bet}), Fluorescence Quenching Rate Constants (k_q), Effective Quenching Distances (r_q), Free Radical Yields (Φ_R), and Rate Constants of GRIP Separation into Free Radicals (k_{esc}) and Back ET within GRIP (k_{bet}) in BN

F	Q	ΔG_{fet}, eV	k_q, 10^{10} M^{-1} s^{-1}	r_q, Å	Φ_R	k_{esc}, 10^8 s^{-1}	k_{bet}, 10^{10} s^{-1}	ΔG_{bet}, eV
CA	o-DMB	−0.06	0.26					−2.93
DCA	Anisole	−0.20	0.31	3.5				−2.55
CA	p-DMB	−0.26	0.52	3.5				−2.73
CA	CN-Ani	−0.28	0.53	3.5				−2.71
DCA	o-DMB	−0.45	0.71	4.8				−2.35
DCA	p-DMB	−0.62	0.87	6.7	0.048	4.18	0.83	−2.18
DCA	CN-Ani	−0.64	0.83	6.7	0.040	4.18	1.00	−2.16
TeCA	o-DMB	−0.91	0.95	7.7	0.017	4.32	2.50	−1.89
DCA	Ani	−0.97	0.95	9.7	0.019	4.12	2.13	−1.83
TeCA	p-DMB	−1.12	1.10	9.0	0.012	4.24	3.49	−1.70
TeCA	CN-Ani	−1.14	1.10	9.1	0.015	4.22	2.77	−1.68
DCA	DMAni	−1.13	1.20	10.0	0.015	4.06	2.66	−1.67
DCA	AS	−1.26	1.10	11.0	0.016	3.83	2.36	−1.54
TeCA	Ani	−1.49	1.20	11.0	0.018	3.83	2.09	−1.33
DCA	PDA	−1.58	1.20	11.0	0.036	3.83	1.02	−1.22
TeCA	DMAni	−1.65	1.30	11.0	0.035	3.83	1.06	−1.17
TeCA	AS	−1.78	1.40	12.0	0.063	3.60	0.53	−1.04
TeCA	PDA	−2.10	1.10	12.0	0.085	3.60	0.39	−0.72

The effective quenching distance r_q was determined by use of the modified Stern−Volmer equation[1] at such high quencher concentrations as 0.1−0.2 M. Even at such high quencher concentrations, the shape of the fluorescence spectrum was not changed. The values for r_q are listed in Table 1. As $r_q > 5$ Å in the region $\Delta G_{fet} < -0.5$ eV, the quenching mechanism in this region is considered to be the long-distance ET. In Figure 2 are shown the plots of r_q versus ΔG_{fet} in BN (○) and AN[4e,f] (△). In both cases, r_q increases linearly with a decrease of ΔG_{fet} and both plots overlap closely with each other. Both plots were obtained for the same fluorescer−quencher pairs. Therefore, the ΔG_{fet} dependence of r_q does not depend on whether the solvent is aliphatic or aromatic.

In the case of the fluorescence quenching in BN due to long-distance ET occurring at diffusion-controlled limit, k_{dif} and d_{cc} in eq 1 may be exchanged by k_q and r_q, respectively. Then, we obtain

$$k_q = 4\pi r_q D N_A \tag{5}$$

The plot of k_q versus r_q for the fluorescence quenching ET in BN (○) is shown in Figure 3, together with that in AN[4e,f] (△).

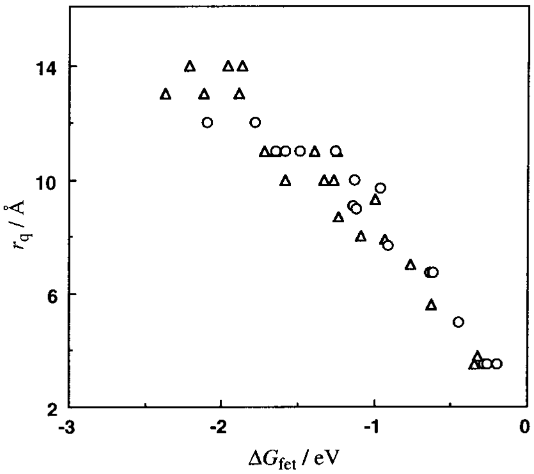

Figure 2. Plots of r_q versus ΔG_{fet}. Solvent: BN (○); AN (△).

