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Exterplex Formation of Poly(3,6-di-*tert*-butyl-9-vinylcarbazole) and Its Dimeric Model Compounds with Dimethyl Terephthalate Studied by Fluorescence Spectroscopy

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ABSTRACT: The emission properties of poly(3,6-di-*tert*-9-vinylcarbazole) (PBVCz) and its dimeric model compounds were investigated in the presence of an electron acceptor, dimethyl terephthalate (DMTP), by fluorescence spectroscopy. In spite of the steric hindrance of *tert*-butyl groups, all these compounds formed a partially-overlapped exterplex, which is in sharp contrast to the fact that the meso isomer of 2,4-bis(3,6-di-*tert*-butyl-9-carbazolyl)pentane (m-BCzPe) and 1,3-bis(3,6-di-*tert*-butyl-9-carbazolyl)propane (BCzPr) do not form any intramolecular excimer. This means that the conformational requirement for the formation of the exterplex is rather loose and that the stabilization energy is larger than that for the formation of the excimer. The kinetic scheme of the exterplex formation was demonstrated by time-resolved fluorescence spectroscopy. The decay analysis revealed that the quenching processes of excited states by DMTP is diffusion-controlled and the rate constants of exterplex formation by exciplex quenching decrease in the order r-BCzPe > m-BCzPe > BCzPr. This suggests that r-BCzPe takes the most favorable conformation in the ground state for forming the partially-overlapped exterplex.

Introduction

An excited triple complex, "exterplex", which is composed of three molecules often plays an important role as an intermediate in photochemical reactions, and it has been a subject of extensive spectroscopic and kinetic studies.[1-9] In 1968, Beens and Weller[1] reported that, for a naphthalene–1,4-dicyanobenzene (p-DCNB) system, the exciplex emission decreases, accompanying a new emission in a longer wavelength region, when the naphthalene concentration is increased. They ascribed this new emission to a DDA type exterplex with an asymmetrical polar structure, which consisted of two naphthalenes (electron donor, D) and p-DCNB (electron acceptor, A). A polymer having pendant aromatic chromophores and dimeric compounds are expected to form an exterplex efficiently due to a high local chromophore concentration. A poly(9-vinylcarbazole) (PVCz)–dimethyl terephthalate (DMTP) system shows a broad emission around 520 nm which appears at a wavelength longer than the exciplex emission. Hoyle and Guillet[7] assigned this emission band to a DDA type exterplex having two carbazolyl chromophores and one DMTP. Similarly to the case of a dimer radical cation,[10-14] the DDA exterplex is stabilized owing to the delocalization between neighboring electron donors of a positive charge produced by photoinduced electron-transfer from D to A. Therefore, the stability of the exterplex depends on the relative conformation, the overlapping, of neighboring chromophores. Masuhara et al.,[8] who investigated the fluorescence properties of *meso*- and *rac*-2,4-di(9-carbazolyl)pentanes (m- and r-DCzPe) in the presence of 1,3-dicyanobenzene, reported that these diastereomers form a different DDA type exterplex; r-DCzPe forms an exterplex in which two carbazolyl (Cz) chromophores overlap partially (partially-overlapped exterplex), while m-DCzPe forms one in which two Cz chromophores overlap completely with each other (fully-overlapped exterplex).

Recently, we studied the fluorescenct behavior of poly(3,6-di-*tert*-butyl-9-vinylcarbazole) (PBVCz), *meso*- and *rac*-2,4-bis(3,6-di-*tert*-butyl-9-carbazolyl)pentanes (BCzPe), and 1,3-bis(3,6-di-*tert*-butyl-9-carbazolyl)propane (BCzPr),[15] the latter two being a dimeric model compound of the former. A *tert*-butyl group introduced in a carbazole (Cz) chromophore is very bulky, and its steric hindrance should be very large. Therefore, in these systems, the neighboring chromophore interaction in an excited state was found to be suppressed: PBVCz and the racemic isomer of BCzPe (r-BCzPe) exhibit a unique excimer whose emission band is slightly shifted from the excited monomer band, while the meso isomer of BCzPe (m-BCzPe) and BCzPr gave no excimer. Thus, the kinetic scheme in the excited states was found to be simplified because of the steric hindrance of the *tert*-butyl groups.

