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Photophysical properties of β-(1-pyrenyl)ethyl *p*-cyanobenzoate in binary solvents of isooctane-ethyl acetate and ethyl acetate-acetonitrile

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Abstract

The effects of solvent polarity on the fluorescence spectra and fluorescence decays of β-(1-pyrenyl)ethyl *p*-cyanobenzoate (P2CN) were investigated in detail using binary solvents consisting of various mixing ratios of isooctane-ethyl acetate or ethyl acetate-acetonitrile (dielectric constants (ε) = 1.94–36.2). Whereas both the intensity and wavelength maxima of an intramolecular exciplex emission (EX) are dependent on the solvent polarity, only the intensity of an emission from the locally excited pyrene (LE) is dependent on the solvents used. When monitored at 377 nm, the picosecond SPC (single photon counting) measurements reveal a slow decay (>150 ns) in addition to a fast decay (<1 ns) of the locally excited P2CN. There are also two decays for the EX which vary the intensity ratios by the monitored wavelength. The decay rate constants, k_{EX1} and k_{EX2}, have a good linear correlation with the dielectric constants of the solvents, indicating that there exist two kinds of exciplexes. It is suggested that the decays of the locally excited-state of P2CN are so fast due to result of the efficient electron transfer that the two kinds of intramolecular exciplexes are formed from the two discrete conformers in the ground state.

Keywords: Intramolecular exciplex; Solvent effect; Pyrene derivatives; Fluorescence lifetimes

1. Introduction

Studies on the structures and dynamic behavior of electron donor–acceptor systems in the excited states are important for understanding the primary processes of photochemical reactions. Straightforward information can be mostly obtained from observation of the fluorescence quenching or exciplex emission (EX) [1–4]. Both phenomena, especially in an intramolecular donor-acceptor system, are significantly influenced by the polarity of a solvent. While the rate of fluorescence quenching increases as the polarity of the solvent increases, an EX is usually observed in the solvent with low to medium polarity [5,6]. We reported the influence of the *p*-substituents and the length of the alkyl chains on the fluorescence quenching and intramolecular exciplex formation in ω-(1-pyrenyl)alkyl *p*-substituted benzoates, PnX (X = H, Cl, CF_3, CN, NO_2; $n = 1$–4), in which two chromophores are connected by a spacer consisting of an alkyl chain and an ester bond [7]. The relationship between the fluorescence quenching by electron transfer and *p*-substituents of PnX was discussed based on the free energy for electron transfer, ΔG_{ET}. The ΔG_{ET} values in both acetonitrile and isooctane were calculated using the oxidation and reduction potentials obtained from the CV measurements of the 1-methoxy-1-pyrenylmethane and methyl *p*-substituted benzoates. While β-(1-pyrenyl)ethyl benzoate with a ΔG_{ET} of 0.07 eV in acetonitrile did not exhibit an EX, β-(1-pyrenyl)ethyl *p*-cyanobenzoate (P2CN) with a ΔG_{ET} of −0.45 eV showed an intramolecular EX in solvents with a wide range of polarities from isooctane to acetonitrile. The extremely small fluorescence quantum yield and lifetime of P2CN even in isooctane ($\Phi_{\mathrm{f}} = 0.068$ and $\tau_{\mathrm{f}} = 0.635$ ns) compared to those of pyrene ($\Phi_{\mathrm{f}} = 0.53$ and $\tau_{\mathrm{f}} = 340$ ns) [8] indicate that photoinduced electron transfer from the pyrene part to the *p*-cyanobenzoate part is quite efficient. We also studied the ground state and excited state conformation of P2CN using NMR, X-ray crystallographic analysis, in addition to the absorption and emission spectra, and the decay analysis. We concluded that in P2CN, the pyrene and *p*-cyanobenzoate parts are roughly situated in a gauche position, from which the exciplex is derived [9,10].

In this report, we investigated the solvent effects on the fluorescence quantum yields and lifetimes of P2CN for various mixing ratios of isooctane-ethyl acetate or ethyl acetate-acetonitrile (ε = 1.94–36.2) Scheme 1 [11,12].

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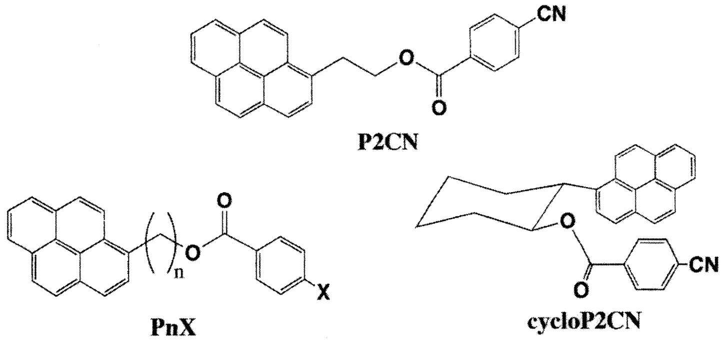

P2CN

PnX

(X = H, Cl, CF_3, CN, NO_2; n = 1-4)

cycloP2CN

Scheme 1.

