Fluorescence dynamics of charge-transfer-complex films of poly(*N*-vinylcarbazole) and 1,2,4,5-tetracyanobenzene and molecular aspects of the disordered structure

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Charge-transfer (CT) fluorescence of poly(*N*-vinylcarbazole) (PVCz) films doped with 1,2,4,5-tetracyanobenzene was investigated in comparison with exciplex (and/or exterplex) fluorescence of PVCz films doped with 1,4-dicyanobenzene by using the nanosecond time-correlated single-photon-counting method. For excitation of PVCz absorption band and CT absorption band, the fluorescence peak in the time-resolved spectra shifted continuously to short wavelength with time. The direction of the shift was opposite to that of the exterplex fluorescence. The dependence of the steady-state CT fluorescence intensity on concentration of the acceptor was also different from the exciplex system. These different behaviours of fluorescence dynamics between the CT and the exciplex systems were discussed from the viewpoint of the overlap of CT and exterplex fluorescence for the CT system and of a morphological change of PVCz films caused by formation of ground-state CT complexes.

(Keywords: poly(*N*-vinylcarbazole); charge-transfer complex; fluorescence dynamics)

INTRODUCTION

Fluorescence properties of poly(*N*-vinylcarbazole) (PVCz) have received considerable attention because of interest in its photoconductive properties, two spectrally distinct excimer fluorescences and a clear relation between photophysical properties and tacticity[1]. Doping of weak electron acceptors such as 1,4-dicyanobenzene (DCNB) into PVCz films causes chemical sensitization of the photoconductivity[2] and gives exciplex fluorescence[3-10]. Relatively stronger acceptors such as 1,2,4,5-tetracyanobenzene (TCNB) form a charge-transfer (CT) complex with the carbazolyl chromophore, and sensitization of the photocurrent in the corresponding CT absorption region and CT fluorescence are observed[11]. Since radiative processes of CT fluorescence as well as exciplex fluorescence are competitive with carrier photogeneration, electric- and magnetic-field effects on steady-state exciplex and/or CT fluorescence have been investigated in detail to clarify the carrier-photogeneration mechanism of PVCz films[5-7,11]. Studies on the dynamics of exciplex and CT fluorescence are indispensable, because observable fluorescence and carrier generation occur in an excited state and these processes are essentially dynamic.

Recently, we have investigated the dynamics of the exciplex fluorescence of PVCz films doped with DCNB and dimethyl terephthalate (DMTP)[9,10]. The exciplex fluorescence peak in time-resolved spectra shifted continuously to long wavelength with time. This behaviour was interpreted by a superposition of various exciplex and exterplex species with temporal characteristics. The exciplex fluorescence showed non-exponential decay with unusually slow tails up to the several microsecond time region, and the decay process was enhanced by applying an electric field. It was impossible to interpret these behaviours only by considering the presence of the various species, because the lifetime of the singlet exciplex and exterplex is shorter than 100 ns. Hence, we proposed that geminate recombination of ion pairs leading to the exciplex and/or exterplex and their dissociation into free carriers were rate-determining steps for the decay process of fluorescent exciplex and/or exterplex states (see the scheme in the 'Discussion' section below). That is, the time constant of the relaxation from the ion pairs to the fluorescent exciplex and/or exterplex seems to be around the microsecond order. Thus, the formation of fluorescent states continues even in the microsecond time region. Since this geminate recombination competes with the electric-field-assisted dissociation into free carriers, the

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decay of the fluorescence can be affected by the electric field.

Since these behaviours are usual as the exciplex and/or exterplex dynamics, we have to confirm their generality by examining the dynamics of CT fluorescence. Concerning low-molecular-weight compounds in solution, fluorescent states of the exciplex and the CT complex, their related ion-pair states and their dynamics have attracted research interest for many years. For example, about 20 years ago, an identical fluorescence state of the exciplex and the CT complex was suggested for the intermolecular complex system, while, for the intramolecular system between the same chromophores as the intermolecular one, a different fluorescent state was suggested[12]. Furthermore, recent femtosecond and picosecond transient absorption spectroscopies have revealed that the dynamics of ion-pair states and their reactivity depend on their production pathway, excitation of CT-complex absorption band and of donor or acceptor absorption band (local excitation)[13]. However, although information about the fluorescence state of the exciplex and the CT complex in photoconductive aromatic vinyl polymer films such a PVCz is of importance for understanding the photoconductivity and the carrier-photogeneration mechanism, there are few reports of whether the fluorescent state of the CT complex and the exciplex and their dynamic behaviour in the films are identical to each other or not.