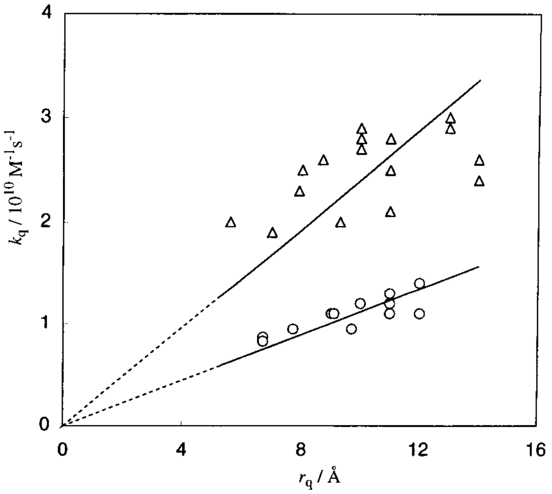

Figure 3. Plots of k_q versus r_q. Solvent: BN (○); AN (△).

Figure 3 seems to ensure the validity of eq 5, although the experimental points are dispersed at random, particularly in the case of AN. The slopes of the plots are 2.4×10^{17} and 1.1×10^{17} M^{-1} s^{-1} cm^{-1} for AN and BN, respectively. With these in eq 5, the average values of D for the fluorescer−quencher pairs in AN and BN are calculated to be 3.1×10^{-5} and 1.5×10^{-5} cm^2 s^{-1}, respectively. The validity of eq 5 is also confirmed by the fact that the average value of D for AN agrees with the reported one, $D = 3.5 \times 10^{-5}$ cm^2 s^{-1} in AN at 298 K.[1] In both cases of AN and BN, the ΔG_{fet} dependence of k_q is attributed to the ΔG_{fet} dependence of r_q according to eq 5. Therefore, the results shown in Figure 3 seem to indicate that the fluorescence quenching ET between aromatic molecules necessarily takes place at the diffusion-controlled limit in the region $\Delta G_{fet} < -0.5$ eV.

If the Stokes−Einstein relation[2] ($D = k_BT/6\pi\eta b$; b is the Stokes radius) is applied for AN with $\eta = 0.341$ cP at 298 K and BN with $\eta = 1.237$ cP at 298 K, the ratio in D of AN to BN is calculated to be 3.6, which is not consistent with the ratio 2.4 in D of the reported one for AN to the above average one for BN. In the later discussion, we adopt the above average value of D for BN as the sum of diffusion coefficients for the electron donor and acceptor (EDA) pairs in BN, because the macroscopic solvent viscosity η is not necessarily the same as the microscopic one.

In the region $\Delta G_{fet} \geq -0.5$ eV, $r_q < 5$ Å. Since it is close to the interplanar separation in the exciplex and the energy gap between the locally excited singlet state and the contact radical pair state is small in this region, fluorescence quenching is considered to be induced by exciplex formation, although

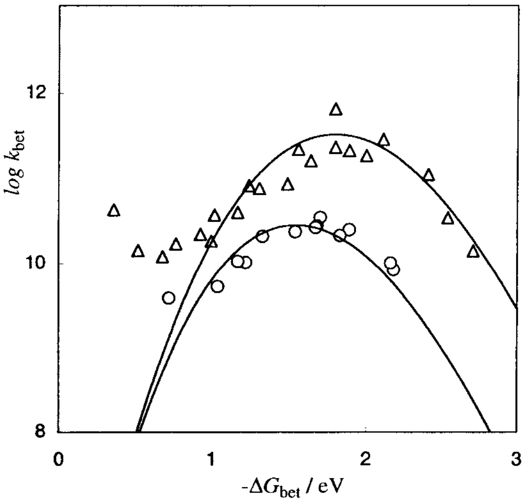

Figure 4. Plots for k_{bet} versus ΔG_{bet}. Solvent: BN (○); AN (△). The solid curve was calculated by use of eqs 8−11 with fitting parameters $\beta = 1.0$ Å^{-1}, $\lambda_{\mathrm{v}} = 0.25$ eV, $r_{\mathrm{A}} = r_{\mathrm{D}} = 3$ Å, $h\nu = 1500$ cm^{-1}, and $r_{\mathrm{bet}} = 10.5$ Å, $|V_0| = 120$ cm^{-1}, and $\lambda_{\mathrm{S}} = 1.33$ eV for BN; $r_{\mathrm{bet}} = 8.0$ Å, $|V_0| = 120$ cm^{-1}, and $\lambda_{\mathrm{S}} = 1.58$ eV for AN.

exciplex fluorescence was not observed. In the region $\Delta G_{\mathrm{fet}} < -0.5$ eV, in contrast, $r_{\mathrm{q}} > 5$ Å, indicating that fluorescence quenching is induced by long-distance ET. Therefore, the switchover of the fluorescence quenching mechanism between exciplex formation and long-distance ET is considered to take place at $\Delta G_{\mathrm{fet}} \approx -0.5$ eV.