Although, the dependency of fluorescence quenching and exciplex formation on solvent polarity has been well discussed [13–16], the influence of the shape of a solvent molecule on solvation has been rarely taken into consideration. Using binary solvents with various mixing ratios to minimize the influence of the shape of a solvent, we found that the solvent affects the decay of the locally excited pyrene (LE) of P2CN different from that of the decay of the exciplex. From these results, the nature and behavior of the excited state species will be discussed.

2. Experimental details

2.1. Synthesis

The preparation of β-(1-pyrenyl)ethyl benzoate (P2CN) and the other compounds were reported in [7].

2.2. General

The UV–VIS absorption spectra were measured using a Hitachi 330 spectrometer. The fluorescence and phosphorescence spectra were measured with a Hitachi 850 fluorophotometer. The fluorescence quantum yields were determined at room temperature relative to that of pyrene (0.53) [8] using the solutions of matched absorbance (ca. 0.1) at the excitation wavelength (313 nm). The fluorescence lifetimes were measured with a photon counting apparatus with a hydrogen arc lamp (Hamamatsu Photophysics, time resolution ca. 1 ns). The picosecond SPC measurements of the fluorescence lifetimes were carried out with a mode-locked Nd–YAG laser using its second harmonic emission of R6G and DCM (310–327 nm) as a picosecond excitation light source [17].

2.3. Determination of dielectric constants (ε) in the binary solvents

The mixed solvents were prepared with isooctane (I), ethyl acetate (E) and acetonitrile (A), and their dielectric constants (ε) at room temperature were determined by the heterodyne beat method using the parallel capacitive oscillator with a fixed frequency as reviewed in [18]. The dielectric constants (ε) should be expressed as

$$C_1 = C_0 + C_x + C_{\mathrm{st}} \tag{2.1}$$

$$C_2 = C_0 + \varepsilon C_x + C_{\mathrm{st}} \tag{2.2}$$

where C_1 and C_2 are the capacitance in absence and presence of solvents. C_0, C_x and C_{st} are the capacitance of a condenser, an empty cell and strays, respectively.

From the Eqs. (2.1) and (2.2), the following equation could be derived:

$$C_1 - C_2 = \Delta C = (\varepsilon - 1)C_x \tag{2.3}$$

$$\varepsilon = \frac{\Delta C}{C_x + 1} \tag{2.4}$$

From Eq. (2.3), the value of C_x was obtained using benzene ($\varepsilon = 2.27$). From Eq. (2.4), the dielectric constants (ε) of the binary solvents were then determined as follows: (1) I, $\varepsilon = 1.94$; (2) I:E = 9:1, $\varepsilon = 2.22$; (3) I:E = 1:1, $\varepsilon = 3.62$; (4) E, $\varepsilon = 6.02$; (5) E:A = 4:1, $\varepsilon = 11.4$; (6) E:A = 1:1, $\varepsilon = 19.4$; (7) A, $\varepsilon = 36.2$.

2.4. Materials

Spectrograde solvents (Fluorosol, supplied by Cica-Merck Co., Ltd.) were used without further purification. For measurements of the absorption and emission spectra and lifetimes, all compounds were purified using repeated column chromatography on silica gel and recrystallization. Their purity was confirmed by an HPLC equipped with UV absorption and fluorescence emission detectors. In the case where impurities were detected even after repeated recrystallization and chromatography, the sample solution was directly collected from the HPLC. The concentrations of the solutions for spectroscopic studies were adjusted to less than 10^{-5} M which had absorbances of less than 0.1 at the excited wavelength. The absence of any intermolecular interactions at that concentration was confirmed. The samples were degassed using freeze-pump-thaw cycles on a high vacuum line and sealed under vacuum.

2.5. Calculation methods

The energies of the singlet and triplet states of P2CN and ethyl pyrene were calculated using the CNDO/S method, without any modification of the original parameters, and the configurational interactions (CI) among all the singly excited configurations.

All ab initio molecular orbital calculations were carried out using Gaussian 98 [19]. The initial geometry of P2CN was based on the results of the X-ray single crystal analysis of P2CN [10]. The total energies of the conformers of P2CN were obtained using a Hartree-Fock SCF calculation with the 6-31G basis set.