Herein, we report the fluorescence properties of these compounds in the presence of DMTP and discuss the steric effect of the *tert*-butyl groups on the exterplex formation. Furthermore, the processes of exterplex formation are clarified by the time-resolved fluorescence spectra and fluorescence decay analysis.

Experimental Section

Materials. Poly(3,6-di-*tert*-butyl-9-vinylcarbazole) (PBVCz), *meso*- and *rac*-2,4-bis(3,6-di-*tert*-butyl-9-carbazolyl)pentanes (m- and r-BCzPe), 1,3-bis(3,6-di-*tert*-butyl-9-carbazolyl)propane (BCzPr), and 3,6-di-*tert*-butyl-9-ethylcarbazole (BEtCz) were synthesized previously.[15,16] PBVCz has a molecular weight of ca. 1×10^6. The diastereoisomers r- and m-BCzPe are model compounds for syndiotactic and isotactic diads, respectively, in a PBVCz chain, and PEtCz is a monomer model for PBVCz.

An electron acceptor, dimethyl terephthalate (DMTP, Wako Pure Chemical Industries) was purified several times by recrystallization. Tetrahydrofuran (THF, Dotite Spectrosol) and toluene (Dotite Spectrosol) were used without further purification.

Measurements. The fluorescence properties of PBVCz and its model compounds were investigated in THF and toluene solvents, respectively, in the presence of DMTP (0.05 M). Fluorescence spectra were recorded with a Hitachi 850 spectrophotofluorometer. Fluorescence decay and time-resolved fluorescence spectra were measured by a single-photon-counting method. The photoexcitation of the 3,6-di-*tert*-butylcarbazole

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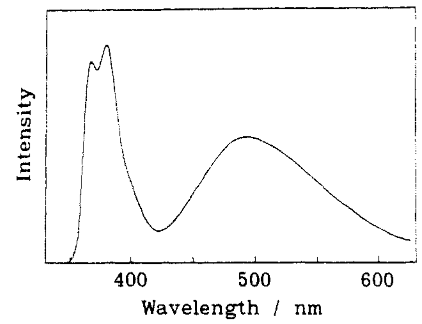


Figure 1. Emission spectrum for the BEtCz-DMTP (0.05 M) system in toluene at 25 °C. The absorbance at 322 nm is about unity.

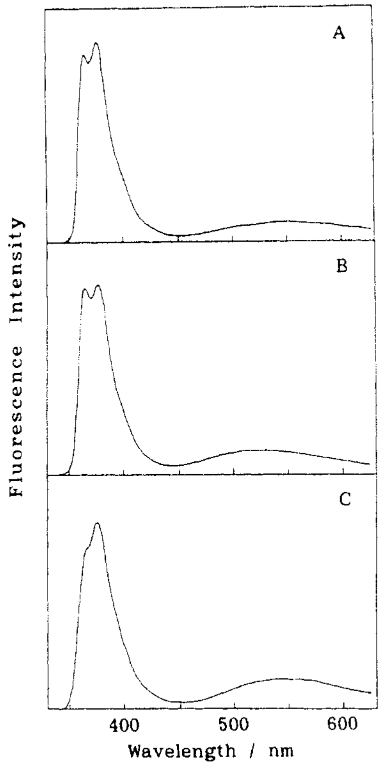


Figure 2. Emission spectra for the dimeric model compound–DMTP (0.05 M) systems in toluene at 25 °C. (A) m-BCzPe; (B) BCzPr; (C) r-BCzPe. The absorbance at 322 nm is about unity.

(BCz) chromophore was made by a 322-nm pulse (fwhm ca. 75 ps) of a Spectra-Physics picosecond synchronously pumped, mode-locked, cavity-dumped dye laser (Models 2020, 342A, 375B, and 344S). The concentration of BCz chromophore was so adjusted as to give about a unit absorbance at 322 nm. All samples were degassed by the freeze–pump–thaw method, and the measurements were carried out in a 1-cm quartz cell at 25 °C.

