Electric Field Effects on Fluorescence Quenching Due to Electron Transfer

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Electric field effects on fluorescence quenching due to electron transfer

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The effect of an external electric field on fluorescence quenching due to electron transfer from a photoexcited electron donor to an acceptor has been analyzed theoretically. The model predicts that at weak fields the variation $\Delta I(c,F)/I(c,0)$ in the steady-state monomer fluorescence intensity induced by an external electric field is proportional to the square of the field strength F and to the concentration of acceptors c. Similar relations have been reported for the fluorescence intensity of ethylcarbazole doped in poly-methyl-methacrylate films in the presence of dimethyl terephthathalate and an external electric field with a strength up to 0.01 V/Å. The effect of the free energy change of the electron transfer reaction on the c and F dependencies of $\Delta I(c,F)/I(c,0)$ has been discussed within the framework of the present model. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1421364]

I. INTRODUCTION

The number of studies concerning the field effect on the initial step of intramolecular and intermolecular electron transfer processes is very limited. The majority of papers relate to dissociation and recombination of the produced radical-ion pairs. These processes are important for explanation of the mechanism of photocarrier generation in, e.g., photoconductive polymers.[1–5] Other studies on external electric field effects on chemical reactions include those on electric field effects on diffusion-controlled bulk recombination.[6–8] The influence of an external electric field on the charge separation in the photosynthetic reaction center has been interpreted in terms of the field effect on the initial step of electron transfer.[9] Recently the extensive measurements of the field-affected fluorescence intensity were made by Ohta and co-workers for systems with donor and acceptor molecules doped in poly-methyl-methacrylate (PMMA) at room temperature. One of the systems investigated by that group was composed of *N*-ethylcarbazole (ECZ) as the electron donor and dimethyl terephthalate (DMPT) as the electron acceptor.[10–12] They have found[10] that the rate of electron transfer from the photoexcited ECZ to DMTP is enhanced by the external electric field, depending on the applied concentration c of DMTP. The influence of the acceptor concentration, which was especially clear in the ECZ electrofluorescence spectra, indicates that the electron transfer rate in PMMA polymer films depends on the average distance or, more precisely, on the distribution of distances between electron donor and acceptor molecules.

Due to a large dipole moment $\boldsymbol{\mu}$, which usually appears in a radical-ion pair produced in the charge separation process, the free energy difference ΔG of this process changes in the presence of an external electric field $\mathbf{F}$. As the electron transfer rate k is a function of the free energy difference,[13–15] we can expect that the rate of reaction producing a radical-ion pair is influenced by $\mathbf{F}$, depending on the magnitude of $\boldsymbol{\mu}$ and its orientation relative to the direction of the applied field. To express quantitatively the contribution of an external electric field to the free energy gap ΔG one should take into account the change of the solvent–solute interaction energy induced by $\mathbf{F}$. It has been shown,[16] however, that this leads to only a small correction, which is less than 10%, with respect to the term $\boldsymbol{\mu}\cdot\mathbf{F}$. Thus, it is acceptable to adopt for the free energy difference the simple formula

$$\Delta G(r,\mathbf{F}) = \Delta G(r) - \boldsymbol{\mu}\cdot\mathbf{F}, \tag{1}$$

and take the Marcus electron transfer rate constant k in the form

$$k(r,\mathbf{F}) = \frac{2\pi}{\hbar} \frac{J^2(r)}{\sqrt{4\pi\lambda(r)k_B T}} \times \exp\left\{ -\frac{[\Delta G(r,\mathbf{F}) + \lambda(r)]^2}{4\lambda(r)k_B T} \right\}, \tag{2}$$

where $\hbar$ is the Planck constant divided by 2π, J is the transfer integral which is determined by the overlap between the initial-state and the final-state electronic wave functions, k_B is the Boltzmann constant, and T is the temperature. The quantity λ is given by the sum

$$\lambda(r) = \lambda_s(r) + \lambda_i. \tag{3a}$$

λ_s is the solvent reorganization energy, which can be expressed in the framework of the dielectric continuum model as

$$\lambda_s(r) = \frac{e^2}{2}\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right)\left(\frac{1}{a} + \frac{1}{d} - \frac{2}{r}\right), \tag{3b}$$