3. Results and discussion

3.1. Fluorescence spectra

The mixed solvents were prepared with isooctane (I), ethyl acetate (E) and acetonitrile (A), and their dielectric constants (ε) at room temperature were determined as follows: (1) I, $\varepsilon = 1.94$; (2) I:E = 9:1, $\varepsilon = 2.22$; (3) I:E = 1:1, $\varepsilon = 3.62$; (4) E, $\varepsilon = 6.02$; (5) E:A = 4:1, $\varepsilon = 11.4$; (6) E:A = 1:1, $\varepsilon = 19.4$; (7) A, $\varepsilon = 36.2$. Fig. 1 shows the fluorescence spectra excited at 313 nm and taken without normalization. It is noted that even in the solvent of lowest polarity (1), the longer wavelength region of the emission from the LE was broadened by an EX. The following trends are observed as the polarity of the solvent increased: 1) the total intensity of the spectra decreased, 2) while the maxima of the LE emission (ca. 377 and 397 nm) were not shifted, the EX maxima was shifted to the longer wavelength (Fig. 2).

Fluorescence quantum yields (Φ_f) obtained relative to that of pyrene are reported in Table 1, in which Φ_{total} is the quantum yield for the total emission, Φ_{LE} is that of the LE emission and Φ_{EX} is that of the EX. The Φ_{LE} values are much smaller than those of pyrene ($\Phi_{Py} \approx 0.53$) in all the solvents used, and significantly decreased as the polarity of the solvents increased. The same tendency was observed both in Φ_{EX} and Φ_{total}. Since the charge transfer between the pyrenyl and the *p*-cyanobenzoyl chromophores in the ground state do not exist as previously shown [9,10], these effects of solvents are ascribed to an intramolecular interaction in the excited state between the two chromophores. The decrease in the Φ_{EX} values in the polar solvents indicates that the exciplex is unstable and rapidly deactivates as the polarity of the solvent increases. Therefore, the exciplex would be rather non-polar in nature. Taking into account that a large decrease in Φ_{LE} of P2CN was observed even in isooctane, intramolecular photoelectron transfer (PET) followed by exciplex formation is the main origin of this fluorescence quenching. If the contribution of the intersystem crossing (ISC) to a triplet state is more important in P2CN than in pyrene itself, it would likely cause the decrease in Φ_{LE} [20,21]. However, we concluded that this was not the case based on the following observations. 1) The emission

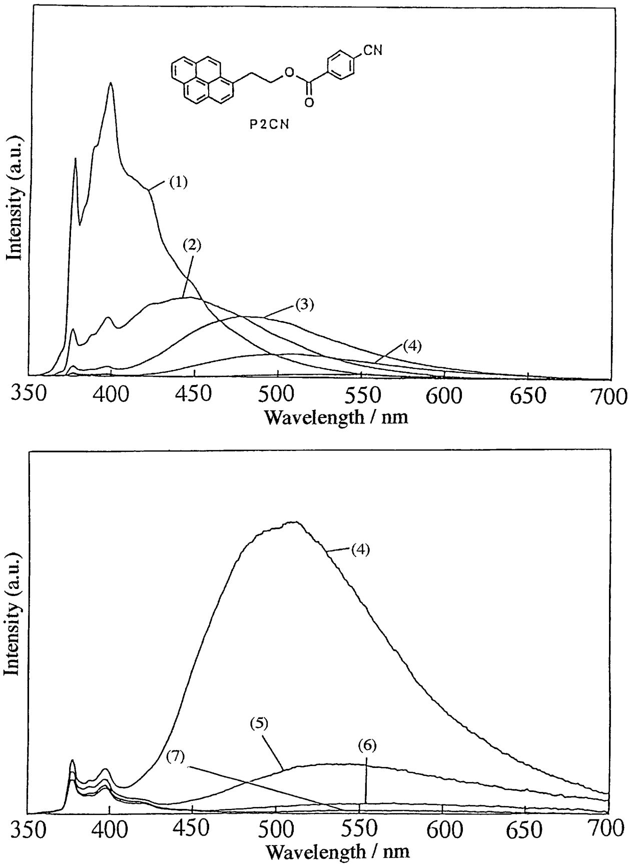

Fig. 1. Fluorescence spectra of P2CN excited at 313 nm in solvents of various Polarities at room temperature. (1) I, $\varepsilon = 1.94$; (2) I:E = 9:1, $\varepsilon = 2.22$; (3) I:E = 1:1, $\varepsilon = 3.62$; (4) E, $\varepsilon = 6.02$; (5) E:A = 4:1, $\varepsilon = 11.4$; (6) E:A = 1:1, $\varepsilon = 19.4$; (7) A, $\varepsilon = 36.2$.

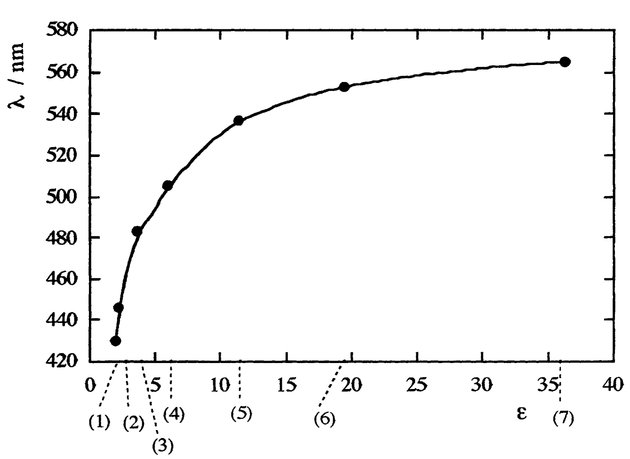

Fig. 2. The plot of exciplex emission maxima (λ/nm) vs. dielectric constants (ε).

