

Time-resolved ion-pair charge transfer fluorescence of bipyridinium salts in various microenvironments

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Abstract

The temperature dependence of ion-pair charge transfer (IPCT) fluorescence was studied by time-resolved spectroscopy in 4,4'-bipyridinium and 2,2'-bipyridinium salts with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate in microcrystals and polymer films at 10–300 K. Time-resolved fluorescence, peaking at 400–460 nm and 500 nm, appeared on excitation of IPCT absorption. A shorter wavelength peak in microcrystals was observed at 440 nm for the 4,4'-bipyridinium salt and at 460 nm for the 2,2'-bipyridinium salt; this peak was independent of temperature. A shorter wavelength peak in polymer films containing the 4,4'-bipyridinium salt was observed to shift from 432 nm → 420 nm → 402 nm with decreasing temperature from 300 K to 10 K, corresponding to the molecular motion of polymer chains. Similarly, a shorter wavelength peak in polymer films containing the 2,2'-bipyridinium salt was observed to shift from 460 nm to 440 nm with decreasing temperature from 300 K to 10 K. The fluorescence decay curves were composed of two fast components ($\tau = 0.3$ –7 ns) and a slow component ($\tau = 12$ –34 ns). The former corresponds to the shorter wavelength peak and the latter to the longer wavelength peak in the IPCT fluorescence spectra of the 4,4'-bipyridinium and 2,2'-bipyridinium salts. A reaction mechanism is proposed on the basis of these results.

Keywords: Time-resolved ion-pair charge transfer fluorescence; Bipyridinium salts; Microcrystal; Polymer film

1. Introduction

Various photochromic systems employing polymeric thin films or Langmuir–Blodgett (LB) films have recently attracted much interest in view of their promising applicability to high-speed and high-density photon-mode optical memory. The photochromism reported so far involves changes in chemical bonds, such as heterolytic cleavage of a pyran ring in spiropyrans or cis–trans isomerization in azobenzenes [1].

Recently, we have reported novel photochromism (photoinduced electrochromism) in organic solutions [2,3], microcrystals [4,5], LB films [6–11] and polymer films [11–15], which is due to the photoinduced electron transfer reaction via the excited state of specific ion-pair charge transfer (IPCT) complexes [16,17] between 4,4'-bipyridinium ion as acceptor and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [18] (abbreviated to TFPB⁻) as donor. The photochemical colouring and thermal fading due to reverse electron transfer are highly reversible in all systems in a deaerated atmosphere [2–15]. The lifetime of the coloured

(blue) state depends markedly on the microenvironment and temperature.

N,N'-Dimethyl-4,4'-bipyridinium TFPB⁻ salts show broad structureless fluorescence with a maximum at 525 nm from the excited IPCT state in 1,2-dimethoxyethane (DME) solutions at room temperature [16,19]. The excitation of the IPCT band ($\lambda_{ex} = 475$ nm) in an oxygen-free atmosphere results in quenching of the IPCT fluorescence accompanied by a remarkable colour change from pale yellow to blue owing to the accumulation of 4,4'-bipyridinium radical cations. After the disappearance of the blue colour in about 1 h at 20 °C in the dark, the IPCT absorbance and fluorescence intensity in DME recover very gradually to equilibrium values [19]. The changes in IPCT fluorescence and colour are repeated reversibly. These results demonstrate that 4,4'-bipyridinium TFPB⁻ salts can be applied to photon-mode optical memories which can be read with either absorption or emission [19]. The decay behaviour of fluorescence, observed on picosecond laser excitation, does not correspond to the formation rate of transient absorption at about 600 nm, which is much faster than the fluorescence decay [15]. The picosecond time-resolved fluorescence spectra of 4,4'-bipyridinium

idium polymer films show a broad, slowly decaying component with a peak at 490 nm and a less broad short-lived component with a peak at about 440 nm at room temperature [20]. The temperature dependence of the time-resolved IPCT fluorescence in polymer films of 4,4'-bipyridinium TFPB⁻ salts has recently been reported [21]. In this study, the temperature dependence of the IPCT fluorescence spectra of 4,4'-bipyridinium and 2,2'-bipyridinium salts with TFPB⁻ in microcrystals and polymer films is discussed.