In the present work, using a nanosecond time-correlated single-photon-counting technique, we have investigated PVCz films doped with TCNB. The electron affinity of TCNB is larger than that of DMTP and DCNB, and the CT complex is formed in the ground state. The results are compared with that of the exciplex fluorescence. Although the electric-field effect on the steady-state CT fluorescence has been discussed[11], time-resolved spectroscopic analysis of the CT fluorescence has never been given as far as we know. This is the first report about comparison of the fluorescent state and of its dynamic behaviour between the exciplex and the CT-complex systems in photoconductive vinyl polymer films with large π-electron pendent groups. The results were discussed in view of a morphological change of PVCz films caused by formation of ground-state CT complexes.

EXPERIMENTAL

PVCz and *N*-isopropylcarbazole (i-PCz) were the same as those in the previous experiment[9,14]. The latter was sublimed *in vacuo* again before use. The alternating copolymer of diethyl fumarate and *N*-vinylcarbazole (DEF:VCz) was prepared by radical polymerization according to the literature[15] and purified by reprecipitations. TCNB was recrystallized from ethanol and subsequently sublimed *in vacuo*. Polycarbonate (PC) was reprecipitated twice from 1,2-dichloroethane solution using methanol. PVCz films were cast on quartz or nesa-coated quartz plates from 1,2-dichloroethane solution containing PVCz and a known amount of TCNB, and were dried under vacuum for several hours. PC films doped with i-PCz and TCNB (i-PCz + TCNB/PC) were cast on quartz plates from dichloromethane solution containing PC, i-PCz and TCNB. If necessary, a semi-transparent gold electrode was evaporated upon the

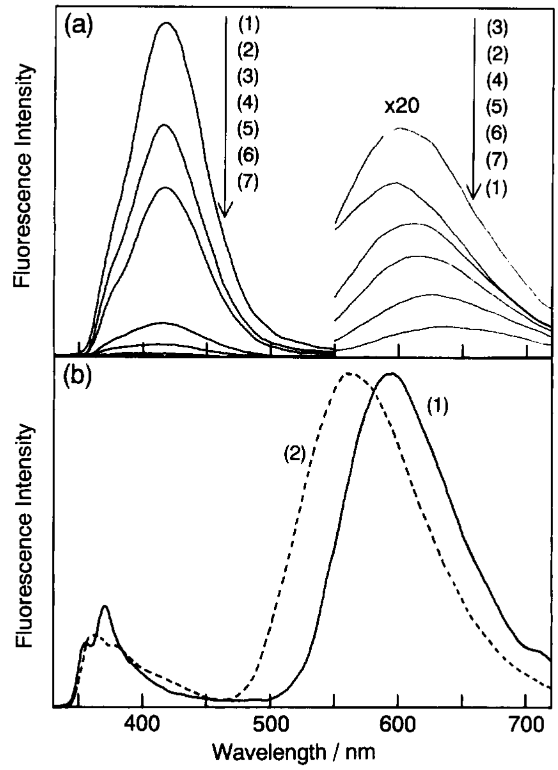


Figure 1 (a) Fluorescence spectra of PVCz films doped with TCNB. TCNB concentration: (1) 0, (2) 0.05, (3) 0.1, (4) 0.5, (5) 1, (6) 2 and (7) 4 mol%. Excitation wavelength is 308 nm (LE excitation). Since fluorescence intensities of samples (1) and (7) are very low in the long- and short-wavelength regions, respectively, their spectra are not shown clearly. (b) Reference fluorescence spectra of (1) i-PCz + TCNB/PC (i-PCz: 40 wt% for PC; TCNB: 2 mol% for i-PCz) and (2) VCz-DEF:TCNB (TCNB: 2 mol% for VCz unit) films