Table 1
Fluorescence quantum yields (Φ_f) of P2CN[a]

	(1) I (ε = 1.94)	(2) I:E = 9:1 (ε = 2.22)	(3) I:E = 1:1 (ε = 3.62)	(4) E (ε = 6.02)	(5) E:A = 4:1 (ε = 11.4)	(6) E:A = 1:1 (ε = 19.4)	(7) A (ε = 36.2)
Φ_{total}[b]	0.068	0.038	0.031	0.011	0.0030	0.0014	0.0004
Φ_{LE}	0.025	0.007	0.001	0.001	0.0003	0.0003	0.0003
Φ_{EX}[c]	0.043	0.031	0.030	0.010	0.0027	0.0011	0.0001

[a] I: isooctane, E: ethyl acetate, A: acentonitrile.

[b] $\Phi_{\text{total}} = \Phi_{\text{LE}} + \Phi_{\text{EX}}$.

[c] $\Phi_{\text{EX}} = \Phi_{\text{EX1}} + \Phi_{\text{EX2}}$.

Table 2
S_1 (eV) and T_n (n = 1–6, eV) energy calculated by CNDO/S method

Ethylpyrene		P2CN	
$S_1 = 3.52$	$T_6 = 3.58$	$S_1 = 3.53$	$T_6 = 3.58$
	$T_5 = 3.43$		$T_5 = 3.29$
	$T_4 = 3.17$		$T_4 = 3.23$
	$T_3 = 3.07$		$T_3 = 3.10$
	$T_2 = 2.92$		$T_2 = 3.05$
	$T_1 = 1.86$		$T_1 = 1.98$

spectra of P2CN in ethanol at 77 K showed a phosphorescence emission with a maximum at 595 nm which was the same as that of pyrene. 2) Because the ratio of phosphorescence versus the fluorescence quantum yields in ethanol at 77 K, $\Phi_p/\Phi_{f\,(\text{LE})}$, was 2×10^{-3} for both P2CN and pyrene, a similar amount of ISC would take place in these two compounds at 77 K and also possibly at room temperature. Besides, the energy gap between S_1 and T_n of P2CN has to be smaller than that of pyrene for the more efficient ISC. The change in the electronic structures induced by the addition of the *p*-cyanobenzoate group to ethylpyrene was estimated using the CNDO/S calculation (Table 2). It predicted that the energy gap between S_1 and any triplet state of P2CN was not small enough to possibly increase the ISC efficiency.

3.2. SPC measurements

Two kinds of decays, fast (<1 ns) and very weak slow (>150 ns) decays were observed in the solvents (4)–(7) when monitored at the emission maxima of the LE (377 nm).[2] The fast and the slow decays in (4) are shown in Fig. 3a–c. The slow decay was not observed due to its extremely low intensity in the solvents of lower polarity such as (1)–(3). Both the fast and slow decays are fitted with a single exponential decay. Because the lifetime of the fast decay was identical with the growing-in time of the EX, it was assigned to the lifetime (τ_{LE}) of the LE. The fluorescence lifetimes and the rate constants in the solvents (1)–(7) are given in Table 3. The τ_{LE} decreased as the polarity of the solvents increased,