2. Experimental details

2.1. Materials

The structures of the compounds employed are shown in Fig. 1. The synthesis of poly(tetrahydrofuran) containing 4,4'-bipyridinium (2.3×10^{-4} mol g⁻¹) as part of the main chain has been reported previously [12,13].

An elastic polymer containing 2,2'-bipyridinium salt as part of the main chain was synthesized by a slight modification of the procedure used for polymeric 4,4'-bipyridinium

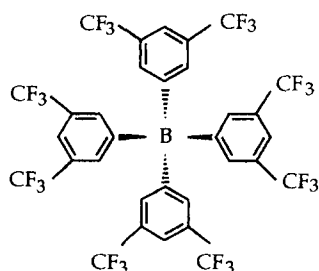
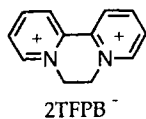
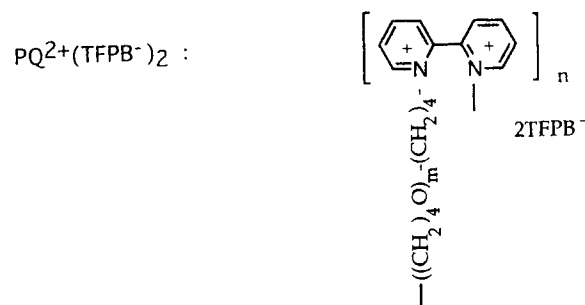
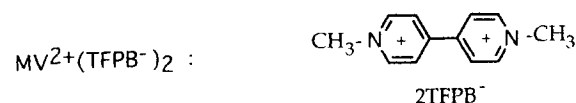
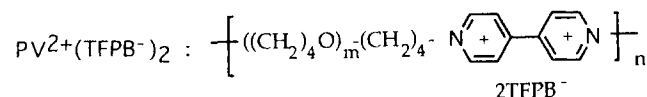


Fig. 1. Structures and abbreviations of the compounds employed.

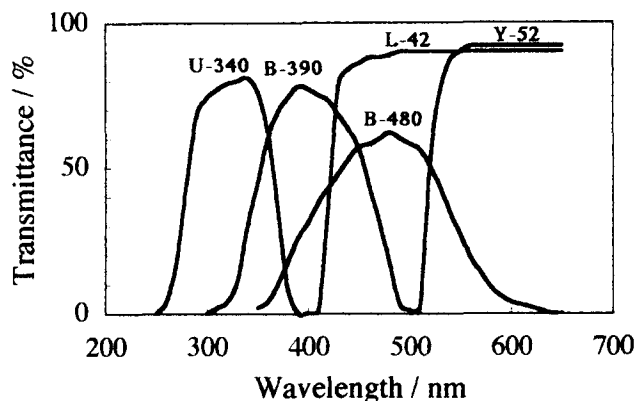


Fig. 2. Characteristics of the bandpass and sharp-cut filters used in the experiment.

salt. Dry tetrahydrofuran (24.45 g) was stirred in N₂ for 15 min at room temperature in the presence of trifluoromethanesulphonic anhydride (1.40 g) as initiator. The solution was then cooled to -70°C and a tetrahydrofuran solution of 2,2'-bipyridine (0.53 g in 10 ml) was added. The mixture was stirred for 7 h at -70°C and for 1 h at 2°C to effect reaction between 2,2'-bipyridine and living dicationic poly(tetrahydrofuran). The highly viscous products were purified by repeated precipitation and washing with water.

The counter anion, CF₃SO₃⁻, of the resulting white polymer was exchanged with TFPB⁻ to yield a pale yellow elastic polymer. Transparent, uniform films were obtained by casting a DME solution of this polymer onto a glass plate.