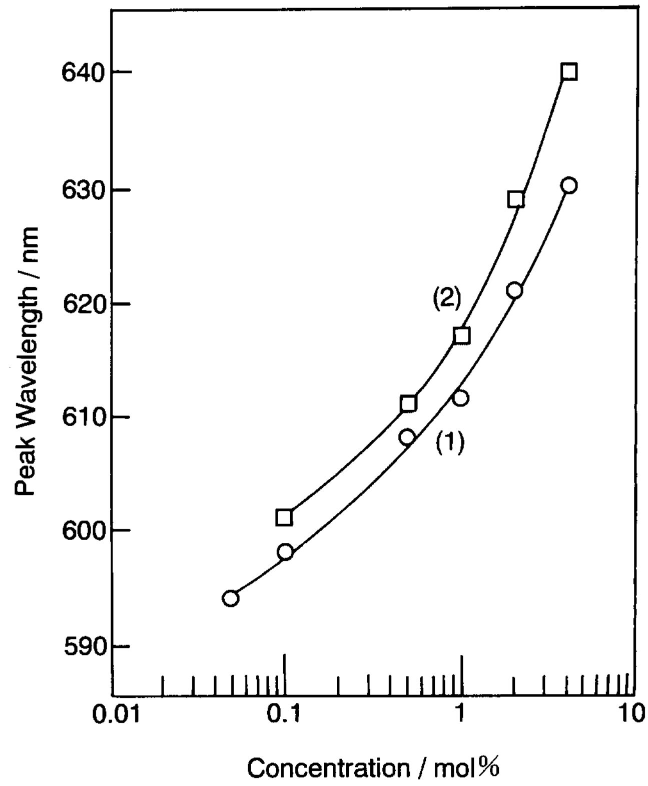


Figure 2 Plot of peak wavelength of CT fluorescence as a function of TCNB concentration: (1) LE (308 nm) excitation and (2) CT (400 nm) excitation

film on nesa-coated quartz plates to prepare a sandwich-type cell. The cell was used for examining electric-field effects on CT fluorescence dynamics.

Time-resolved fluorescence spectra and fluorescence rise and decay curves were measured with the apparatus described in a previous paper[9]. All the measurements were performed under vacuum. Spectra were not corrected for the detector sensitivity.

RESULTS

First, although absorption below 350 nm of PVCz films containing ground-state CT complexes is due to an overlap of both non-complexed and complexed carbazolyl chromophores, we call phenomenologically excitation of the PVCz absorption band 'LE excitation' and discriminate it from excitation of the CT absorption band ('CT excitation'). Fluorescence spectra of PVCz films undoped and doped with TCNB (PVCz:TCNB) for LE excitation ($\lambda_{ex} = 308$ nm) are shown in *Figure 1*. Fluorescence spectra of the i-PCz+TCNB/PC and VCz-DEF:TCNB films are also shown as a reference of a monomeric model system (hereafter they are called monomeric model systems). The spectrum of the undoped PVCz film consists of the sandwich excimer fluorescence ($\lambda_{max} = 420$ nm) and the partial overlap excimer one ($\lambda_{max} = 370$ nm). By doping with TCNB, the host fluorescence is quenched and is replaced by the CT fluorescence, the peak of which shifts to long wavelength from 595 to 640 nm with increasing TCNB concentration, as shown in *Figure 2*. Also on CT excitation ($\lambda_{ex} = 400$ nm), the CT fluorescence shows a peak shift to long wavelength with increasing TCNB concentration. These peaks were at longer wavelength compared with those of the CT fluorescence observed for LE excitation (*Figure 2*). The CT fluorescence of the monomeric model systems is observed in the shorter-

