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External electric field effects on exciplex formation of 1,1-diphenylpropene with chiral 1,4-naphthalenedicarboxylate in PMMA polymer films

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Abstract

Fluorescence of (−)-bis(1,2;4,5-di-*O*-isopropylidene-β-D-fructopyranyl) 1,4-naphthalenedicarboxylate (NDC) co-doped with 1,1-diphenylpropene (DPP) in a PMMA polymer film is quenched by an external electric field, which however enhances the fluorescence from an exciplex formed between DPP and NDC. This contrasting fluorescence behavior is attributable to the enhanced efficiency of exciplex formation. The magnitudes of the difference in dipole moment and molecular polarizability between the ground state and the excited state of NDC or DPP have been also determined from the Stark shift of the absorption and emission spectra. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electric field effect; Control of photochemical reaction; Asymmetry photochemistry; Exciplex fluorescence; Chiral sensitizer; Electroabsorption spectrum; Electrofluorescence spectrum

1. Introduction

Asymmetry photochemistry is one of the current topics. In particular, photosensitized enantiodifferentiating reactions have attracted much attention, and the effects of temperature, pressure, solvent polarity, concentration and chiral substituent on the optical yield have been extensively examined, in order to elucidate the factors which control the enantiodifferentiating process and the structure of intervening exciplex and in order to optimize the optical yields as well as the chemical reaction yields [1–3].

Bimolecular enantiodifferentiating polar addition of methanol to 1,1-diphenylpropene (DPP) sensitized by chiral alkyl naphthalene(di)carboxylates was shown to give the adduct 1,1-diphenyl-2-methoxypropane in moderate optical yields [4]. The mechanism of these enantiodifferentiating reactions was interpreted by assuming an exciplex formation between excited sensitizer and substrate [4]. It has been proposed that a diastereomeric exciplex pair, which is subjected to an enantioface-selective nucleophilic attack by alcohol, is formed upon photoexcitation of the sensitizer. The chemical and optical yields of photoproduct are determined by the formation efficiency of the exciplex pair and by the differences in stability and reactivity of the intervening diastereomeric exciplex pairs, respectively. If one can alter the formation rate, stability, and/or reactivity of diastereomeric exciplexes by external factors, therefore, not only the chemical yields but also the optical yields can be controlled. In most cases, there is a severe tradeoff relationship between the chemical and optical yields [5,6]. Hence, it is a challenging task to develop a new methodology or to introduce an external factor which can enhance both of the chemical and optical yields simultaneously.

It is well known that the application of an electric field to a molecule induces the Stark shift of absorption and emission spectra, and the direction and magnitude of the shift critically depend on the electric dipole moment or molecular polarizability of the states involved [7,9].[2] Applied electric fields may also influence the electronic coupling between the

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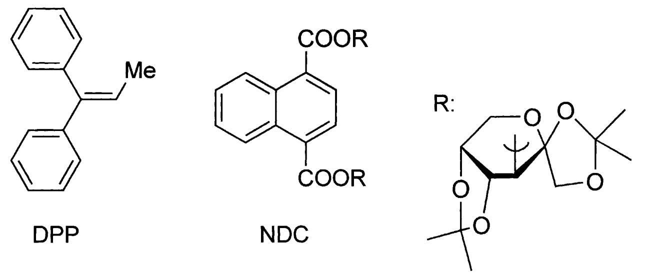


Fig. 1. Molecular structure of DPP and NDC.

initial and final states involved in the electron transfer, which depends on the overlap of the wavefunctions of the donor and acceptor. As a result, chemical reaction dynamics can be affected by an electric field. In fact, it has been demonstrated in the study of fluorescence spectra under an electric field that photoinduced electron transfer processes are significantly influenced by an external electric field [10–15], affording either reduced or enhanced intensity of exciplex fluorescence [13,16–19], when the exciplex fluorescence appears as a result of photoinduced electron transfer. Thus, the formation rates and lifetimes of exciplex intermediates can be controlled in some cases by an electric field.

In view of the foregoing studies on the electric field effects upon fluorescent donor–acceptor systems, it is sensible to assume that the electric field can alter the formation rate and stability of exciplex intermediates. If this is indeed the case, one can control the enantiodifferentiating photoreaction pathway and eventually the optical yield of photoproduct just by applying an electric field to the system. In the present study, we have investigated the electric field effects on the absorption and emission spectra of chiral (−)-bis(1,2;4,5-di-*O*-isopropylidene-β-D-fructopyranyl) 1,4-naphthalenedicarboxylate (NDC) doped in a PMMA polymer film in the presence and absence of DPP; for structures, see Fig. 1. Based on the results, we elucidate the electric field effects on the exciplex formation process and discuss the possibility of controlling enantiodifferentiating photochemical reaction by an electric field. The magnitudes of the difference in electric dipole moment and molecular polarizability between the excited state and the ground state are also evaluated for DPP, NDC and fluorescent exciplex by analyzing the Stark shift of the absorption and fluorescence spectra.