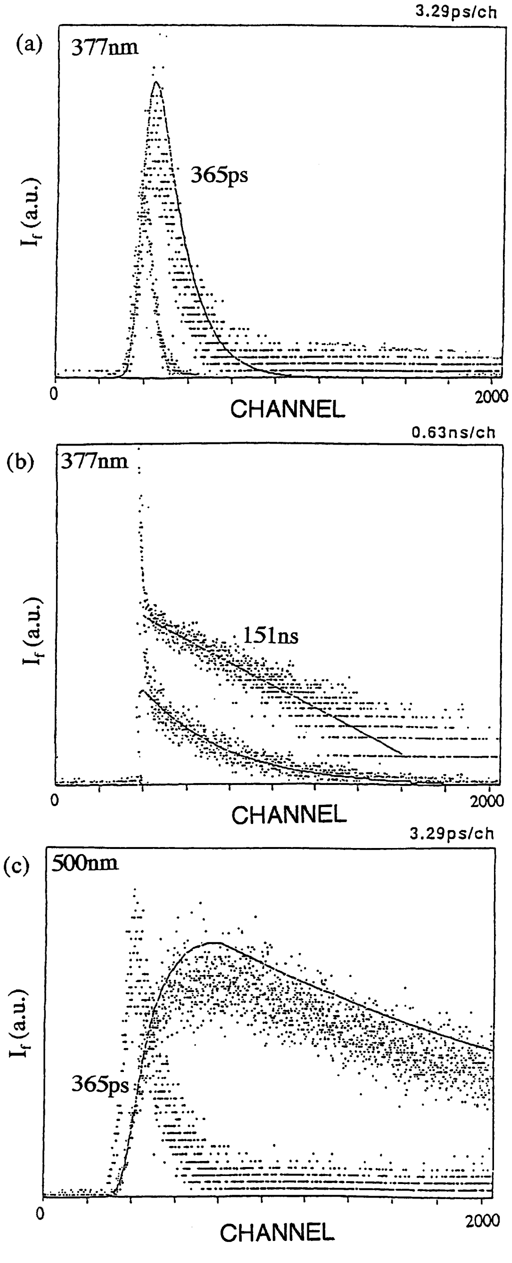

Fig. 3. Decay curve for the fast decay (a), its enlarged curve for the slow decay (b) monitored at 377 nm and for the exciplex decay (c) monitored at 500 nm in ethyl acetate.

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[2] In order to exclude the possibility of the impurity contamination, several samples were prepared using P2CN from the various purified batches. These slow decays were extremely weak but always observed, therefore, they were analyzed as a single exponential decay, using χ^2 of 1.1–1.4.

Table 3
Fluorescence lifetimes (τ) and kinetic constants (k) of P2CN[a]

	(1) I ($\varepsilon = 1.94$)	(2) I:E = 9:1 ($\varepsilon = 2.22$)	(3) I:E = 1:1 ($\varepsilon = 3.62$)	(4) E ($\varepsilon = 6.02$)	(5) E:A = 4:1 ($\varepsilon = 11.4$)	(6) E:A = 1:1 ($\varepsilon = 19.4$)	(7) A ($\varepsilon = 36.2$)
$\tau_{\rm LE}$ (ps)[b]	635	460	381	365	276	247	230
$\tau_{\rm SD}$ (ns)[b,c]	NO[d]	NO[d]	NO[d]	151	178	180	>190
$\tau_{\rm EX1}$ (ns)[e]	16.0	7.35	4.65	3.92	1.26	0.67	0.31
$\tau_{\rm EX2}$ (ns)[e]	41.4	17.2	12.5	9.61	4.58	2.78	1.50
$k_{\rm LE}$ ($10^9\,{\rm s}^{-1}$)	1.57	2.17	2.62	2.74	3.62	4.05	4.35
$k_{\rm SD}$ ($10^6\,{\rm s}^{-1}$)	–	–	–	6.5	5.6	5.5	<5.3
$k_{\rm EX1}$ ($10^7\,{\rm s}^{-1}$)	6.25	13.6	21.5	25.5	79.4	149	323
$k_{\rm EX2}$ ($10^7\,{\rm s}^{-1}$)	2.42	5.81	7.97	10.4	21.8	36.0	66.7

[a] I: isooctane, E: ethyl acetate, A: acentonitrile.
[b] Monitored at 377 nm.
[c] $\tau_{\rm SD}$ and $k_{\rm SD}$ are the lifetime and the kinetic constant of the slow decay.
[d] NO: not observed.
[e] Monitored at 500 nm.

for example, 635 ps in (1) and 230 ps in (7), due to the acceleration of the intramolecular PET in a polar solvent, thus, resulting rapid formation of an intramolecular exciplex. On the other hand, the lifetime of the slow decay increased in a more polar solvent, for example, 150 ns in (4) and 190 ns in (7). It can be understood that the species with the slow decay has an ionic character so that it is stabilized in a polar solvent. In contrast, cycloP2CN gave only one kind of decay, a fast decay ($\tau_{\rm LE} = 66$ ps), when measured under the same instrumental conditions(Fig. 4). As previously reported, the exciplex formation in cycloP2CN was very efficient since the two chromophores are in a rigid gauche conformation: $\Phi_{\rm LE}/\Phi_{\rm EX}$ for P2CN and cycloP2CN were 0.10 and 0.02, respectively. By comparing the structure and the fluorescence properties of P2CN and cycloP2CN, it can be said that the slow decay is related to a transient species, other than the exciplex, generated after PET from the locally LE. However, this has not been fully characterized.

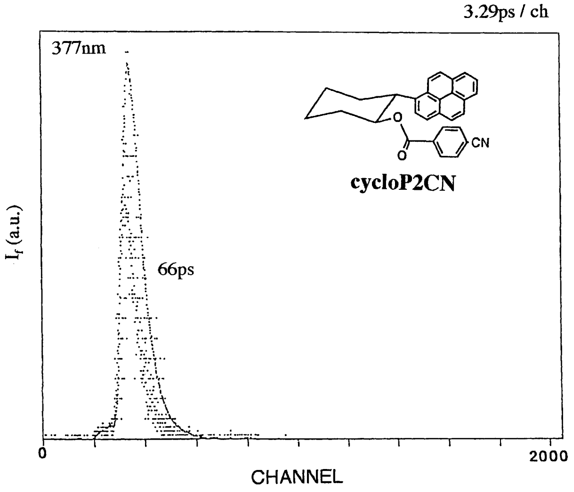

Fig. 4. Fluorescence decay curve of cycloP2CN monitored at 377 nm in ethyl acetate.