To confirm that the quenching mechanism in the region $\Delta G_{\mathrm{fet}} \geq -0.5$ eV is the exciplex formation, the heavy atom effects on the triplet yield Φ_{T} and the free radical yield Φ_{R} in fluorescence quenching were studied using Br−anisole and Br−DMAni as quenchers. If fluorescence quenching is induced by exciplex formation, Φ_{T} is expected to be strongly enhanced by a heavy atom substitution on the quencher, because the intersystem crossing within the exciplex can be strongly enhanced by a heavy atom involved in the fluorescer and/or quencher.[4b] If fluorescence quenching is induced by long-distance ET, in contrast, Φ_{T} is not so much enhanced by the heavy atom substitution.[4b]

In the case of the DCA−anisole pair with $\Delta G_{\mathrm{fet}} = -0.20$ eV, Φ_{T} increases from 0.11 to 0.86 by the Br substitution, whereas Φ_{R} decreases that from 0.089 to 0.010, indicating that the fluorescence quenching is induced by exciplex formation. In the case of the DCA−DMAni pair with $\Delta G_{\mathrm{fet}} = -1.13$ eV, in contrast, Φ_{T} is only 0.004 even upon the Br substitution whereas Φ_{R} decreases from 0.015 to 0.010, indicating that the fluorescence quenching is not induced by exciplex formation but by long-distance ET.

Thus, the ΔG_{fet} dependence of quenching mechanism does not depend on whether the solvent is aliphatic or aromatic.

3.2. Back Electron Transfer within GRIP. Flashing of the solution containing fluorescer (10^{-4} to 10^{-5} M) and quencher (1−6 mM) gives the transient absorption due to fluorescer radical anion and quencher radical cation.

When fluorescence quenching is induced by long-distance ET for producing GRIP, Φ_{R} may be given by eq 4. According to the Tachiya theory,[9] k_{esc} for oppositely monocharged GRIP ($\mathrm{D}^{\bullet+}/\mathrm{A}^{\bullet-}$) is given by

$$k_{\mathrm{esc}} = Dr_{\mathrm{c}}/[r_{\mathrm{q}}^{\,3}\{\exp(r_{\mathrm{c}}/r_{\mathrm{q}}) - 1\}] \tag{6}$$

Here, r_{c} is the Onsager distance and D has been evaluated to be 1.5×10^{-5} cm^2 s^{-1}:

$$r_{\mathrm{c}} = e^2/\epsilon k_{\mathrm{B}}T \tag{7}$$

Here, k_{B} is the Boltzman constant. r_{c} is calculated to be 22.2 Å in BN.

The k_{esc}'s were calculated by use of eq 6, as listed in Table 1. The k_{bet}'s were calculated from the Φ_{R}'s by use of eqs 4, as listed in Table 1. In Figure 4, the k_{bet}'s are plotted with respect to ΔG_{bet} (○). k_{bet} may be given by[10−13]

$$k_{\mathrm{bet}} = \left(\frac{4\pi^3}{h^2\lambda_{\mathrm{S}}k_{\mathrm{B}}T}\right)^{1/2}|V|^2 \times \sum_{w=0}^{\infty}\left(\frac{e^{-S}S^w}{w!}\right)\exp\left\{-\frac{(\lambda_S + \Delta G_{\mathrm{bet}} + wh\nu)^2}{4\lambda_{\mathrm{S}}k_{\mathrm{B}}T}\right\} \tag{8}$$

Here

$$\lambda_S = e^2/8\pi\epsilon_0(1/r_{\mathrm{A}} + 1/r_{\mathrm{D}} - 2/r_{\mathrm{bet}})(1/n^2 - 1/\epsilon) \tag{9}$$

$$|V|^2 = |V_0|^2 \exp[-\beta\{r_{\mathrm{bet}} - (r_{\mathrm{A}} + r_{\mathrm{D}})\}] \tag{10}$$

$$S = \lambda_{\mathrm{v}}/h\nu \tag{11}$$

r_{D} and r_{A} are the radii of electron donor and acceptor, r_{bet} is their center-to-center separation at the instant of back ET, and n and ϵ are the solvent refractive index and the solvent dielectric constant.