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where e is the electronic charge, ϵ_{op} and ϵ_s are the solvent optical and static dielectric constants, and a and d are the radii of an electron acceptor and donor, respectively. λ_i in Eq. (3a) stands for the vibrational reorganization energy connected with the average skeletal vibrations of the donor and acceptor molecules and can be assumed as equal to 0.3 eV.[17] The rate constant (2) depends on the applied electric field and also on the donor–acceptor distance r. The latter dependence comes through the reorganization energy (3), the transfer integral[18] J,

$$J^2(r) = J_0^2 \exp\{-\beta[r-(a+d)]\}, \tag{4}$$

the dipole moment μ, and the energy gap ΔG at zero electric field[19]

$$\Delta G(r) = \Delta G_0 - \frac{e^2}{\epsilon_s r}. \tag{5}$$

J_0 and β in Eq. (4) are the constant parameters appropriate to a given donor–acceptor system and have the meaning of the transfer integral at the encounter distance and the attenuation constant of the transfer integral, respectively. ΔG_0 in Eq. (5) is the standard Gibbs free energy gap, equivalent to $\Delta G(\infty)$.

In the present paper we investigate, starting from the rate constant (2), the effect of an external electric field on the initial step of intermolecular electron transfer process, which creates radical-ion pairs with a distribution of distances r. This field effect can be observed experimentally as an enhanced quenching of the fluorescence emitted by excited monomers (e.g., donors), or as an enhanced exciplex (ion-pair) fluorescence resulting from electron transfer reaction. Our model provides an expression for the change $\Delta I(c,F)/I(c,0)$ in the steady-state fluorescence intensity of the excited donor in the presence of acceptors and weak external electric fields $\mathbf{F}$, and relates it directly to the experimental results of Ohta et al.[10]

II. MODEL

Our treatment is based on the calculation of the survival probability $P(t,\mathbf{F})$ of an excited donor and is in accord with the approach presented in Refs. 20 and 21. Suppose that donor molecules are excited at time $t=0$. In the absence of electron acceptors their excitation disappears with the rate constant k_0, which is assumed to describe the processes other than electron transfer and independent of the acceptor concentration c. We can write this rate constant as $k_0 = 1/\tau_0$, where τ_0 is the monomer fluorescence lifetime measured at $c=0$. When acceptors are present, the donor fluorescence is quenched additionally by electron transfer processes to the acceptor molecules. We assume that the donor and acceptor molecules are randomly distributed within the matrix and their positions do not change on the time scale of experiments considered.

Let $k(r_i,\mathbf{F})$ denote the rate constant for electron transfer from an excited donor molecule at the origin to the acceptor molecule placed at $\mathbf{r}_i$, where $r_i = |\mathbf{r}_i|$. If N is the total number of acceptor molecules in the volume V, then the probability that the excited donor will survive at time t can be expressed as

$$P(t,\mathbf{F}) = \exp\left[-tk_0 - t\sum_{i=1}^{N} k(r_i,\mathbf{F})\right]. \tag{6}$$

The rate constant $k(r_i,\mathbf{F})$ is assumed to have the Marcus form (2) and its dependence on the external electric field $\mathbf{F}$ comes through the free energy change ΔG of the electron transfer reaction in accordance with Eq. (1). The decay described by Eq. (6) depends on the arrangement of acceptor molecules around the electron donor. The experimental observable is the statistical average of $P(t,\mathbf{F})$ over all such arrangements. Hence, with $u(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ denoting the probability density of finding acceptor molecule 1 at a position $\mathbf{r}_1$, 2 at $\mathbf{r}_2$, etc., the ensemble averaged survival probability $P(t,\mathbf{F})$ of the excited monomer takes the form

$$P(t,\mathbf{F}) = \exp(-tk_0) \int_V \int_V \cdots \int_V \exp\left[-t\sum_{i=1}^{N} k(r_i,\mathbf{F})\right]$$
$$\times u(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N. \tag{7}$$

For a uniform distribution of acceptors we have

$$u(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \frac{1}{V^N}. \tag{8}$$