2. Experimental

DPP and NDC, synthesized and purified according to the procedures reported in a previous paper [4], were used in this study. PMMA (MW = 120 000, Aldrich) was purified by a precipitation with a mixture of methanol and benzene and by an extraction with hot methanol. Spectral grade benzene was used as solvent without further purification.

NDC or a mixture of NDC and DPP was dissolved into a benzene solution containing PMMA of different concentrations. The resulting benzene solution, containing NDC/PMMA or NDC/DPP/PMMA, was poured onto ITO-coated quartz substrate by a spin coating method, and polymer films were evaporated in vacua to eliminate benzene completely. The concentration of DPP was ranged from 0 to 20 mol% in its ratio to that of the monomer unit of PMMA, while that of NDC was in the range 1–5 mol%. After casting and drying the polymer film, a semi-transparent aluminum film was deposited by the vacuum vapor deposition technique. Aluminum and ITO films were used as electrodes. The thickness of the polymer films was determined by using a thickness measurement system (Nanometrics, M3000). The thickness of the sample used for the optical measurements was typically 0.5 μm. Unless otherwise stated, the excitation wavelength of ca. 337 nm was chosen for the fluorescence measurements, since the field-induced change in absorption intensity (ΔA) of NDC is negligibly small at that wavelength.

All the optical spectra were measured at room temperature under vacuum conditions. Plots of ΔA or the field-induced change in fluorescence intensity (ΔI_F) as a function of wavelength, which are denoted by E-A spectrum and E-F spectrum, respectively, were measured using electric field modulation spectroscopy with the same apparatus as reported in our previous paper [20]. As occasion demands, a conversion from wavelength to wavenumber in abscissa of the spectra was made. A sinusoidal a.c. voltage was applied, and the value of ΔA or ΔI_F was detected with a lock-in amplifier at the second harmonic of the modulation frequency. Hereafter, applied electric field is denoted by $\boldsymbol{F}$, and its strength is represented in r.m.s.

3. Theoretical background

A shift of energy level is induced in general by $\boldsymbol{F}$, depending on the electric dipole moment and molecular polarizability of the system examined. As a consequence of the level shift, absorption as well as emission spectra are expected to be changed by $\boldsymbol{F}$. An expression for such a field-induced change in absorption intensity as well as in emission intensity was derived by Liptay and co-workers [9,21]. By assuming that the original isotropic distribution in rigid matrices such as PMMA polymer films is maintained even in the presence of $\boldsymbol{F}$, the change in absorption intensity at wavenumber, ν, in the presence of $\boldsymbol{F}$, i.e. $\Delta A(\nu)$, may be given by the following equation [9,22]:

$$\Delta A(\nu) = (f\boldsymbol{F})^2 \times \left\{ A\,A(\nu) + B\nu \frac{\mathrm{d}[A(\nu)/\nu]}{\mathrm{d}\nu} + C\nu \frac{\mathrm{d}^2[A(\nu)/\nu]}{\mathrm{d}\nu^2} \right\} \quad (1)$$

where *f* represents the internal field factor. The coefficient *A* depends on the change in transition dipole moment, and *B* and C are given by the following equations:

$$B = \frac{\Delta\bar{\boldsymbol{\alpha}}/2 + (\Delta\boldsymbol{\alpha}_{\mathrm{m}} - \Delta\bar{\boldsymbol{\alpha}})(3\cos^2\chi - 1)/10}{hc} \tag{2}$$

$$C = (\Delta\boldsymbol{\mu})^2 \frac{[5 + (3\cos^2\xi - 1)(3\cos^2\chi - 1)]}{30h^2c^2} \tag{3}$$

where h represents the Planck's constant and c the light speed. Here, $\Delta\boldsymbol{\mu}$ and $\Delta\boldsymbol{\alpha}$ are the differences in electric dipole moment and polarizability tensor, respectively, between the ground (g) and excited (e) states, and are given by the following equations:

$$\Delta\boldsymbol{\mu} = |\Delta\boldsymbol{\mu}|, \qquad \Delta\bar{\boldsymbol{\alpha}} = \tfrac{1}{3}\mathrm{Tr}(\Delta\boldsymbol{\alpha}) \tag{4}$$

where $\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_{\mathrm{e}} - \boldsymbol{\mu}_{\mathrm{g}}$ and $\Delta\boldsymbol{\alpha} = \boldsymbol{\alpha}_{\mathrm{e}} - \boldsymbol{\alpha}_{\mathrm{g}}$. $\Delta\boldsymbol{\alpha}_{\mathrm{m}}$ denotes the diagonal component of $\Delta\boldsymbol{\alpha}$ with respect to the direction of the transition dipole moment, χ the angle between the direction of $\boldsymbol{F}$ and the electric vector of the excitation light, and ξ the angle between the direction of $\Delta\boldsymbol{\mu}$ and the transition dipole moment.