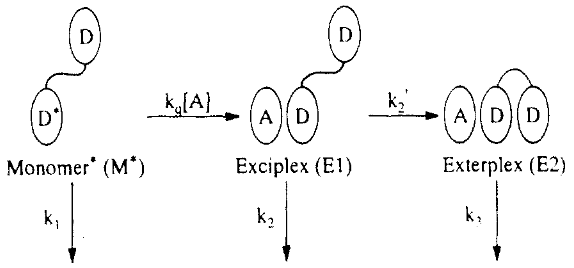
Results and Discussion

Figure 1 shows the emission spectrum of the BEtCz–DMTP system in toluene. The exciplex emission was observed at ca. 495 nm besides the monomer emission having a vibrational structure. This exciplex emission was somewhat shifted to longer wavelengths than that of the EtCz–DMTP system at ca. 480 nm.[17] This is considered to be due to the effect of *tert*-butyl substitution. On the other hand, the dimeric model compounds show a broad emission at a wavelength (ca. 540 nm) longer than the exciplex emission besides the monomer and/or the excimer emissions (Figure 2).[15] This broad emission band was ascribed to a DDA exterplex consisting of two BCz chromophores and DMTP. The DDA exterplex is stabilized owing to the delocalization between neighboring D chromophores of a positive charge produced by photoinduced electron transfer from D to A. Beens and Weller[1] estimated the stabilization energy (ΔE) using the following equation.

$$\Delta E = \nu'_{\max} - \nu''_{\max} \qquad (1)$$

where $\nu'_{\max}$ and $\nu''_{\max}$ are the peak wavenumbers of DA exciplex emission and DDA exterplex emission, respectively. According to eq 1, for all dimeric model compounds having BCz chromophores, the stabilization by the charge delocalization was estimated to be ca. 0.21 eV. This is comparable to the stabilization energy (0.25 eV) of the partially-overlapped exterplex for r-DCzPe, which shows an exterplex emission band around 520 nm with DMTP.[8] m-DCzPe forms a fully-overlapped exterplex with an emission band around 560 nm, and its stabilization energy was estimated to be ca. 0.42 eV.[8] Due to the steric hindrance of *tert*-butyl groups, all BCz dimeric model compounds do not form the fully-overlapped exterplex but form the partially-overlapped one, which is not as stable as the partially-overlapped exterplex of r-DCzPe. It is noteworthy that m-BCzPe and BCzPr form the partially-overlapped exterplex, though they form no excimer.

Scheme I
Exterplex Formation Scheme for the m-BCzPe and BCzPr Systems



By introducing *tert*-butyl groups, the formation scheme of the exterplex becomes very simple, especially in the case of m-BCzPe and BCzPr. Scheme I shows the formation process of the exterplex for the m-BCzPe and BCzPr systems. Since they do not form any excimer, only the quenching of the monomer excited state by DMTP is taken into account. The monomer excited state is quenched by DMTP with the rate constant k_q and forms the exciplex. The exciplex changes its conformation and forms the exterplex by neighboring chromophore interaction with the rate constant, k_2'. In this scheme, k_1, k_2, and k_3 are the rate constants of the deactivation processes which contain the fluorescence and radiationless transitions. The dissociation of the exciplex and the exterplex to the monomer excited state is neglected. The exciplex formation by quenching of the monomer excited state and subsequent exterplex formation were confirmed by the time-resolved emission spectra as shown in Figure 3 for the m-BCzPe system. The solid line indicates the emission spectrum in the time range from 1.7 to 3.3 ns. Along with the monomer emission, a broad emission was observed in the longer wavelength region. To investigate what this broad band is assigned to, the monomer emission was subtracted from this spectrum by using the emission spectrum at $t = 0$ as the monomer emission band. As shown by the broken line, the subtracted spectrum gives a broad emission band around 500 nm. This corresponds to the exciplex emission for the BEtCz–DMTP system. In the time range from 30 to 40 ns, the exterplex emission was observed at around 540 nm as shown by the dash-dotted line in Figure 3. This suggests that the exciplex