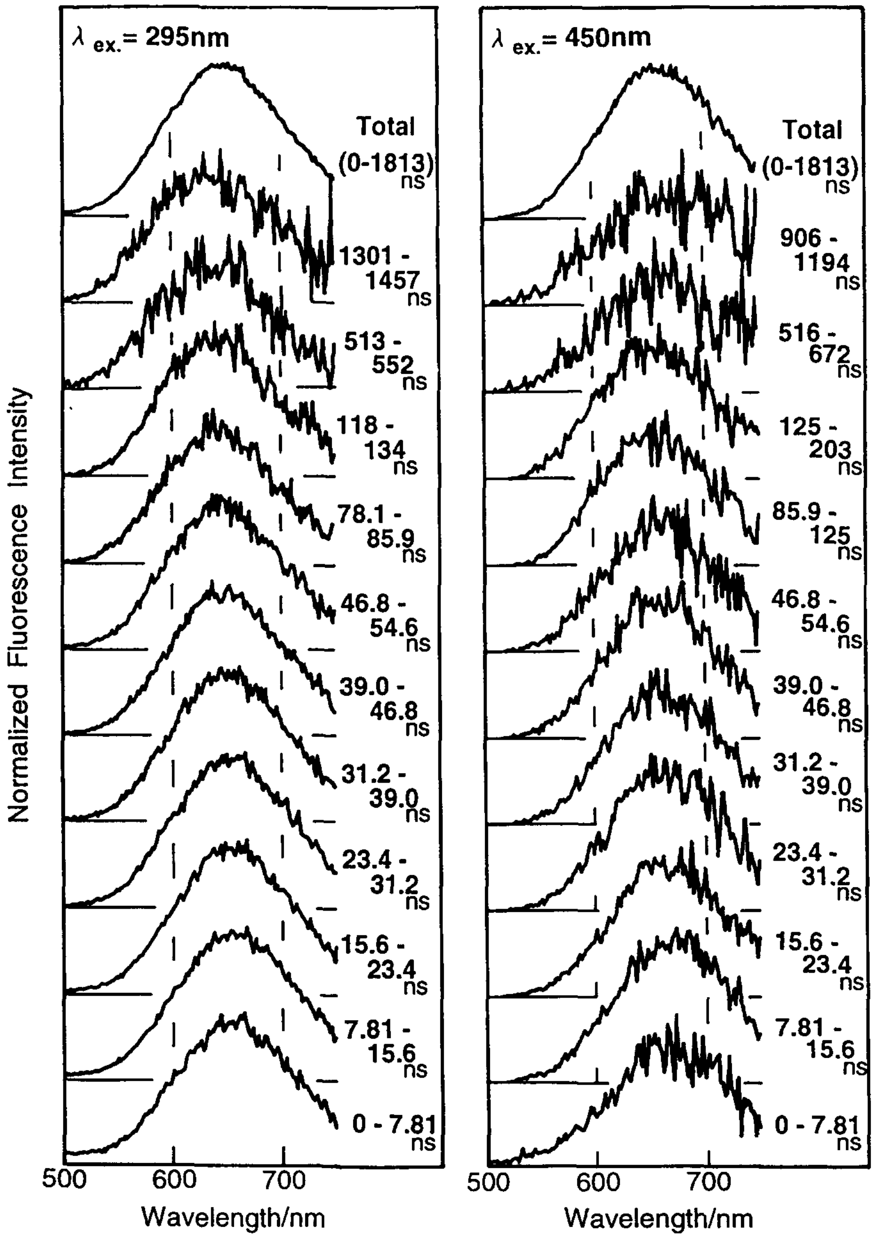


Figure 3 Normalized time-resolved CT fluorescence spectra of PVCz films doped with TCNB (2 mol%) excited at 295 nm (LE excitation) and 450 nm (CT excitation). The time window is given in the figure

wavelength region than that of PVCz:TCNB films (*Figure 1*).

On CT excitation of PVCz:TCNB films, the CT fluorescence intensity increased monotonically with an increase in TCNB concentration. For LE excitation, however, the CT fluorescence intensity increases with an increase in TCNB concentration up to ca. 0.1 mol% and decreases at a concentration higher than 0.5 mol%, while the host fluorescence decreased monotonically (*Figure 1*). On the contrary, the exciplex (exterplex) fluorescence intensity of PVCz:DMTP films increased monotonically with an increase in dopant concentration[3,4]. That is, for LE excitation, the dependence of the CT fluorescence intensity upon dopant concentration is quite different from that for the exciplex (exterplex) system.

Time-resolved CT fluorescence spectra of the PVCz:TCNB (2 mol%) film for LE and CT excitation (295 and 450 nm, respectively) are shown in *Figure 3*, where each spectrum is normalized at the maximum intensity and was not corrected for the wavelength dependence of the instrumental response function. Under both excitation conditions, the peak of the CT fluorescence continuously shifts to short wavelength with time. *Figure 4* shows the shift of the fluorescence peak in the time-resolved fluorescence spectra. It is worth noting that the direction of the peak shift of the CT fluorescence (to short wavelength) is opposite to that of the fluorescence of the exciplex system such as a PVCz:DCNB film (to long wavelength) and that the amount and the position of the fluorescence peak shift are different between both the excitation conditions. The peak of the CT fluorescence in the time-resolved fluorescence spectra of the VCz-DEF:TCNB (2 mol%) monomeric model film shifted also to short wavelength (to high wavenumber) with time, as shown in *Figure 4*. The amount of the blue shift of the CT fluorescence is larger for the polymer system than for the monomeric model one.