Electric field-induced change in fluorescence intensity, i.e. $\Delta I_{\mathrm{F}}(\nu)$, observed at the second harmonic of the modulation frequency in a polymer film is also given by an equation similar to Eq. (1), i.e. by a linear combination of the fluorescence spectrum and its first and second derivative spectra. The first and second derivative components correspond to the spectral shift and the spectral broadening resulting from the difference in molecular polarizability and electric dipole moment between the fluorescent state and the ground state, respectively. Let us consider an extreme system where no nonradiative process occurs and the excited molecules dissipate excitation energy only through the emissive processes. In such a case, the emission intensity does not change even in the presence of $\boldsymbol{F}$, as far as the numbers of the excited molecules are the same. Even when the transition dipole moment is changed by $\boldsymbol{F}$, the fluorescence quantum yield (intensity) is not affected by $\boldsymbol{F}$, although the fluorescence lifetime is changed. When a molecule is excited, it always comes down to the ground state through emissive processes. On the other hand, when a nonradiative process competes with the emissive processes, the field-induced change in transition dipole moment as well as in nonradiative process will cause a change in fluorescence intensity. Therefore, the component of the E-F spectrum, which gives the same shape as the emission spectrum, corresponds to the field-induced change in emission quantum yield. Hence, evaluating the magnitude of the change in emission intensity provides us with the information about the electric field effects on excitation dynamics.

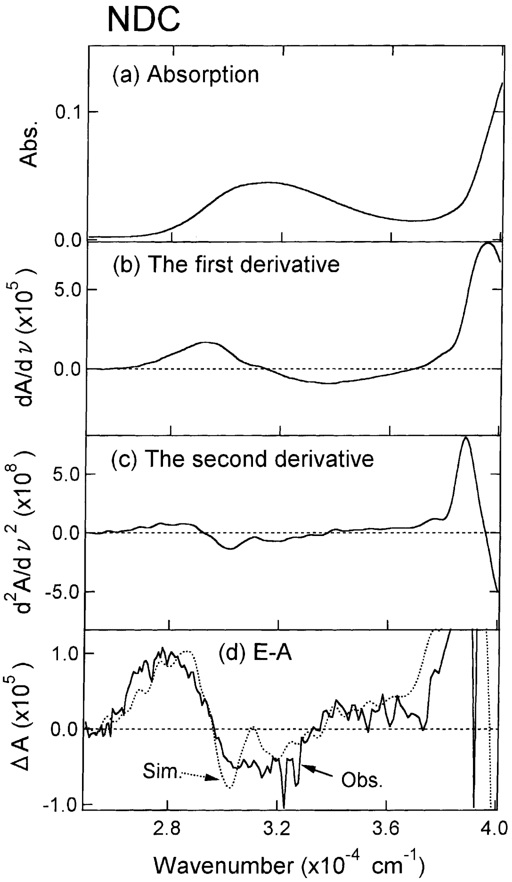


Fig. 2. Absorption spectrum, its first and second derivative spectra and E-A spectrum of NDC at 1.0 mol% doped in a PMMA film (from top to bottom). The simulated E-A spectrum is also shown in (d) by a dotted line. Applied field strength was 1.0 MV cm^{-1}.

4. Results and discussion

We first discuss the results of the measurements of the E-A spectra of NDC and of a mixture of NDC and DPP doped in a PMMA polymer film. Both of the field-induced change in emission quantum yield and in absorption intensity are jointly responsible for the field-induced change in emission intensity. Then, the measurements of the E-A spectra are essential not only for the evaluation of the Stark shift upon excitation to each absorption band but also for finding the adequate excitation wavelength for the measurements of the E-F spectra. The E-A spectra of 1 mol% NDC in PMMA are shown in Fig. 2, together with the absorption spectrum and its first and second derivative spectra. The E-A spectra of NDC in the region 26 000–35 000 cm^{-1} can be simulated quite well by a linear combination of the absorption spectrum and its first and second derivative spectra (see Eq. (1)). The E-A spectra of a mixture of 1.0 mol% NDC and various concentrations of DPP in PMMA were also obtained. The results obtained with a mixture of 5 mol% DPP and 1 mol% NDC in PMMA are shown in Fig. 3. The absorption spectrum of the mixture is resolved into the spectra of DPP and NDC. The first and second derivative spectra of each absorption spectrum are also shown in Fig. 3. The absorption intensity of DPP is negligibly weak below 32 000 cm^{-1}. The absorption maximum of NDC at around 31 700 cm^{-1} slightly shifts to the red in the presence of DPP, and the magnitude of the shift increases slightly with increasing the