Substitution of Eq. (8) in Eq. (7) yields

$$P(t,\mathbf{F}) = \exp(-tk_0)\left\{\frac{1}{V}\int_V \exp[-tk(r,\mathbf{F})]d\mathbf{r}\right\}^N$$
$$= \exp(-tk_0)\left\{1 - \frac{1}{V}\int_V [1-e^{-tk(r,\mathbf{F})}]d\mathbf{r}\right\}^{cV}, \tag{9}$$

where $c=N/V$. Since $k(r,\mathbf{F})$ drops to zero with increasing r, the integral in Eq. (9) approaches a finite value with increasing V. Taking the limit $V\to\infty$ we obtain

$$P(t,\mathbf{F}) = \exp(-tk_0)\exp\left\{-c\int_V [1-e^{-tk(r,\mathbf{F})}]d\mathbf{r}\right\}. \tag{10}$$

Choosing the z axis along the external electric field $\mathbf{F}$ and denoting the polar angle of the dipole moment $\boldsymbol{\mu}=e\mathbf{r}$ of the produced ion-pair state by θ we can rewrite Eq. (10) as

$$P(t,F) = \exp\left\{-tk_0 - 2\pi c\right.$$
$$\left.\times \int_{a+d}^{\infty}\int_0^{\pi} [1-e^{-tk(r,\mathbf{F})}]r^2 \, dr \sin\theta \, d\theta\right\}, \tag{11}$$

where $F=|\mathbf{F}|$ is the strength of the applied field. In the absence of the electric field (11) reduces to[20,21]

$$P(t,0) = \exp\left\{-tk_0 - 4\pi c\int_{a+d}^{\infty} [1-e^{-tk(r,0)}]r^2 \, dr\right\}. \tag{12}$$

When the electric field is weak, the survival probability (11) can be expanded in terms of F as

$$P(t,F) = P(t,0)\left[1 - \frac{cF^2}{6}\int_{a+d}^{\infty} M(t,r)e^{-tk(r,0)}r^2 \, dr\right], \tag{13}$$

where

$$M(t,r) = \frac{\pi k(r,0)t\mu^2}{[k_B T\lambda(r)]^2}\{[\Delta G(r)+\lambda(r)]^2$$
$$\times [1-tk(r,0)]-2k_B T\lambda(r)\}, \tag{14}$$

$\mu = |\boldsymbol{\mu}|$, and $\Delta G(r)$ is given by Eq. (5).

The steady-state monomer fluorescence intensity is obtained by integrating the survival probability $P(t,F)$ over time t,

$$I(c,F) = k_f \int_0^\infty P(t,F)dt, \tag{15}$$

and its variation induced by the external electric field is

$$\frac{\Delta I(c,F)}{I(c,0)} = \frac{I(c,F)}{I(c,0)} - 1, \tag{16}$$

where k_f is the radiative rate constant. If the electric field is weak, Eq. (16) can be rewritten as

$$\frac{\Delta I(c,F)}{I(c,0)} = F^2 \eta(c,\Delta G_0), \tag{17}$$

where

$$\eta(c,\Delta G_0)$$
$$= -\frac{1}{6}c\frac{\int_0^\infty P(t,0)\int_{a+d}^\infty M(t,r)\exp[-tk(r,0)]r^2\,dr\,dt}{\int_0^\infty P(t,0)dt}. \tag{18}$$

As is clear from the last two expressions, the values of I and ΔI depend on both the concentration of acceptors c in the considered matrix and the strength of the applied field F. Equation (17) predicts that at weak electric fields the quantity $\Delta I(c,F)/I(c,0)$ is proportional to F^2. This relation can be directly compared with the corresponding experimental data.

III. COMPARISON WITH EXPERIMENT

Equation (17) allows us to link our model to available experimental data. To perform the calculations based on this equation we should know, however, the values of the parameters for a particular electron donor–acceptor system. Within the framework of the dielectric continuum model these parameters appear in Eqs. (1)–(5). As the system for verification of our model we choose a mixture of ECZ and DMTP doped in PMMA polymer film. This system was studied experimentally by Ohta and co-workers.[10] We can assume that in a rigid matrix, such as a PMMA polymer film, the originally generated isotropic distribution of dopants is maintained even in the presence of an applied electric field.

The physical properties of the PMMA matrix at room temperature (298 K) are as follows:[22] the density 1.19 g/cm^3, the static dielectric constant $\epsilon_s = 3.6$, the optical dielectric constant $\epsilon_{op} = 1.05\,n^2$, and the refractive index $n = 1.489$. We assume the radii of the acceptor and donor molecules as $a = d = 3$ Å.