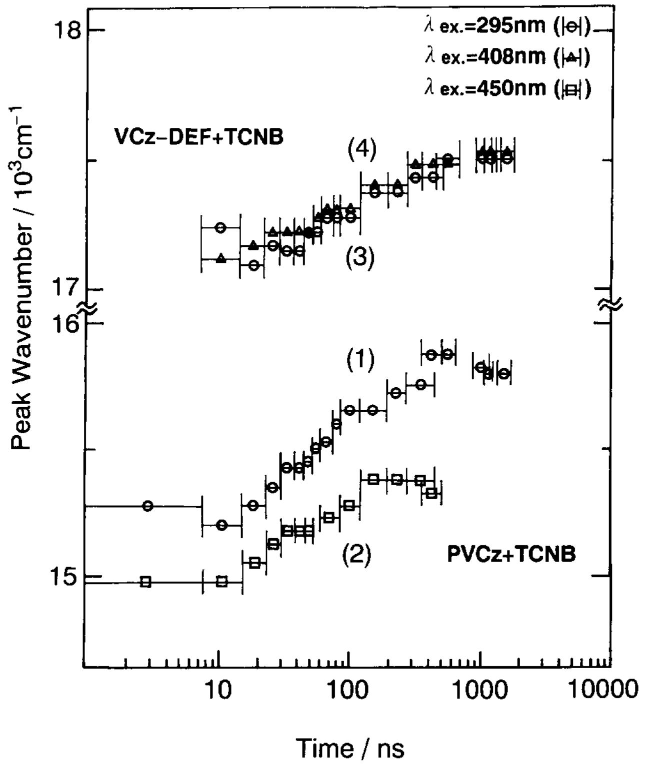


Figure 4 Fluorescence peak wavenumber as a function of time, obtained from time-resolved spectra corrected for the detector sensitivity. PVCz films doped with TCNB (2 mol%): (1) LE (295 nm) excitation and (2) CT (450 nm) excitation. VCz-DEF:TCNB (2 mol%) films: (3) LE (295 nm) excitation and (4) CT (408 nm) excitation

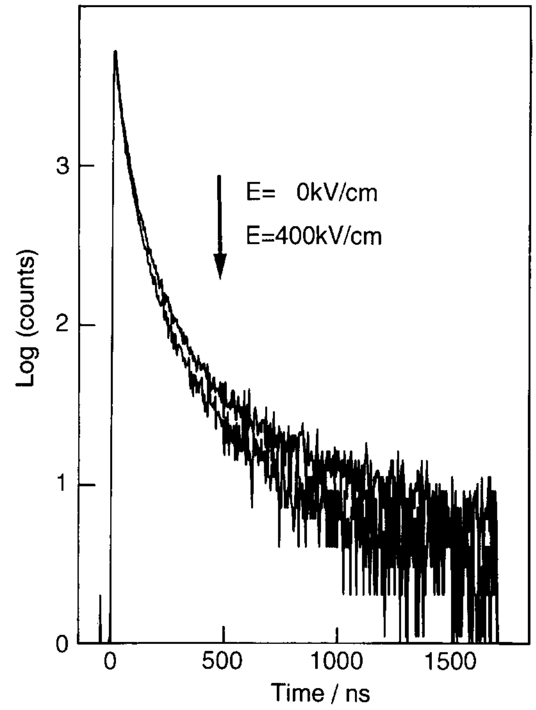
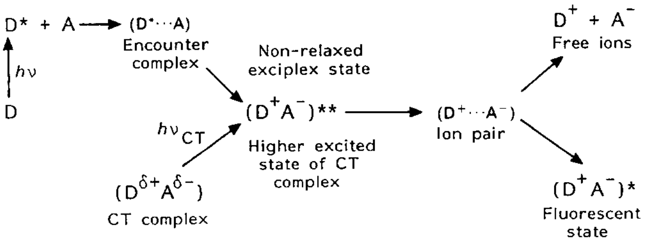


Figure 5 Charge-transfer fluorescence decay curves of PVCz films doped with TCNB (2 mol%) with and without an applied electric field of 400 kV cm^{-1}. Excitation wavelength is 330 nm

Yokoyama *et al.* reported that the steady-state CT fluorescence of PVCz:TCNB films was quenched by applying an electric field[11]. The decrease in the CT fluorescence intensity depends upon the applied electric field strength, which was interpreted well in terms of the Onsager theory. However, measurement of the CT fluorescence decay curve with an applied electric field has never been performed until now, although such an investigation is of importance for elucidating the dynamics of the carrier-photogeneration mechanism. Decay curves of the CT fluorescence of the PVCz:TCNB (2 mol%) film observed at 630 nm with and without the applied electric field (400 kV cm^{-1}) are shown in *Figure 5*. The excitation wavelength was 330 nm. The decay curves do not obey an exponential function and show a long tail in the microsecond time region. Using the 1/e lifetime of the fluorescence, at which the intensity becomes 1/e of the initial value, as a measure of the fluorescence decay, the time of the CT fluorescence was 35 ns. This 1/e lifetime is much smaller than that of the exciplex fluorescence of the PVCz:DCNB (2 mol%) film (280 ns at 540 nm), and the long tail of the CT fluorescence is also shorter than that of the exciplex fluorescence. The initial intensity of the decay curve of the CT fluorescence is decreased by applying an electric field, and the decay is enhanced by it. The total fluorescence intensity was decreased by applying an electric field, which is in agreement with the result reported by Yokoyama *et al.* for the steady-state CT fluorescence[11]. This electric-field-induced decay time decrement was also observed for the exciplex fluorescence[9,10], although the decrement was small compared with the CT fluorescence.

The CT fluorescence decay for CT excitation was faster than that for LE excitation.



Scheme 1 Most probable mechanism for formation of fluorescent states

DISCUSSION

Before discussing the present results, we describe a mechanism that was proposed for the formation of fluorescent exciplex and CT states without information about the fluorescence dynamics. The results on electric-field-induced exciplex and CT fluorescence quenching[5,6,11] and the magnetic-field effect on exciplex fluorescence[7] and photoconductivity[16] suggest *Scheme 1* as the most probable mechanism for the formation of the fluorescent states.