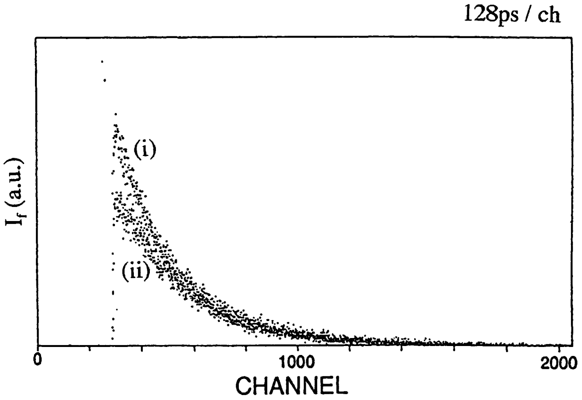

Fig. 5. Fluorescence decay curve of P2CN in (1) (isooctane, $\varepsilon = 1.94$): (i) detected at 460 nm, (ii) detected at 500 nm.

The most note-worthy characteristic is that the shape of the decay curve of the exciplex of P2CN was found to be dependent on the monitored wavelength. Fig. 5 is an example of the decays in (1) (isooctane) monitored at (i) ca. 460 nm using a V40 filter and at (ii) ca. 500 nm using a VG50 filter.[3] A similar wavelength dependency was observed in all solvents (1)–(7). All decay curves were better fitted with the sum of two exponentials. These results indicate that there exist at least two kinds of exciplexes, EX1 and EX2, whose lifetimes and emission spectra are different from each other. Their decay lifetimes, $\tau_{\rm EX1}$ and $\tau_{\rm EX2}$, respectively, were obtained as shown in Table 3 by analyzing the decay curves to be the sum of two exponentials. On the other hand, only one kind of rise time is found, therefore, EX1 and EX2 have almost the same growing-in times within the accuracy of the picosecond SPC measurements.

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[3] The following band path filters or their combination are used for monitoring the decays: (D2 + 35) (340–400 nm maximum at ca. 370 nm), (V40) (320–490 nm, maximum at 400 nm), (VB46 + L39) (360–590 nm, maximum at 460 nm), (VG50) (390–580 nm, maximum at 500 nm).

The intensity ratio of the fluorescence from two components, I_1/I_2, is given by the Eq. (3.2) which is derived from a fluorescence decay function (3.1) consisting of two components:

$$G(t) = a_1 \exp\left(\frac{-t}{\tau_1}\right) + a_2 \exp\left(\frac{-t}{\tau_2}\right) \tag{3.1}$$

where τ_i is the decay lifetime and a_i the pre-exponential factor of the decay obtained from the maximum height of the deconvoluted decay curve. The intensity of the fluorescence, I_i, is given by $a_i\tau_i$. The total amount of the fluorescence emission, I $(I_1 + I_2)$, is represented by $I = \int G(t)\,\mathrm{d}t = a_1\tau_1 + a_2\tau_2$, so that

$$\frac{I_1}{I_2} = \frac{a_1\tau_1}{a_2\tau_2} \tag{3.2}$$

Therefore, the values of $I_{\mathrm{EX1}}/I_{\mathrm{EX2}}$ give the outline of the emission spectra of EX1 and EX2, when the decays are

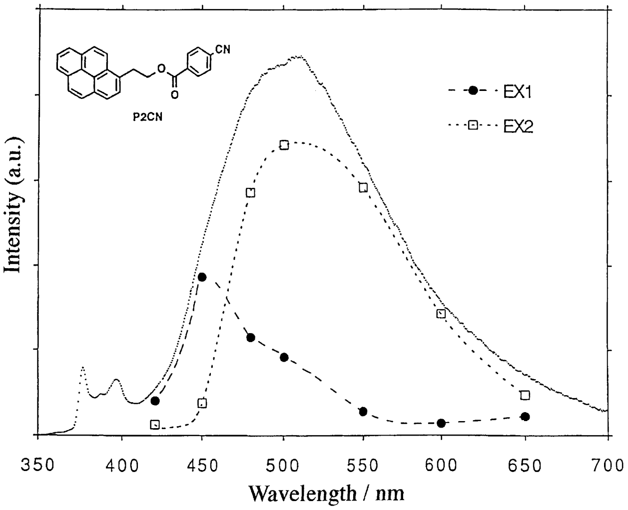

Fig. 6. The outline of the fluorescence spectra of two exciplex (EX1 and EX2) of P2CN in (4) (ethyl acetate, $\varepsilon = 6.02$).