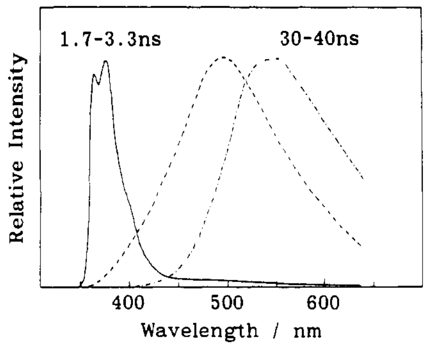


Figure 3. Time-resolved emission spectra for the m-BCzPe–DMTP (0.05 M) system in toluene at 25 °C observed at 500 (a) and 640 nm (b). The solid and dash–dotted lines show the emission spectra in the time range from 1.7 to 3.3 ns and from 30 to 40 ns, respectively. The broken line indicates the spectrum in the time range from 1.7 to 3.3 ns after subtracting the monomer emission.

is mainly formed in the earlier stage and that the exterplex is formed subsequently. The time dependence of the emission spectrum for the BCzPr system was essentially the same as that for m-BCzPe.

According to this scheme, the rise and decay functions of the monomer excited state (M*), the exciplex (E1*), and the exterplex (E2*) are expressed by the following equations.

$$[\mathrm{M}^*] \propto \exp(-t/\tau_{\mathrm{M}}) \tag{2}$$

$$[\mathrm{E1}^*] \propto -\exp(-t/\tau_{\mathrm{M}}) + \exp(-t/\tau_{\mathrm{E1}}) \tag{3}$$

$$[\mathrm{E2}^*] \propto T_1 \exp(-t/\tau_{\mathrm{M}}) - T_2 \exp(-t/\tau_{\mathrm{E1}}) + (T_2 - T_1) \exp(-t/\tau_{\mathrm{E2}}) \tag{4}$$

$$T_1 = (\tau_{\mathrm{M}}^{-1} - \tau_{\mathrm{E2}}^{-1})^{-1}, \qquad T_2 = (\tau_{\mathrm{E1}}^{-1} - \tau_{\mathrm{E2}}^{-1})^{-1}$$

where τ_{M}, τ_{E1}, and τ_{E2} are the lifetimes of the monomer excited state, the exciplex, and the exterplex, respectively. Figure 4 shows the decay curves observed at 500 nm (Figure 4a) and at 640 nm (Figure 4b). As a main component, the former decay curve contains the exciplex emission, and the latter, the exterplex emission. These decay curves were simulated by the three-exponential function as the sum of the exciplex (eq 3) and the exterplex emission (eq 4). The solid line shows a simulation line. The best-fit three-exponential functions ar as follows.

$$I_{500}(t) = -0.848 \exp(-t/0.96) + 0.881 \exp(-t/6.57) + 0.229 \exp(-t/40.99) \tag{5}$$

$$I_{640}(t) = -0.779 \exp(-t/2.01) - 0.075 \exp(-t/6.57) + 0.966 \exp(-t/40.99) \tag{6}$$

Since the lifetime, τ_{M}, of the monomer excited state is nearly in the limit of measurability in this time range, the experimental error is large. Therefore, τ_{M} was determined by means of the decay curve at 365 nm, where the contribution of the exciplex and the exterplex emissions can be neglected. Thus, a τ_{M} value of ca. 1.8 ns was obtained. Then τ_{M}, τ_{E1}, and τ_{E2} were evaluated to be 1.8, 6.6, and 41.0 ns, respectively.