For the exciplex system, a singlet excited state D* in PVCz films migrates through carbazolyl chromophores, encounters an acceptor A, and forms an encounter complex (D*···A). The complex goes through a rapid electron transfer and changes to a non-relaxed exciplex state $(D^+A^-)^{**}$. This state has an excess energy and undergoes a thermalization of the excess energy, giving an ion-pair state $(D^+\cdots A^-)$ with inter-ionic distance r_0. Relaxation from the ion pair to the relaxed fluorescent exciplex state $(D^+A^-)^*$ occurs in competition with the electric-field-assisted thermal dissociation into free carriers $D^+ + A^-$. For the CT-complex system, CT excitation produces the higher excited CT state (the second CT excited state in the present system)[11].

Recently, in order to obtain information on the dynamics of exciplex fluorescence, we have measured time-resolved spectra of the exciplex fluorescence and have examined the electric-field effect on the decay curve of the exciplex fluorescence[9]. On the basis of the results, we have proposed the following modification of *Scheme 1*. Multiple exciplex and exterplex species $(DD^+A^-)^*$ with various relative configurations between donors and acceptor should be considered as the exciplex fluorescence state $(D^+A^-)^*$. Multiple ion pairs with various inter-ionic distances, which are composed of carbazolyl dimer cation and acceptor anion $(DD^+\cdots A^-)$, should be considered as the ion-pair state $(D^+\cdots A^-)$. Moreover, the rate-determining step for the fluorescence decay process is the geminate recombination of the ion pair to the fluorescent state $(DD^+A^-)^*$ and the dissociation of the ion pair to free carriers $D^+ + A^-$ and/or $DD^+ + A^-$.

If one accepts *Scheme 1* and/or the modified one, the dynamics of the CT fluorescence is expected to be quite similar to that of the exciplex fluorescence. As mentioned above, however, the peak of time-resolved fluorescence spectra continuously shifted to short and long wavelengths for CT and exciplex systems, respectively. The 1/e lifetime was short (35 ns) and long (280 ns) for CT and exciplex systems, respectively. Furthermore, the intensity of the steady-state CT fluorescence for LE excitation increases and then decreases with an increase in the acceptor concentration, whereas the intensity of the exciplex fluorescence increases monotonically. These results suggest that fluorescence properties of the CT system are remarkably different from those of the exciplex system.

In the case of CT systems, since the degree of complex formation in the ground state is incomplete in films, the films contain two types of acceptor: acceptors that form CT complexes with carbazolyl chromophores and non-complexed acceptor molecules. CT excitation around 450 nm produces directly an excited CT state. For LE excitation, however, the following three processes that produce the CT fluorescent state should be considered. First is direct excitation of the CT complex to the excited state. This is due to an overlap of CT absorption and PVCz absorption bands. Second is that the singlet excited state of the carbazole migrates effectively through carbazolyl chromophores, encounters non-complexed acceptors and produces the excited CT complex. This is the same as the exciplex formation process. (In the present paper, we call the CT fluorescence due to this mechanism the exciplex (or exterplex) one.) Third is that the singlet excited state of the carbazole encounters the ground-state CT complex and produces the excited CT complex. The fluorescence dynamics of the excited CT complex formed via this process is considered to resemble the first one, because the energy migration of the singlet excited state in films is too fast to detect it with the time resolution of the present experiment.

Formation of fluorescent 2:1 CT complex via excitation of 1:1 CT complex

The steady-state CT fluorescence for CT excitation was observed in the longer-wavelength region than that for LE excitation (*Figure 2*). This is explained by considering that the fluorescence spectrum of the latter is composed of both the CT and the exciplex fluorescence and that the exciplex fluorescence emits at short wavelength and has high quantum yield compared with the CT fluorescence.

On CT excitation, the CT fluorescence of PVCz:TCNB films was observed in the long-wavelength region compared with those of the monomeric model systems. This indicates that the CT fluorescence of the latter systems is mainly due to a complex composed of one carbazolyl chromophore and one TCNB molecule (1:1 complex) and that the CT fluorescence of PVCz:TCNB films is attributed to a triple complex formed between two carbazolyl chromophores and one TCNB molecule (2:1 complex). This is supported by the following three observations. First is that i-PCz is distributed homogeneously in PC films and does not form a dimer that leads to excimer upon excitation[17]. Second is that the undoped VCz–DEF films do not show excimer fluorescence clearly. Third is that exciplex fluorescence studies on monomeric and bichromophoric model compounds (*meso*- and *rac*-2,4-di(*N*-carbazolyl)pentane) of PVCz in the presence of 1,3-dicyanobenzene revealed that the exterplex fluorescence is observed at long wavelength compared with the exciplex one[18], and that the exterplex formation has been confirmed also in PVCz–DMTP solution[19] and in PVCz films doped with DMTP and DCNB[9].