The values of ΔG_0, J_0, and β have been obtained by fitting Eq. (12) to the time-resolved donor fluorescence intensity for the acceptor concentration $c = 2$ mol % (the third
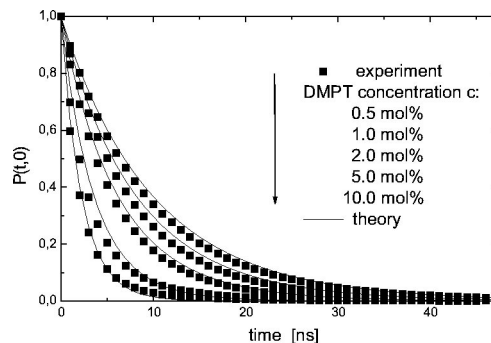

FIG. 1. Survival probability of the excited ECZ (1 mol %) with different concentrations of DMTP (0.5; 1.0; 2.0; 5.0; 10.0 mol % from top to bottom). Lines correspond to the theoretical predictions based on Eq. (12) for $F = 0$ V/Å and closed squares are the experimental data (Ref. 10) on fluorescence decays of ECZ normalized to unity.

curve in Fig. 1) and Eq. (16) to the field-induced variation in the steady-state fluorescence intensity measured for various values of c (Fig. 3). The optimization procedure employed the nonlinear regression method based on the Levenberg–Marquardt algorithm. The values of the parameters, which are appropriate for the two curves, are as follows: $\Delta G_0 = -0.912$ eV, $\beta = 0.445$ Å^{-1}, $J_0 = 4.29\times10^{-4}$ eV.

Closed squares in Fig. 1 show the fluorescence decays of ECZ in a mixture of ECZ and DMTP with different concentrations of DMTP. These decays were taken from Ref. 10, but the maximum fluorescence intensity for each curve has been normalized to unity. The concentration of ECZ was constant in all experiments and equal to 1 mol % in the molar ratio to the monomer unit of PMMA. The acceptor concentration was ranged from 0.5 to 10 mol %. The lines in Fig. 1 show the functions $P(t,0)$ fitted to the experimental decay curves. It is worth noting that the donor fluorescence in the absence of acceptors shows a single-exponential decay with a lifetime of 12.5 ns. It corresponds to the rate constant $k_0 = 8\times10^7$ s^{-1}, which was used in the present calculations.

Figure 2 shows the variation $\Delta I(c,F)/I(c,0)$ in the steady-state fluorescence of the excited donor in the presence of the DMTP acceptors with concentration of 2 mol % as a
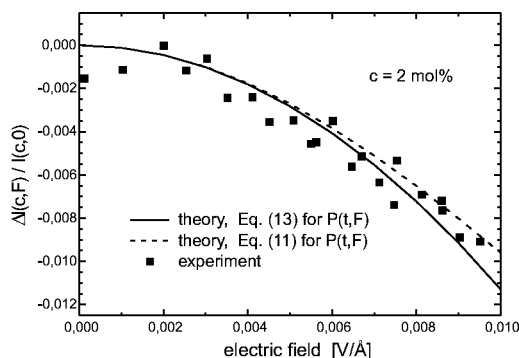