2.2. Measurements

Polymer films and microcrystals were thoroughly degassed in a cryostat with Iwatani Plantech ultralow-temperature cooling units. The fluorescence decay curve and time-resolved fluorescence spectra were measured on a Horiba NAES-700F with a nanosecond N₂ lamp (NFL-700) in vacuo at a controlled temperature. For time-resolved emission spectral measurements, U-340 and B-390 bandpass filters for 400–432 nm emission and a B-390 bandpass filter for 500 nm emission were used to excite the IPCT absorption band alone. For time-resolved excitation spectra, B-390 and L-42 filters or B-480 and Y-52 filters were used to monitor the IPCT fluorescence at 400–432 nm. The transmittance spectra of these filters are shown in Fig. 2. The fluorescence decay curve and time-resolved fluorescence spectra were measured after about 5 min at a given temperature.

The differential scanning calorimetry (DSC) thermogram was recorded using a MAC Science DSC 3100 thermal analysis station from 150 to 340 K with a heating rate of 5 K min⁻¹ and between 320 and 220 K with a cooling/heating rate of 1 K min⁻¹.

3. Results

Fig. 3 shows the time-resolved fluorescence spectra of 4,4'-bipyridinium and 2,2'-bipyridinium salts with TFPB⁻ in

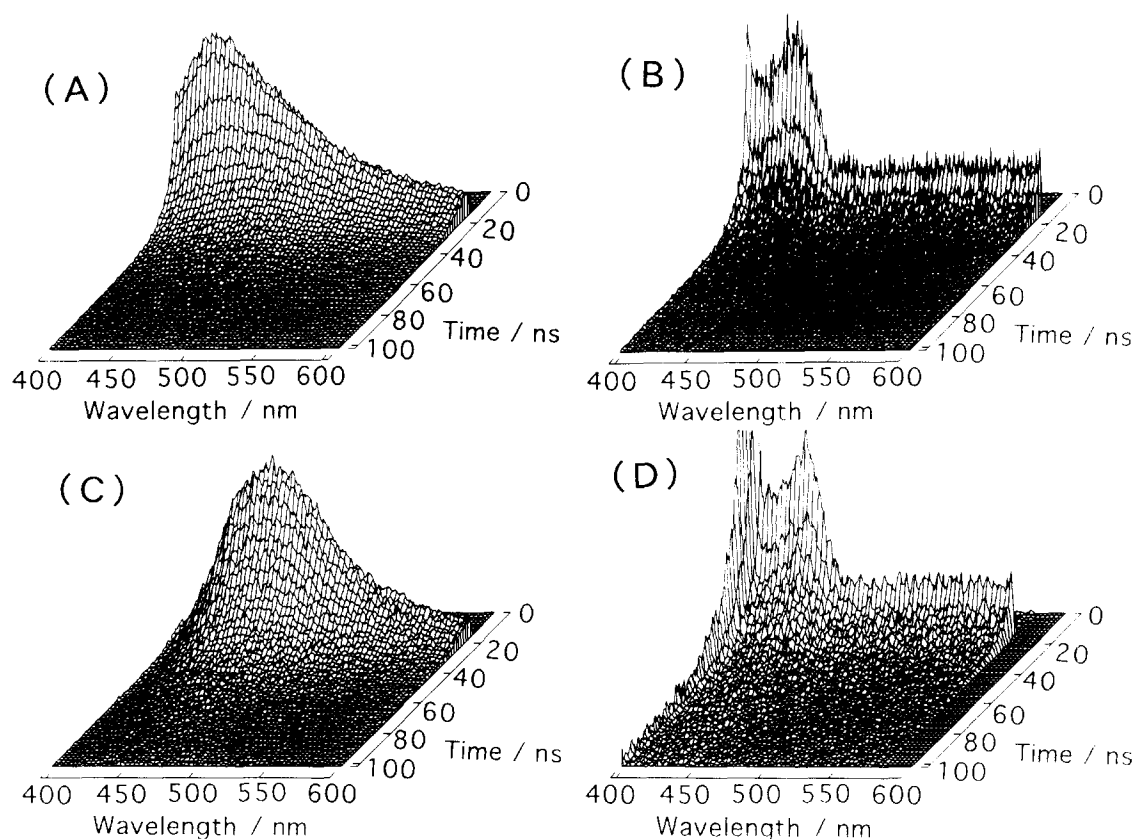


Fig. 3. Time-resolved fluorescence spectra of bipyridinium salts in microcrystals and polymer films excited at 350–400 nm at room temperature: (A) $PV^{2+}(TFPB^-)_2$; (B) $MV^{2+}(TFPB^-)_2$; (C) $PQ^{2+}(TFPB^-)_2$; (D) $DQ^{2+}(TFPB^-)_2$.