Both the shape of the absorption spectrum and its energy position are identical among the CT complexes of PVCz:TCNB in film and in solution, and the

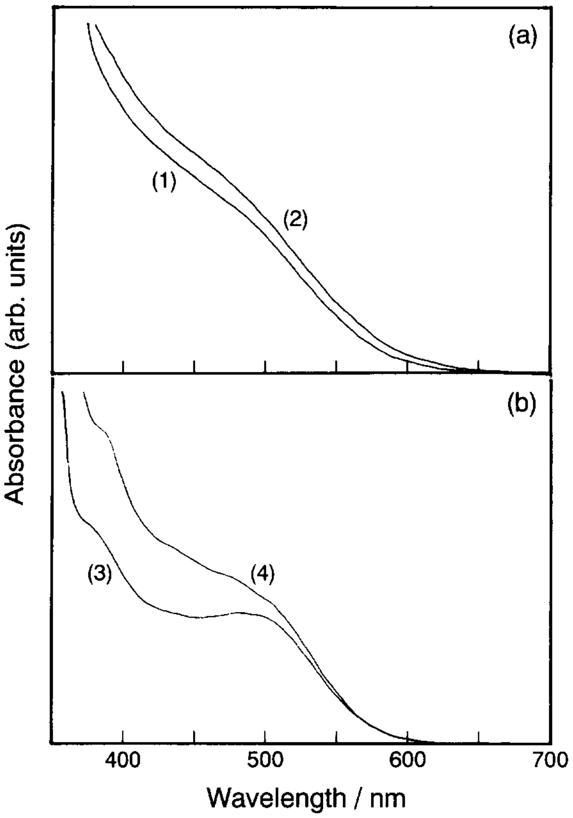


Figure 6 Charge-transfer absorption spectra. (a) PVCz–TCNB complex: (1) 1,2-dichloroethane solution, [PVCz] = 0.13 M, [TCNB] = 0.016 M; (2) PVCz:TCNB (2 mol%) film. (b) i-PCz–TCNB complex: (3) 1,2-dichloroethane solution, [i-PCz] = 0.085 M, [TCNB] = 0.022 M; (4) i-PCz + TCNB/PC (40 wt%, 2 mol%) film

CT complex of the monomeric model systems (*Figure 6*). In solution, the 1:1 stoichiometry of ground-state CT complexes of PVCz and its related compounds with various acceptor molecules was confirmed by the continuous-variation method[20]. Concerning ground-state CT complexes in PVCz films, Weiser performed a compositional analysis of PVCz films doped with 2,4,7-trinitro-9-fluorenone (TNF) of various concentrations and determined the degree of complex formation in PVCz films[21]. The present result of the absorption spectra combined with the result of the compositional analysis of PVCz:TNF suggests 1:1 stoichiometry of the ground-state CT complex of carbazolyl chromophore with TCNB molecule in PVCz films doped with TCNB (1:1 complex in the ground state). As a consequence, the difference in the stoichiometry between the ground and excited states in PVCz films proposes that the excitation of ground-state 1:1 CT complexes creates fluorescent 2:1 CT complexes. This suggests complicated dynamics in the excited state.

Excited triple complexes with various relative geometrical structures of donors and acceptor

In the time-resolved fluorescence spectra, the CT fluorescence of PVCz:TCNB films for CT excitation shifts continuously to short wavelength. The exciplex/exterplex fluorescence of PVCz:DCNB and PVCz:DMTP films showed a shift to long wavelength with time[9]. The shift of the latter to long wavelength was considered to be attributed to a superposition of exterplex species with various relative geometrical structures of donors and acceptor. The shift of the former to short wavelength is also considered to be attributed to temporal characteristics of excited triple complexes $(DD^+A^-)^*$ with various relative configurations among two donors and one acceptor (2:1 complex). That is, the geometry of carbazole dimer cation (DD^+) and the relative geometrical structure of DD^+ to A^- in the excited triple complex take diverse distribution, and each excited triple complex emits and decays independently.