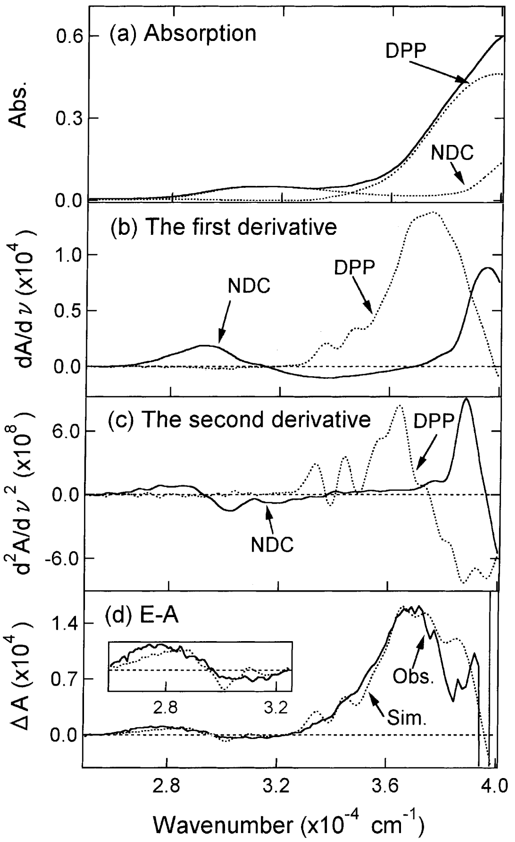


Fig. 3. Absorption spectrum, its first and second derivative spectra and E-A spectrum of a mixture of NDC (1.0 mol%) and DPP (5.0 mol%): (a) absorption spectrum is resolved into the spectra of NDC and DPP (dotted line); (b) the first derivative spectra of NDC (solid line) and DPP (dotted line); (c) the second derivative spectra of NDC (solid line) and DPP (dotted line); (d) E-A spectrum of a mixture observed with a field strength of 1.0 MV cm^{-1} and the simulated spectrum (dotted line).

DPP concentration. The observed E-A spectra of a mixture of NDC and DPP are well simulated by a sum of the spectra of NDC and DPP. The results of the simulation with a mixture of 1 mol% NDC and 5 mol% DPP are also shown in Fig. 3(d). The magnitudes of $\Delta\mu$ and $\Delta\alpha$ upon excitation of NDC at ~32 000 cm^{-1} and DPP at ~39 000 cm^{-1} are evaluated from the contribution of the first and second derivative components, and are listed in Table 1. These values are nearly independent of the DPP concentration.

Table 1
The magnitude of $\Delta\mu$ and $\Delta\alpha$ between the excited state and the ground state of DPP, NDC and exciplex

	$\Delta\mu$ (D)	$\Delta\alpha$ ($4\pi\varepsilon_0$Å^3)
DPP[a]	3.9	40
NDC[a]	4.6	9
NDC[b]	5.2 (6.7)[c]	200 (200)[c]
Exciplex	5.5	350

[a] Estimated from E-A spectra.
[b] Estimated from E-F spectra.
[c] Estimated from E-F spectra in the presence of DPP.

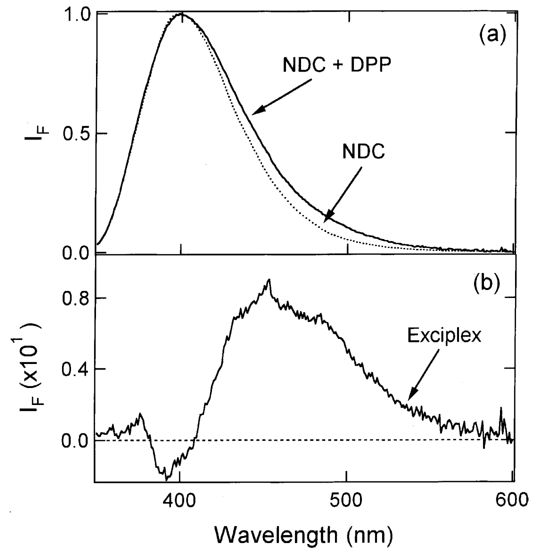


Fig. 4. (a) Fluorescence spectrum of a mixture of NDC (1.0 mol%) and DPP (20 mol%) doped in PMMA, and the fluorescence spectrum of NDC (1.0 mol%) which is shifted to the red by 1.0 nm (dotted line); (b) exciplex fluorescence spectrum obtained by subtracting the spectrum of NDC from that of a mixture of NDC and DPP. The maximum intensity is normalized to unity in both spectra in (a).