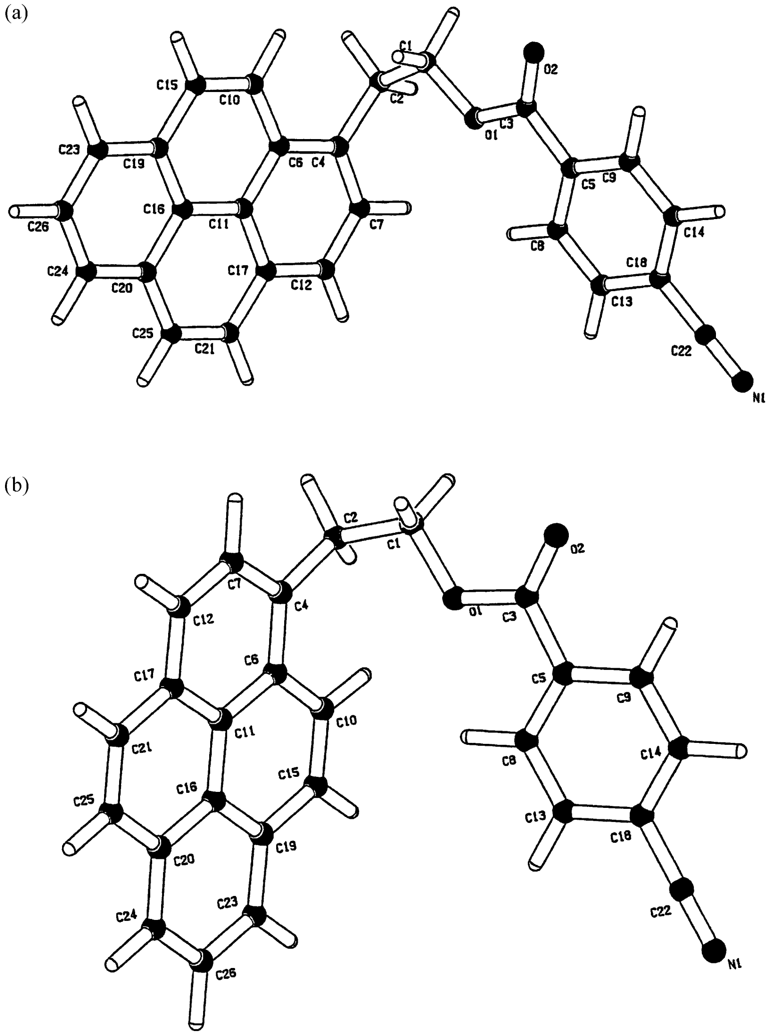

Fig. 7. The geometries of two kinds of exciplexes obtained by ab initio molecular orbital calculations. Total energy were (a) 2.0 kcal mol^{-1} and (b) 2.1 kcal mol^{-1}, respectively.

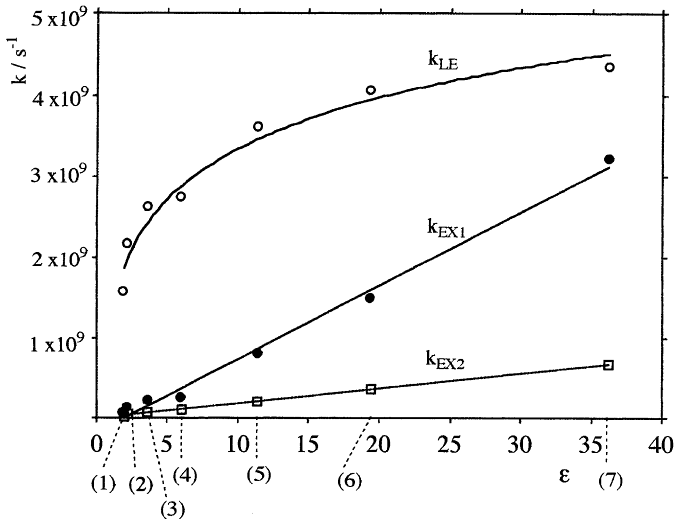

Fig. 8. The plots of the kinetic constants (k_{LE}, k_{EX1} and k_{EX2}) vs. ε.