The fluorescence decay for CT excitation ($\lambda_{ex} = 450$ nm) is faster than that for LE excitation and showed a tail in the time region up to ca. 1 μs. Since the lifetime of the excited singlet state of the CT complex (excited triple complex) is usually less than 100 ns, it is impossible to interpret the long tail of the CT fluorescence only by considering the presence of excited triple complexes with various relative configurations. Hence, we adopt the same consideration as used for the interpretation of the exciplex/exterplex fluorescence decay curve with a long tail. That is, the fluorescent CT state that is responsible for the tail is produced via the geminate recombination of ion pairs formed by CT excitation. The ion pairs also take a variety of inter-ionic separations r_0. Hence the fluorescent state of 2:1 CT complexes is formed through two routes: one is via ion-pair states and the other is not.

Difference in fluorescence dynamics between exterplex and triple CT-complex systems

The fluorescence for LE excitation shows a non-exponential decay curve with a long tail up to the microsecond time region and the decay process is enhanced by applying an electric field (*Figure 5*). These behaviours are also observed for the exciplex/exterplex system such as a PVCz:DCNB film[9,10] and, hence, are interpreted by the same consideration as that for the exciplex/exterplex system. That is, the geminate recombination of multiple ion pairs to fluorescent states and the competing dissociation to free carriers are the rate-determining steps for the decay process of fluorescent states.

For LE excitation, as mentioned above, both CT and exterplex fluorescence are observed. Since the exterplex fluorescence decay of PVCz:TCNB films as well as the PVCz:DCNB exciplex system is determined by the geminate recombination of ion pairs, the exterplex fluorescence, which is expected to show a long tail in the decay curve, should be observed even after the decay of the CT fluorescence with short decay time. That is, comparing the time-resolved fluorescence spectra for CT excitation with those for LE excitation, we expect that we will observe the shift of the exterplex fluorescence to long wavelength even after the shift of the CT fluorescence to short wavelength stops. As shown in *Figure 4*, however, such a fluorescence peak shift was not observed. This result suggests that the fluorescence dynamics of exterplexes that are formed between two carbazolyl chromophores and one acceptor with large electron affinity is different from those of an acceptor with small electron affinity. That is, the exterplex fluorescence dynamics depends on the electron affinity of the acceptor.

The exciplex fluorescence peak shift to short wavelength (high wavenumber) for the monomeric model system (VCz–DEF:TCNB (2 mol%)) is observed in the short-wavelength (high-wavenumber) region compared with the PVCz system. This supports the interpretation that the CT fluorescence of PVCz:TCNB films is attributed to the 2:1 complex and suggests that 1:1 complexes of

VCz–DEF:TCNB films also have different relative configuration between carbazolyl chromophore and TCNB and decay independently.

Molecular aspects of disordered structure and morphological change

In the present and earlier papers[9], in order to interpret the fluorescence peak shift in the time-resolved spectra, we proposed ion pairs with various inter-ionic distances, various exciplexes/exterplexes and various excited triple complexes, where the geometry of carbazole dimer cation (DD^+) and the relative geometrical structure of DD^+ to A^- in the state take diverse distribution. The presence of such multiple species in PVCz films is due to fluctuations of the distances between carbazolyl chromophores and of their mutual orientation. Such a positional disorder results in a large spread of site energies. From a physical point of view, Bassler pointed out the importance of energetic disorder of amorphous organic materials. For example, he took PVCz as a prototypical system, and investigated inhomogeneous broadening of the absorption band[22], hole transport[22,23], singlet exciton motion[24] and recombination kinetics of geminate electron–hole pairs[25]. The present result is one piece of evidence to show the importance of the fluctuation due to the positional disorder, which is clarified on the basis of dynamic molecular aspects.

The different fluorescence properties between the exterplex and the CT complex and the difference in the fluorescence dynamics observed for exterplexes formed between two carbazolyl chromophores and an acceptor with different electron affinity may be due to the presence or absence of ground-state CT complexes. That is, formation of the ground-state CT complex seems to induce a change of relative geometrical structure of carbazolyl chromophores (morphological change) in PVCz films. On the other hand, weak electron acceptors (exterplex system) are incorporated without any particular interaction with carbazolyl chromophores. Thus the morphology of PVCz films changes with the electron affinity of doped acceptors.

We have recently measured transient absorption spectra of PVCz thin films doped with acceptors by a new laser photolysis method, monitoring transmittance change under a total internal multi-reflection condition[26]. The absorption spectrum of PVCz cation in the PVCz–TCNB system was relatively sharper than that in the PVCz–DCNB one, and the migration coefficient of a hole was larger in the exciplex system than in the CT one[10,27]. These results also suggest the morphological change of PVCz films caused by the formation of the ground-state CT complex. That is, even if the dopant concentration is small, the morphological change induced by the formation of the ground-state CT complex is suggested by fluorescence spectroscopy.

The present paper is the first one concerning the CT fluorescence dynamics in photoconductive vinyl polymer films with large π-electron pendent groups. The behaviour is quite complicated, and more detailed experimental work and analysis are necessary.

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