FIG. 2. Dependence of the fluorescence intensity change $\Delta I(c,F)/I(c,0)$ of the excited ECZ in the presence of DMTP acceptor (concentration $c = 2$ mol %) on the external electric field strength F. The full line corresponds to the theoretical predictions based on Eq. (17) with survival probability $P(t,F)$ given by Eq. (13). The dotted line shows $\Delta I(c,F)/I(c,0)$ obtained based on $P(t,F)$ given by exact expression (11). Solid squares are the experimental data (Ref. 10).
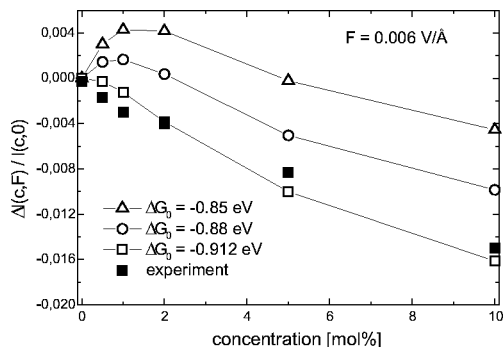
FIG. 3. Dependence of the fluorescence intensity change $\Delta I(c,F)/I(c,0)$ of the excited ECZ on concentration of DMTP doped in PMMA films obtained at $F=6\times10^{-3}$ V/Å. Open symbols correspond to the theoretical predictions based on Eq. (16) with $\Delta G=-0.912$ eV (open squares), -0.88 eV (open circles), and -0.85 eV (open triangles), respectively. Solid squares are the experimental data (Ref. 10).
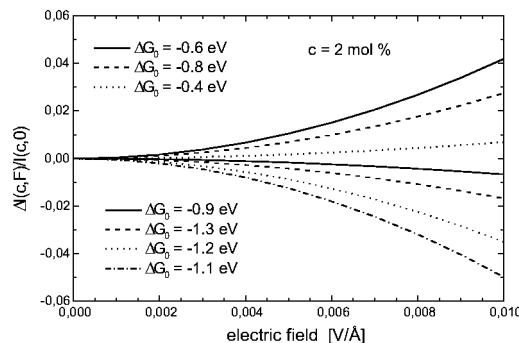

FIG. 4. Dependence of the fluorescence intensity change $\Delta I(c,F)/I(c,0)$ of the excited ECZ in the presence of DMTP acceptor on the external electric field strength F calculated for various values of the free energy change ΔG_0. The upper and the lower legends correspond, respectively, to the curves in the upper and the lower parts of the figure. The concentration of DMTP equals $c=2$ mol %.

function of the external electric field strength F. The squares represent the experimental values measured by the Ohta group, whereas the full line was evaluated from Eqs. (17) and (18) with the aforementioned values of the parameters. Although experimental points are scattered, the theoretical curve seems to predict properly the trend of the experimentally obtained dependence. Note that Eq. (17) has been obtained from the Taylor expansion (13) of the exact expression (11) for the survival probability of the excited donor state, $P(t,F)$, which is valid at small F. To show accuracy of Eq. (17) we should compare it with the quantity $\Delta I(c,F)/I(c,0)$ calculated based on Eqs (15) and (11). The F dependence of this quantity is presented in Fig. 2. As can be seen, the approximate function (full line) does not deviate appreciably from the exact function (dotted line) if the applied electric field strengths F is lower than 0.007 V/Å.

Equations (17) and (18) also predict that the quantity $\Delta I(c,F)/I(c,0)$ should be approximately proportional to the acceptor concentration c. Rigorously speaking, however, in Eq. (18) $P(t,0)$ also depends on c and this dependence causes some deviation from the linear relationship, as shown in Fig. 3. The closed squares in Fig. 3 represent the experimental values taken from Ref. 10 and the theoretical values of $\Delta I(c,F)/I(c,0)$ calculated with the free energy change $\Delta G_0=-0.912$ eV are represented by the open squares. Like in the previous case, agreement between theory and experiment seems to be reasonably good.

IV. EFFECT OF THE FREE ENERGY CHANGE ON THE ELECTRIC FIELD DEPENDENCE OF FLUORESCENCE INTENSITY

The results presented in Sec. III show that for the particular donor–acceptor system our model correctly reproduces the variation in the steady-state monomer fluorescence intensity induced by the applied electric field. In this section we present some theoretical predictions on the electric field effects on the steady-state monomer fluorescence intensity for other electron-transfer systems with different values of the standard free energy change ΔG_0.[22]

The additional curves with open symbols plotted in Fig. 3 for ΔG_0 equal to -0.88 and -0.85 eV illustrate how the electric field effect depends on the quencher concentration for other values of ΔG_0. Except for the free energy change, the values of the parameters employed in the calculation of these curves were exactly the same as those which produce the curve for $\Delta G_0=-0.912$ eV. Figure 3 shows that for the systems with less negative values of the free energy change the steady-state monomer fluorescence intensity can be enhanced by the external electric field. This behavior is rather unexpected although it has been recently observed experimentally for a methylene-linked compound of phenanthrene and phthalimide in a PMMA polymer film.[23]

According to our predictions, if $\Delta G_0=-0.85$ eV, the fluorescence intensity is enhanced by the field of strength $F=6\times10^{-3}$ V/Å in a range of acceptor concentrations from 0 to about 5 mol %. With further increase of c the fluorescence intensity is suppressed by $\mathbf{F}$. When the free energy difference takes the value of -0.88 eV, the field-induced enhancement of fluorescence is limited only to $c<2.1$ mol %. For more negative values of ΔG_0 the quenching occurs in the whole range of acceptor concentrations.