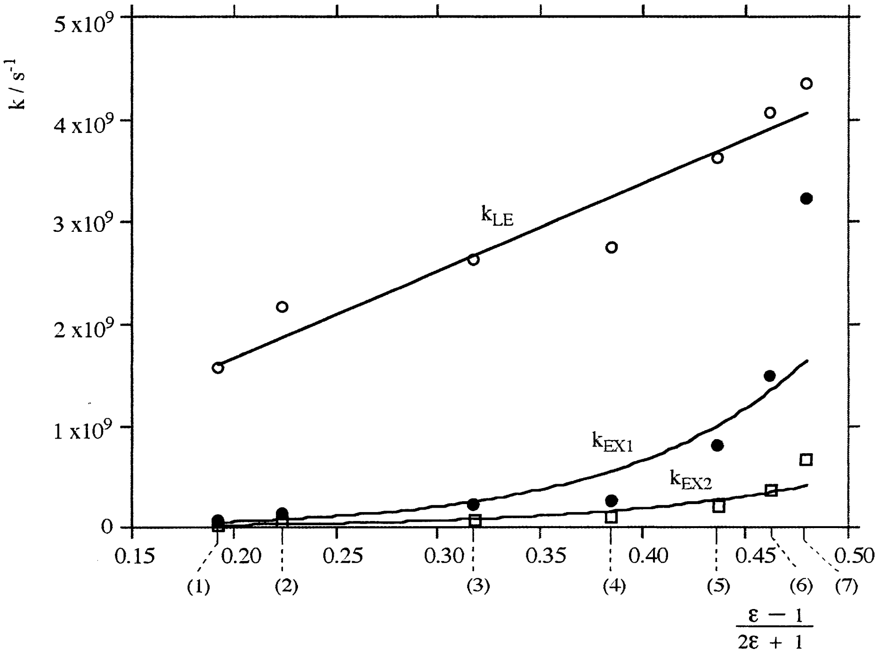

Fig. 9. The plots of the kinetic constants (k_{LE}, k_{EX1} and k_{EX2}) vs. $(\varepsilon - 1)/(2\varepsilon + 1)$.

monitored at several wavelength intervals.[4] Fig. 6 shows the outline spectra of the exciplexes in the solvent (4) thus obtained. They clearly show that the emission of EX2 is stronger and located in the longer wavelength region than that of EX1. Considering that EX1 and EX2 have almost the same growing-in time, they may both come from roughly gauche conformers, only differing in mutual geometrical disposition of the pyrene and benzoate chromophores. To examine whether this is reasonable, ab initio calculations were carried out using the structure obtained from the X-ray single crystal analysis as the initial geometry of P2CN [10]. Two conformers, that would be precursors of the two exciplexes, were obtained (Fig. 7). One of them is exactly the same as that obtained from the X-ray analysis. The other has a similar gauche conformation as to the pyrene and *p*-cyanobenzoate,

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[4] Because the picosecond SPC measurements with the glass filters could not give accurate values for the wavelength, the nanosecond SPC measurements were carried out by monitoring with a 10 nm band-path length spike filter.

but their relative orientation is different. The energy difference between the two conformers is 0.1 kcal mol^{-1}. By a slight rotation around the C_1–C_2 bond, both of these conformers produce the respective overlapping of the two chromophores. Since the decay of the locally excited state is extremely fast, these ground state conformers may give the corresponding, yet distinct exciplexes. There are some precedents in which the ground state conformers as well as the excited state conformers have been assumed to interconvert to give a single exciplex with different rise times [2]. However, P2CN is one of the rare examples to give two kinds of exciplexes from conformers of similar conformation.

3.3. *Influence of solvent polarity on the kinetic constants*

To estimate the nature of the excited species of P2CN, the rates of the decay, k $(1/\tau)$ were plotted versus two kinds of solvent parameters. The rates of the decays, k_{EX1} and k_{EX2}, were linearly correlated with the dielectric constants of the solvents (ε) with fairly good correlation factors ($R = 0.996$ and 0.998, respectively), but not with the Kirkwood function, $f_\varepsilon = (\varepsilon - 1)/(2\varepsilon + 1)$ (Figs. 8 and 9). The observation that the plots of k_{EX1} and k_{EX2} versus ε were on separate lines indicates the existence of two exciplexes. While a plot of the rates of the decay of the locally excited P2CN versus ε did not result in a linear correlation as shown in Fig. 8, a plot of k_{LE} versus f_ε exhibited a roughly linear correlation with $R = 0.962$ (Fig. 9). Namely, the effects of the solvents on the decay of the locally excited P2CN was different from that on the decay of the exciplexes. We believe that this reflects the difference in the properties of these excited species. Although, the meaning of these correlation of the decays with the solvent parameters has not yet been clarified, it is the first example in an intramolecular donor-acceptor system to demonstrate that there is a difference between the nature of the locally excited species and the nature of the exciplexes.

4. Conclusions

We demonstrate here by means of the solvent and wavelength dependency of the decays that P2CN forms two kinds of exciplexes. The decay measurements at 377 nm showed that there are two kinds of decays: a fast decay assigned to the decay of the locally LE of P2CN and a slow decay that originated from a transient species other than the exciplexes formed after PET. P2CN is one of the unique molecules among those to form intramolecular exciplexes by the following two reasons. First, the deactivation processes can be distinctively observed due to the extraordinary short decay lifetime among the bichromophoric compounds containing pyrene. Secondly, the decay of the locally excited state is so fast that when excited, the ground state conformers have no time to transform into the most stabilized exciplex; i.e., the exciplexes are directly formed from the corresponding ground state conformers.

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