As already reported, a mixture of DPP and NDC shows broad exciplex fluorescence with a peak at ~460 nm upon excitation of NDC, along with the fluorescence emitted from the locally excited state of NDC [4]. Hereafter, the latter fluorescence is called as the monomer fluorescence of NDC, which shows a maximum at ~400 nm. With increasing the DPP concentration, the intensity of the exciplex fluorescence relative to the monomer fluorescence of NDC increases. Fluorescence spectrum of a mixture of NDC (1 mol%) and DPP (20 mol%) in a PMMA film is shown in Fig. 4, together with the spectrum of NDC (1 mol%) in PMMA. The latter spectrum is shifted to the red by ~1 nm, and the wavelengths at the peak maxima are taken to be the same in both spectra. By subtracting the 1 nm-shifted fluorescence spectrum of NDC from the fluorescence spectrum of the mixture, the exciplex fluorescence spectrum shown in Fig. 4 was obtained. A small maximum and a minimum at ~390 nm are regarded as artifacts, which are incorporated in the tentative analysis.

Fig. 5 shows the E-F spectra of the mixture of NDC and DPP in various ratios, where the concentration of NDC is fixed at 1 mol%, while the DPP concentration ranges from 0 to 20 mol%. The E-F spectra of NDC in the presence of DPP were completely different from that of NDC in the absence of DPP. The E-F spectrum of NDC is well simulated by a linear combination of the monomer fluorescence spectrum of NDC and its first and second derivative spectra as shown in Fig. 6. From the first and second derivative parts, the magnitudes of $\Delta\alpha$ and $\Delta\mu$ between the fluorescent state and the ground state of NDC are determined, as listed in Table 1. It is believed that a component which possesses the same shape with the fluorescence spectrum is necessary

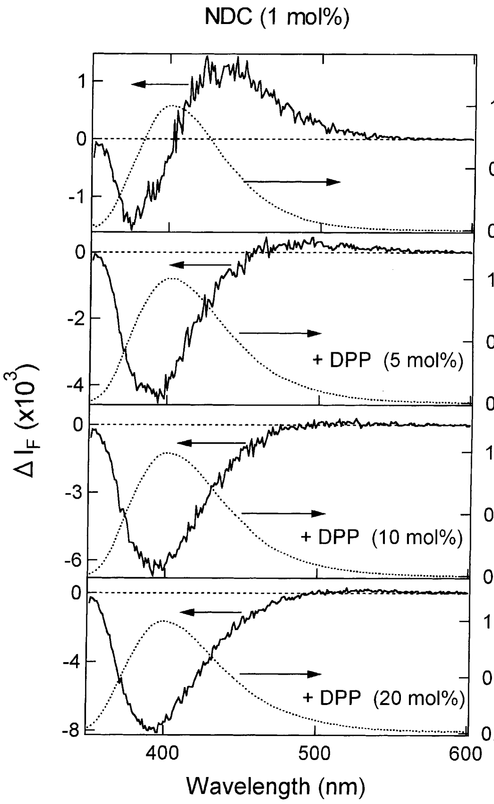


Fig. 5. E-F spectra of NDC and a mixture of NDC and DPP with a field strength of 1.0 MV cm^{-1}. The concentration of NDC is 1.0 mol% in every case, and the DPP concentration is 0, 5.0, 10.0 and 20.0 mol%, respectively (from top to bottom). Fluorescence spectra observed simultaneously are shown by a dotted line; the maximum intensity is normalized to unity.