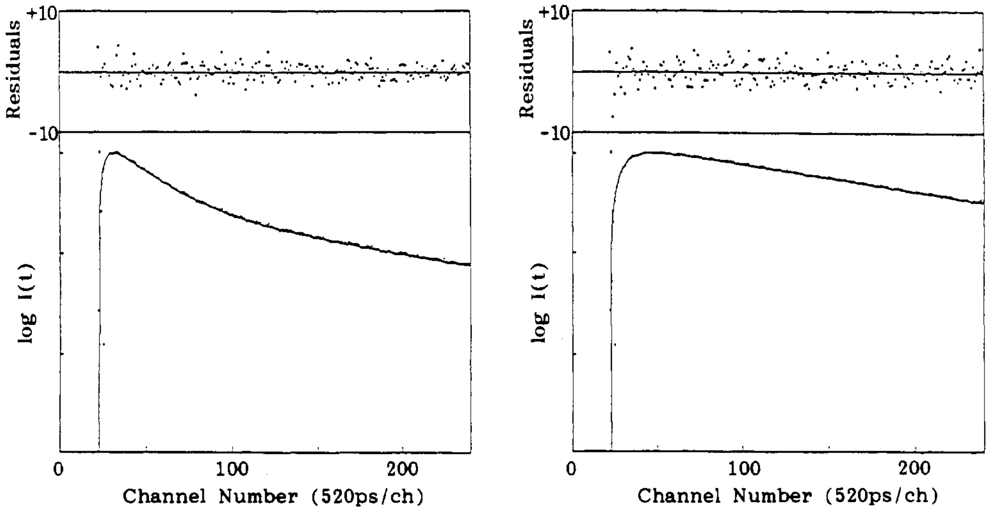
For the BCzPr system, each lifetime was determined in the same way. The lifetime τ_{M} was determined to be 1.8 ns by the decay curve at 365 nm. Figure 5 shows the decay curves at 500 nm (Figure 5a) and at 640 nm (Figure 5b) for the BCzPr system. These decay curves were simulated by the three-exponential function, and the following functions were obtained.

$$I_{500}(t) = -0.917 \exp(-t/0.90) + 0.429 \exp(-t/9.23) + 0.759 \exp(-t/30.12) \tag{7}$$

$$I_{640}(t) = -0.992 \exp(-t/1.75) - 0.200 \exp(-t/9.23) + 1.329 \exp(-t/30.12) \tag{8}$$

For the BCzPr system, τ_{M}, τ_{E1}, and τ_{E2} were found to be 1.8, 9.2, and 30.1 ns, respectively.

On the other hand, this scheme cannot be applied to the r-BCzPe system, since r-BCzPe forms the excimer. Therefore, Scheme II was assumed. In this scheme, the equilibrium between the monomer excited state and the excimer is taken into account and is assumed to be reached much more rapidly than the other processes.[1] Since the quenchings of both the monomer excited state and the excimer by DMTP are considered to be diffusion-controlled,[9] the quenching rate constants (k_{q}) for both processes are assumed to be equal. The constants k_1, k_2,



(a) (b)

Figure 4. Rise and decay curves of fluorescence for the m-BCzPe–DMTP (0.05 M) system in toluene at 25 °C observed at 500 (a) and 640 nm (b). The solid line indicates the simulation line by the three-exponential function.