To fit the theory and experiment as best we can, the parameters other than r_{bet} were assumed to be the same as used in previous work on the same EDA pairs in AN: the reactant vibrational reorganization energy, $\lambda_{\mathrm{v}} = 0.25$ eV; the average energy of active vibrational mode, $h\nu = 1500$ cm^{-1}; the radii of electron donor and acceptor, $r_{\mathrm{D}} = r_{\mathrm{A}} = 3$ Å; the attenuation parameter, $\beta = 1$ Å^{-1}; the electron exchange matrix element at contact distance of the EDA pair, $|V_0| = 120$ cm^{-1}. The best fitting curve was obtained by setting $r_{\mathrm{bet}} = 10.5$ Å (according to eq 9, $\lambda_{\mathrm{S}} = 1.33$ eV), as shown in Figure 4. The upward deviation of the plot at $\Delta G_{\mathrm{bet}} = -0.72$ eV ($\Delta G_{\mathrm{fet}} = -2.10$ eV) suggests that the primary quenching products is not only the ground-state GRIP, ($\mathrm{D}^{\bullet+}/\mathrm{A}^{\bullet-}$), but also the excited-state GRIP, ($\mathrm{D}^{\bullet+*}/\mathrm{A}^{\bullet-}$) or ($\mathrm{D}^{\bullet+}/\mathrm{A}^{\bullet-*}$).[4c] Therefore, the fitting between the theory and experiment is almost good. The difference in the ΔG_{bet} dependence of k_{bet} between AN and BN is only due to the differences in r_{bet} and λ_{S} between AN and BN. The longer distance of r_{bet} in BN than AN may result from the difference in the solvent viscosity: In BN with higher viscosity, the back ET takes place at separation around r_{q}, because the rate of diffusion decreases with increase of solvent viscosity. Then, the upward deviation of the plots in the region $\Delta G_{\mathrm{bet}} < -2.0$ eV may be attributed to the shorter quenching distance such as $r_{\mathrm{q}} = 6.7$ Å compared with the distance ($r_{\mathrm{bet}} = 10.5$ Å) used for the theoretical calculation: In BN, the back ET tends to take place at separation close to r_{q} before the geminate radical pair species diffuses up to their separation of 10.5 Å.

Therefore, the ΔG_{bet} dependence of k_{bet} does not depend on whether the solvent is aliphatic or aromatic as long as the difference in the rate of diffusion is taken into account.

Finally, we have to confirm that eq 8 and the parameters employed for drawing the theoretical curve for BN can reproduce the plot of k_{q} versus ΔG_{fet} in the region -2.0 eV <

$\Delta G_{\text{fet}} < -0.5$ eV, where fluorescence quenching is induced by long-distance ET.

Applying the steady-state approximation to Scheme 1 we obtain

$$k_q = k_{\text{dif}}\, k_{\text{fet}}/(k_{\text{fet}} + k_{-\text{dif}}) \tag{12}$$

k_{fet} can be calculated by use of eq 8 together with the above fitting parameters and r_q. If there is no Coulombic interaction between the fluorescer and quencher, $k_{-\text{dif}}$ may be given by[9]

$$k_{-\text{dif}} = D/r_q^{\;2} \tag{13}$$

Therefore, we obtain

$$1/k_q = 1/k_{\text{dif}} + 1/k_{\text{el}} \tag{14}$$

Here

$$k_{\text{el}} = k_{\text{fet}}(k_{\text{dif}}/k_{-\text{dif}}) \tag{15}$$

From eqs 13 and 1 with setting $d_{cc} = r_q$ we obtain

$$k_{\text{dif}}/k_{-\text{dif}} = 4\pi r_q^{\;3} N_A \tag{16}$$

In the present case, r_q ranges from 6.7 to 12 Å and hence $k_{\text{dif}}/k_{-\text{dif}}$ ranges from 2.3 to 13 M^{-1}. The values for k_{fet} in the region $-2.0 < \Delta G_{\text{fet}} < -0.5$ eV can be calculated by use of eqs 8−11 and r_q listed in Table 1. Thus, $k_{\text{el}} = k_{\text{fet}}(k_{\text{dif}}/k_{-\text{dif}})$ ranges from 2.8×10^{11} s^{-1} (for $r_q = 6.7$ Å) to 4.5×10^{10} s^{-1} (for $r_q = 12$ Å), whereas k_{dif} ranges from 7.6×10^9 M^{-1} s^{-1} (for $r_q = 6.7$ Å) to 1.3×10^{10} M^{-1} s^{-1} (for $r_q = 12$ Å). As $k_{\text{el}} \gg k_{\text{dif}}$, eq 14 is reduced to $k_q \approx k_{\text{dif}:}$ The fluorescence quenching ET takes place at the diffusion-controlled limit in the region $-2.0 < \Delta G_{\text{fet}} < -0.5$ eV. Therefore, the validity of eq 5 obtained by exchanging k_{dif} for k_q and d_{cc} for r_q is confirmed in the region $-2.0 < \Delta G_{\text{fet}} < -0.5$ eV.

4. Conclusions

(1) Figure 3 confirms the validity of eq 5, indicating that the fluorescence quenching ET between aromatic molecules in a highly polar solvent is necessarily the diffusion-controlled process in the region $-2.0 < \Delta G_{\text{fet}} < -0.5$ eV.

(2) Both fluorescence quenching ET and back ET are not affected by the kind of solvent, i.e., aliphatic AN and aromatic BN, if the difference in the solvent characteristics such as dielectric constant, diffraction index, and viscosity are taken into account. Therefore, the solvent-mediate superexchange mechanism does not participate in the photoinduced ET reactions in BN. The π-electron of BN is not considered to participate in the superexchange ET.

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