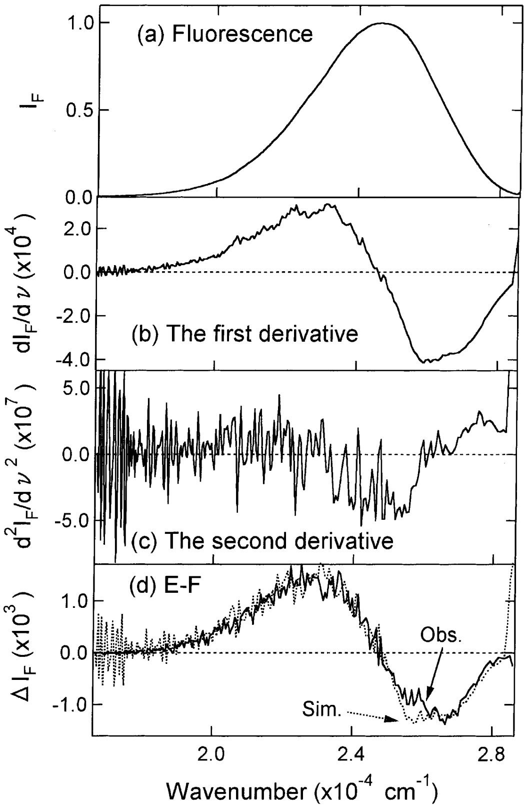


Fig. 6. Fluorescence spectrum of NDC (a), its first derivative spectrum (b), the second derivative spectrum (c) and the E-F spectrum observed with a field strength of 1.0 MV cm^{-1} (d). The simulated E-F spectrum is shown by a dotted line in (d).

for the simulation of the E-F spectrum, but this component is very small, implying that the excitation dynamics in the fluorescent state of NDC is practically unaffected by $\boldsymbol{F}$ in the absence of DPP.

The results of the simulation of the E-F spectrum of a mixture of NDC (1 mol%) and DPP (20 mol%) are shown in Fig. 7, together with the fluorescence spectra of monomer and exciplex and their first and second derivative spectra. If only the spectral broadening and spectral shift take place in the presence of $\boldsymbol{F}$, the integrated intensity of the E-F spectra should be zero. As shown in Figs. 5 and 7, however, the integrated intensity of the E-F spectra of a mixture of NDC and DPP is obviously negative, indicating that the monomer fluorescence of NDC in the mixture is quenched by $\boldsymbol{F}$. Actually, the E-F spectrum was simulated by using the sum of the linear combinations of the fluorescence and its first and second derivative spectra for both monomer fluorescence of NDC and exciplex fluorescence. By evaluating the Stark shift, the $\Delta\alpha$ and $\Delta\mu$ values for the monomer as well as exciplex fluorescence have been determined, as shown in Table 1. The simulation was also made for a mixture of 1 mol% NDC and 5 or 10 mol% DPP. The evaluated values of $\Delta\mu$ or $\Delta\alpha$ are nearly the same for the two samples, and only the magnitude of the quenching of the monomer fluorescence of NDC significantly depends on the DPP concentration. Note that the field-induced change in fluorescence intensity (ΔI_F) could be determined both for monomer fluorescence and for exciplex fluorescence, by evaluating the component which corresponds to the same shape as the fluorescence spectra. In contrast to the monomer fluorescence of NDC, which is significantly quenched by $\boldsymbol{F}$ in the presence of DPP, exciplex fluorescence is slightly enhanced by $\boldsymbol{F}$. The magnitudes of ΔI_F for both fluorescence emissions are shown in Fig. 8, as a function of the DPP concentration. As the DPP concentration increases, the magnitude of the quenching of the monomer fluorescence increases (see Fig. 8). The fluorescing process of NDC is considered to compete with the exciplex formation with DPP, which will be described later.

In the previous study on enantiodifferentiating polar photoaddition [4], a series of 1,1-diphenyl-1-alkenes as substrates, alcohols as nucleophile, and chiral naphthalene(di)carboxylates as photosensitizers were employed in order to elucidate the enantiodifferentiation mechanism and also to enhance the enantiomeric excess (ee) of the product. The photoaddition reactions were performed under a variety of conditions, including solvent and temperature, to give varying chemical and optical yields. For example, photoirradiation of a mixture of NDC, DPP, and methanol led to the anti-Markovnikov addition of methanol to DPP, yielding