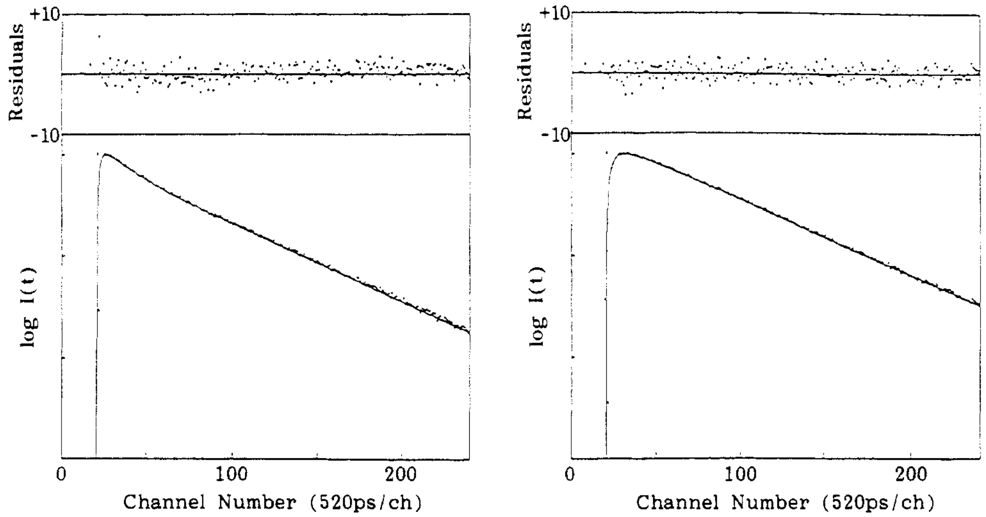
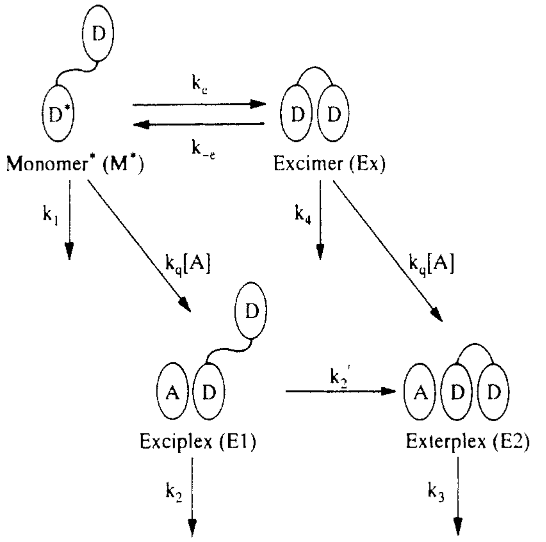


Figure 5. Rise and decay curves of fluorescence for the BCzPr–DMTP (0.05 M) system in toluene at 25 °C observed at 500 (a) and 640 nm (b). The solid line indicates the simulation line by the three-exponential function.

Scheme II
Exterplex Formation Scheme for the r-BCzPe System



k_3, and k_4 are the rate constants of the deactivation processes of each excited state. In this case, the exterplex is formed in two processes; one is via the excimer and the other is via the exciplex. The rapid exterplex formation via the excimer was confirmed by the time-resolved emission spectra, as shown in Figure 6. The solid curve gives the emission spectrum in the time range from 1.7 to 3.3 ns. Along with the monomer and the excimer emissions, a broad emission band was observed in the longer wavelength region. The monomer and the excimer emissions were subtracted by using the emission spectrum at $t = 0$. The subtracted spectrum is shown by the broken line. It is a broad emission around 540 nm which is mainly ascribed to the exterplex emission. This suggests that the exterplex is formed in an earlier stage in contrast to the cases of the m-BCzPe and BCzPr systems. In the later stage from 30 to 40 ns (the dash–dotted line), the relative intensity in the shorter wavelength region is decreased and the one in the longer wavelength region is increased as compared with the subtracted spectrum in the time range from 1.7 to 3.3 ns. This indicates that the exterplex formation process via the exciplex is slow.

This exterplex formation scheme approximately leads to the following rise and decay functions of the monomer excited state, the excimer, the exciplex, and the exterplex.

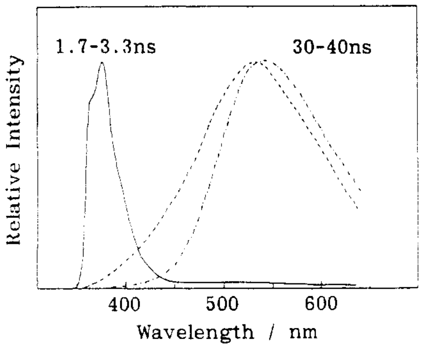


Figure 6. Time-resolved emission spectra for the r-BCzPe–DMTP (0.05 M) system in toluene at 25 °C. The solid and the dash–dotted lines show the emission spectra in the time range from 1.7 to 3.3 ns and from 30 to 40 ns, respectively. The broken line indicates the spectrum in the time range from 1.7 to 3.3 ns after subtracting the monomer and excimer emissions.