The dependence of $\Delta I(c,F)/I(c,0)$ on the field strength F is presented in Fig. 4 for the values of the free energy change ranging from -1.3 up to -0.4 eV. In Fig. 4 the acceptor concentration is fixed at $c=2$ mol %. All curves show the quadratic dependence of the field-induced variation in the steady-state monomer fluorescence intensity on F, but the strength of this dependence is strongly affected by the assumed value of the free energy change. Moreover, as in Fig. 3, we observe the enhancement of fluorescence for less negative values of ΔG_0 and the quenching for more negative values. However, the strength of the F dependence of $\Delta I(c,F)/I(c,0)$ does not change monotonously with ΔG_0. This is illustrated in Fig. 5, where we show the coefficient η for the F^2 term in the expression $\Delta I(c,F)/I(c,0)$ as a function of the free energy change for a variety of acceptor concentrations c. Negative values of η represent the field-induced reduction of fluorescence intensity, whereas positive
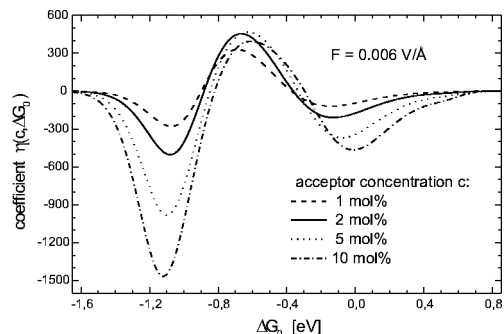
FIG. 5. Coefficient η for the F^2 term in the expression $\Delta I(c,F)/I(c,0)$ plotted as a function of the free energy change ΔG_0 for several different acceptor concentrations c.

values correspond to the fluorescence enhancement. As can be seen, all the curves have two distinct minima and one maximum. The first minimum at $\Delta G_0 \cong -1.1$ eV is very deep, whereas the second minimum is shallow and broad and its position shifts from -0.14 to 0 eV as the concentration of acceptors increases from 1 to 10 mol %. The depths of these minima depend significantly on c. The maximum value of η also depends on c. The functions $\eta(c, \Delta G_0)$ pass through zero twice, at about -0.3 eV and in the energy range from -0.8 to -0.9 eV, depending on the value of c.

V. CONCLUDING REMARKS

We theoretically investigated the external electric field effect on fluorescence quenching in the electron donor and acceptor systems. Starting from the basic model we evaluated the expression for the steady-state monomer fluorescence intensity $I(c,F)$ as a function of acceptor concentration c and the field strength F. We found that its variation $\Delta I(c,F)/I(c,0)$, induced by an applied electric field, properly reproduces the available experimental data.[10] Within the present model we predicted that for some values of the free energy change ΔG_0 and the acceptor concentration c the electric field can enhance the monomer fluorescence intensity instead of quenching. Such a field-induced enhancement of fluorescence has been recently reported experimentally for a donor and acceptor with a fixed distance.[23] In the present model the distance r between donor and acceptor molecules is distributed and the field-induced variation in the steady-state fluorescence intensity is expressed as the integral over r. In order to understand the origin of the fluorescence enhancement due to the external electric field, it is more pref-

erable to analyze a simpler system, in which donor and acceptor molecules are kept at a fixed distance. Such studies are in progress in our laboratory.

Although the model, which employs the simplest form of the Marcus equation (2), is able to reproduce experimental results rather well, admittedly it is oversimplified. We can improve it by taking into account: (i) the more exact expression for the contribution of intramolecular vibrations[17] in the electron transfer rate expression, (ii) the influence of the Stark effect on the measured values of the emission intensity change ΔI of ECZ, and (iii) the Lorentzian correction[24] f to the external electric field $\mathbf{F}$, which affects the value of ΔG for electron transfer process and is of the order of $f \approx (\epsilon_s + 2)/3 \approx 1.87$ for the PMMA system.

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