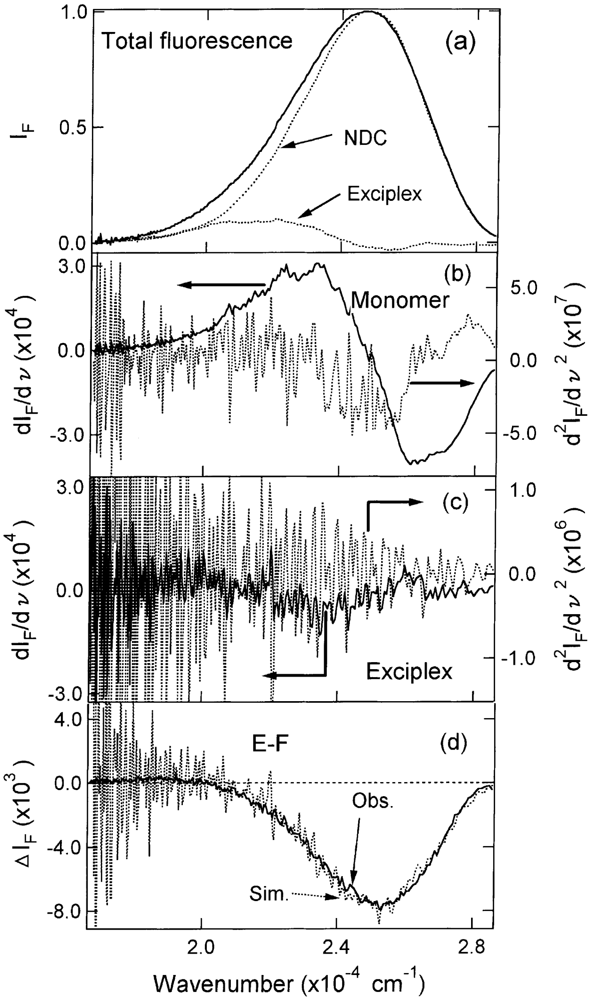


Fig. 7. Fluorescence spectrum of a mixture of NDC (1.0 mol%) and DPP (20 mol%) and the resolved monomer and exciplex fluorescence spectra (a), the first and second derivative spectra of the monomer fluorescence (b) and of the exciplex fluorescence (c), and the E-F spectrum observed with a field strength of 1.0 MV cm^{-1} (d). The simulated E-F spectrum is shown by a dotted line in (d).

the (*S*)-(−)-adduct as the major enantiomeric product in 15.7% ee at 25°C. The monomer fluorescence of NDC was quenched by adding DPP with accompanying generation of exciplex fluorescence, which was in turn quenched by further adding methanol. These photochemical and photophysical results were reasonably accounted for in terms of the reaction mechanism involving a diastereomeric exciplex pair, which are equilibrated with the excited sensitizer, and the reaction Scheme 1 has been proposed [4]. This is a chiral version of the mechanism proposed for the photoaddition of methanol to DPP sensitized by 9,10-dicyanoanthracene [23]. In this mechanism, the diastereomeric exciplexes are subjected to the enantioface-selective nucleophilic attack of alcohol at different rates to give the enantiomeric photoadducts.

If Scheme 1 is applicable even in PMMA films, the present results that the fluorescence of NDC in the presence of DPP is quenched and the exciplex fluorescence is enhanced by applying electric field mean that the equilibrium between the diastereomeric exciplexes and excited NDC, i.e. k_q/k_{-q} in Scheme 1, is appreciably affected by $\boldsymbol{F}$. The present field effects on fluorescence are very similar to those observed for the photoinduced electron transfer processes [12,13,18], where fluorescence emitted from the locally excited state of molecules is quenched by $\boldsymbol{F}$, as a result of the field effects on the initial step of the photoinduced electron transfer. The field-induced quenching of the monomer fluorescence of NDC as well as the field-induced enhancement of the exciplex fluorescence observed in the present study also suggests that the rate constant of the initial step of exciplex formation (k_q) becomes larger in the presence of $\boldsymbol{F}$, which results in the increase of the ratio of k_q/k_{-q} in Scheme 1.