$$[\mathrm{M}^*] \propto \exp(-t/\tau_{\mathrm{M}}), \qquad [\mathrm{E}^*] \propto \exp(-t/\tau_{\mathrm{M}}) \tag{9}$$

$$[\mathrm{E1}^*] \propto -\exp(-t/\tau_{\mathrm{M}}) + \exp(-t/\tau_{\mathrm{E1}}) \tag{10}$$

$$[\mathrm{E2}^*] \propto (k_2'T_3 - K^{-1})T_1 \exp(-t/\tau_{\mathrm{M}}) - k_2'T_2T_3 \exp(-t/\tau_{\mathrm{E1}}) + [k_2'T_3(T_2 - T_1) + K^{-1}T_1] \exp(-t/\tau_{\mathrm{E2}}) \tag{11}$$

$$T_1 = (\tau_{\mathrm{M}}^{-1} - \tau_{\mathrm{E2}}^{-1})^{-1}, \quad T_2 = (\tau_{\mathrm{E1}}^{-1} - \tau_{\mathrm{E2}}^{-1})^{-1}, \quad T_3 = (\tau_{\mathrm{M}}^{-1} - \tau_{\mathrm{E1}}^{-1})^{-1}, \quad K = k_e/k_{-e}$$

where K is the equilibrium constant between the monomer excited state and the excimer. These equations are expressed by the three-exponential function using their lifetimes (τ_{M}, τ_{E1}, and τ_{E2}). Figure 7 shows the decay curves observed at 500 nm (Figure 7a) and at 640 nm (Figure 7b). By simulating the decay curve using the three-exponential function, the following decay functions were obtained.

$$I_{500}(t) = -0.914 \exp(-t/0.60) + 0.590 \exp(-t/3.76) + 0.670 \exp(-t/46.94) \tag{12}$$

$$I_{640}(t) = -0.963 \exp(-t/1.55) - 0.076 \exp(-t/3.76) + 1.146 \exp(-t/46.94) \tag{13}$$

The lifetime τ_{M} was determined to be 1.7 ns by analyzing

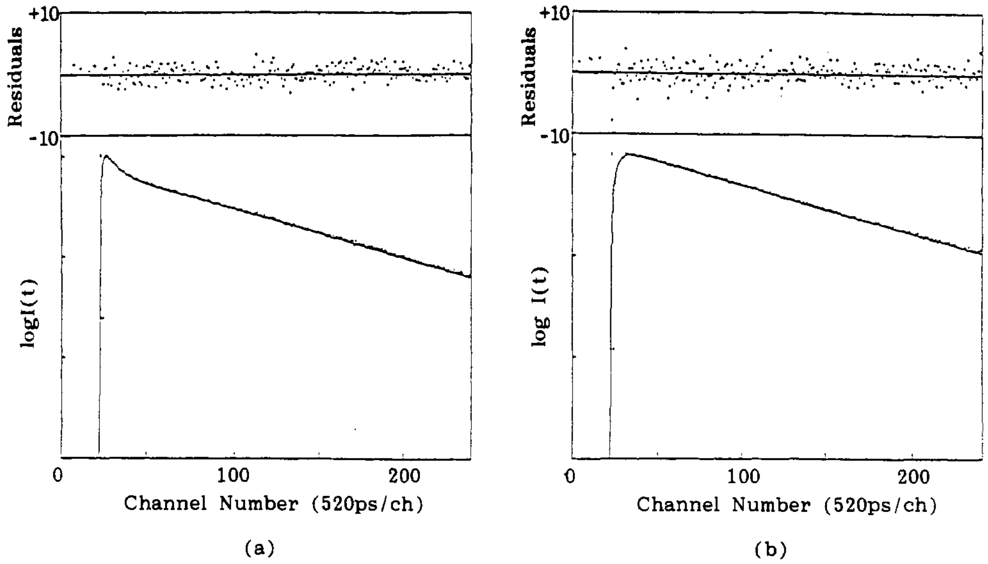


Figure 7. Rise and decay curves of fluorescence for the r-BCzPe-DMTP (0.05 M) system in toluene at 25 °C observed at 500 (a) and 640 nm (b). The solid line indicates the simulation line by the three-exponential function.