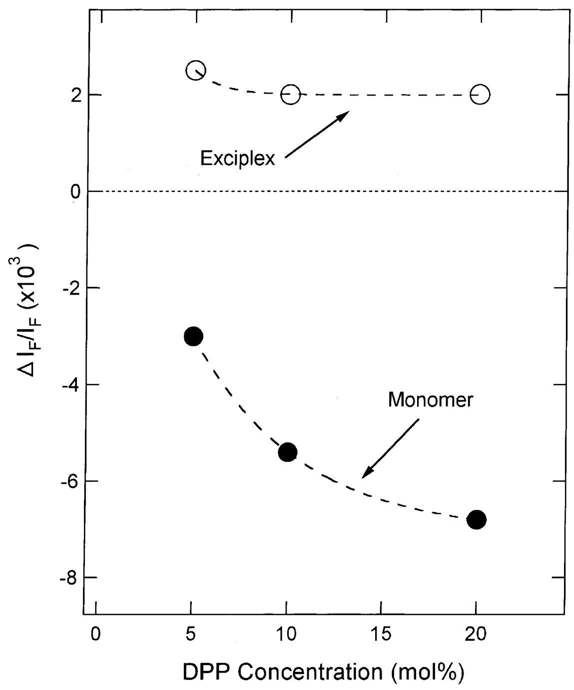
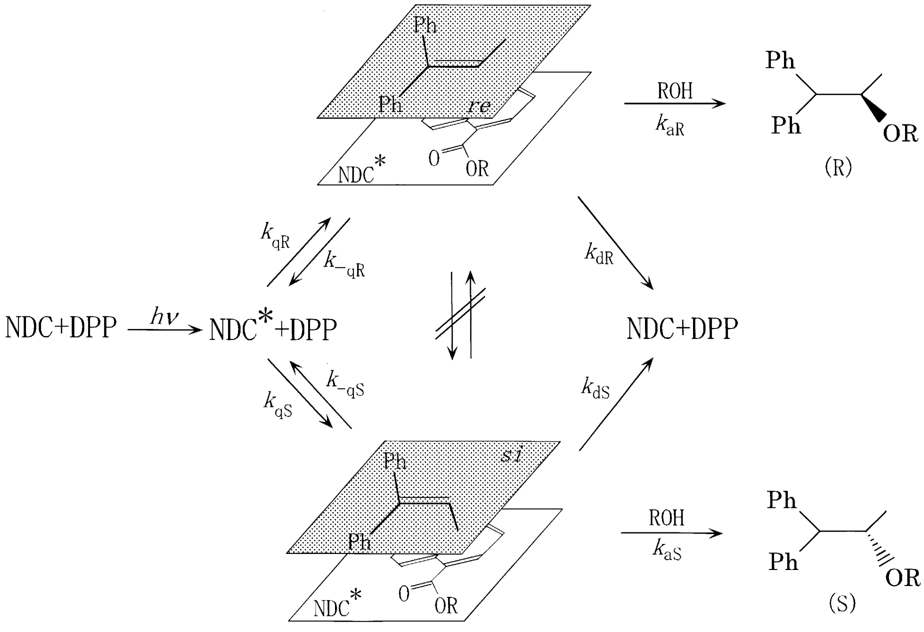


Fig. 8. Plots of the field-induced change in intensity (ΔI_F) relative to the intensity of each of the monomer fluorescence and exciplex fluorescence as a function of DPP concentration.

From the viewpoint of the reactivity/selectivity control by an electric field, the present results are encouraging, indicating that the chemical yield can be altered by $\boldsymbol{F}$, provided that the photoadduct is produced through an exciplex intermediate. The relative stability between the diastereomeric exciplexes is considered to be the major source of the enantioselectivity in the asymmetric photoaddition of alcohol to the exciplexes formed by DPP and NDC; the selectivity depends on the relative equilibrium constant for the formation of K_S/K_R, where $K = k_q/k_{-q}$ in Scheme 1. Hence, it is anticipated in principle that not only the chemical but also optical yields can be manipulated by $\boldsymbol{F}$. The difference in stability or activation energy of two diastereomeric exciplexes in Scheme 1 can be as large as



Scheme 1.

~0.4 kcal/mol as estimated from the optical yield, although the E-F spectra in a polymer film give no direct evidence in support of the presence of two distinct exciplexes. Under the electric field of 1.0 MV cm^{-1}, however, the energy level of an exciplex with an electric dipole moment of 5 D can be changed by up to 0.25 kcal/mol. If the two exciplexes possess unequal dipole moments, the Stark shift under an electric field of 1.0 MV cm^{-1} can appreciably discriminate each of them through the different stabilization energy. In other words, the formation rates of two diastereomeric exciplexes should be differently affected by $\boldsymbol{F}$. As judged from the enhanced exciplex fluorescence at the expense of monomer fluorescence under the applied electric field, the exciplex formation is obviously accelerated by $\boldsymbol{F}$ and the degree of acceleration may differ for each of the diastereomeric exciplexes. These considerations lead us to a working hypothesis that the applied electric field can enhance both the chemical and the optical yields of the enantiodifferentiating photosensitization, which usually conflict with each other, exhibiting a tradeoff relationship in most conventional asymmetric photoreactions [4].

We therefore measured the E-F spectra of a mixture of NDC and DPP in a PMMA polymer film containing benzil alcohol (up to 10 mol%). However, no appreciable effect of the addition of the alcohol was not observed in the E-F spectra. This seems reasonable, since the mobility of the alcohol is greatly reduced in such a rigid matrix as PMMA and is not enough to attack the intermediate at least at room temperature. In order to elucidate the field effects on the optical yield, further study is obviously needed, e.g., in solution or in more soft polymer matrices or at higher temperatures, where both exciplex and alcohols can move freely.

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