Table I
Lifetimes of the Monomer Excited State (τ_M), the Exciplex (τ_{E1}), and the Exterplex (τ_{E2}), Quenching Rate Constants (k_q), and Exterplex-Formation Rate Constants (k_2') for the Dimeric Model Compound Systems

	τ_M/ns	τ_{E1}/ns	τ_{E2}/ns	$k_q/10^9$ M^{-1} s^{-1}	$k_2'/10^8$ s^{-1}
BEtCz	1.8	59.3		9.8	
r-BCzPe	1.7	3.8	46.9	10.1	2.5
m-BCzPe	1.8	6.6	41.0	9.5	1.4
BCzPr	1.8	9.2	30.1	9.5	0.92

the decay curve at 365 nm. In this way, τ_M, τ_{E1}, and τ_{E2} for r-BCzPe were estimated to be 1.7, 3.8, and 46.9 ns, respectively.

The rate constant of quenching (k_q) by DMTP and the rate constant of the exterplex formation (k_2') from the exciplex were calculated by using the lifetimes according to each formation scheme. Table I shows the results together with the lifetime data. The quenching rate constant is ca. 1 × 10^{10} M^{-1} s^{-1} for all systems. The quenching process is an exothermic reaction enough to be diffusion-controlled.[17] The rate constants k_2' decrease in the order r-BCzPe > m-BCzPe > BCzPr. This is due to the difference between the ground-state conformation and the exterplex one. r-BCzPe is considered to form an exterplex with the least conformational change of the three. The exterplex for r-BCzPe has the longest lifetime of the three. This suggests that r-BCzPe forms the most stable exterplex. These BCz dimeric model compounds do not form a fully-overlapped exterplex. Thus, r-BCzPe was found to have the most favorable conformation for forming the partially-overlapped exterplex.

Figure 8 shows the emission spectrum of the PBVCz-DMTP system in THF. Besides the monomer and the excimer emissions, a broad emission in the longer wavelength region was observed around 540 nm. This broad band is similar to the exterplex emission for the dimeric model compound systems described previously. PBVCz is also considered to form a partially-overlapped exterplex.

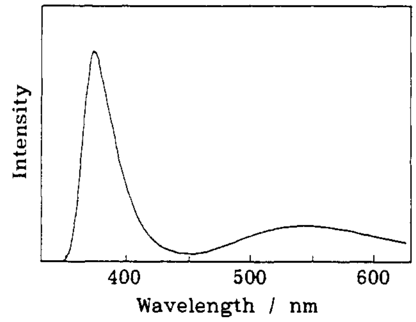


Figure 8. Emission spectrum for the PBVCz-DMTP (0.05 M) system in THF at 25 °C. The absorbance at 322 nm is about unity.

Conclusion

We found that PBVCz and its dimeric model compounds form a DDA-type exterplex with a partially-overlapped conformation and that the involved interaction is somewhat weakened due to the steric hindrance of the *tert*-butyl groups compared with the one for the exterplex of the carbazolyl chromophore. The formation of the exterplex was observed even in m-BCzPe and BCzPr, which form no excimers. This means that the conformational requirement for the stabilization of the exterplex is not so strict compared to that of the excimer and that the stabilization energy by the charge delocalization is larger than that of the excimer. The exterplex formation process was clarified by time-resolved fluorescence spectroscopy; for m-BCzPe and BCzPr, the exterplex is formed via the exciplex, while for r-BCzPe it is formed both via the fast process of the excimer quenching by DMTP and via the slow process of the exciplex quenching by the other BCz chromophore. The fluorescence decay analysis revealed that the quenching process of the excited state by DMTP is diffusion-controlled (k_q = 1 × 10^{10} M^{-1} s^{-1}) and the rate constants of the exciplex quenching by the conformational change become smaller in the order r-BCzPe > m-BCzPe > BCzPr. Furthermore, the lifetimes of the exterplex also decrease in this order. These results suggest that r-BCzPe has the most favorable conformation in the ground state for taking a partially-overlapped conformation in the excited state and forms the most stable exterplex.

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