microcrystals and polymer films excited at 350–400 nm at room temperature. The fluorescence spectra are observed in the wavelength range 400–600 nm with peaks at 432 nm (A), 440 nm (B), 460 nm (C) and 460 nm (D). The sharp peaks around 400 nm in the fluorescence spectra in Figs. 3(B) and 3(D) for $MV^{2+}(TFPB^-)_2$ and $DQ^{2+}(TFPB^-)_2$ in microcrystals are due to the scattering of excitation light. The fluorescence bands of $PV^{2+}(TFPB^-)_2$ and $PQ^{2+}(TFPB^-)_2$ in polymer films (Figs. 3(A) and 3(C)) are much broader than those of $MV^{2+}(TFPB^-)_2$ and $DQ^{2+}(TFPB^-)_2$ in microcrystals. These results clearly indicate that the IPCT fluorescence spectra are affected by the structure of the acceptor and the microenvironment.

The fluorescence peak of $PQ^{2+}(TFPB^-)_2$ is blue shifted from 460 nm at 275 K to 440 nm at 250 K (with decreasing temperature) and red shifted from 440 nm at 275 K to 460 nm at 300 K (with increasing temperature), whereas no shifts are observed below 250 K, as shown in Fig. 4. Such a temperature dependence in $PQ^{2+}(TFPB^-)_2$ films corresponds to the glass transition temperature at 221 K, the crystallization at 267 K on cooling and the melting at 285 K on heating, as shown by the DSC thermogram (rate, 5 K min^{-1}) in Fig. 5. The slower rate of cooling at 1 K min^{-1} shifts the crystallization temperature to 275 K. Similarly, the fluorescence peak of $PV^{2+}(TFPB^-)_2$ shifts to shorter wavelengths from 432 nm at 300 K to 420 nm at 200 K (with decreasing temperature), whereas no temperature dependence of the peak at 402

nm is observed below 100 K, as shown in Fig. 6. The fluorescence band broadens with increasing temperature above 250 K in $PQ^{2+}(TFPB^-)_2$, as shown in Fig. 4, and above 200 K in $PV^{2+}(TFPB^-)_2$, as shown in Fig. 6 [21]. Another fluorescence peak at about 510 nm is observed on excitation at 460 nm of $PQ^{2+}(TFPB^-)_2$, similar to that previously reported for $PV^{2+}(TFPB^-)_2$ [21]. The relative intensity of this fluorescence band at about 510 nm increases with increasing temperature. The fluorescence spectra of $MV^{2+}(TFPB^-)_2$ and $DQ^{2+}(TFPB^-)_2$ in microcrystals, at 440 and 460 nm respectively, are not dependent on the temperature. The DSC thermograms of $MV^{2+}(TFPB^-)_2$ and $DQ^{2+}(TFPB^-)_2$ from 150 to 340 K show no transition.

Fig. 7 shows the time-resolved fluorescence excitation spectra of $PQ^{2+}(TFPB^-)_2$ at room temperature monitored at 460 nm (A) and 500 nm (B). The fluorescence excitation spectrum corresponds to the IPCT absorption spectrum, except for the shorter wavelength region below 380 nm, where the fluorescence quantum yield is very low due to photodissociation of the IPCT complexes. The fluorescence excitation spectrum monitored at 460 nm shows peaks at 350, 375 and 400 nm (Fig. 7(A)). The fluorescence excitation spectrum monitored at 500 nm shows an additional peak around 460 nm (Fig. 7(B)). For the emission band at 500 nm, the time-resolved fluorescence excitation spectrum exhibits a small ‘‘rise’’ at 350–400 nm as shown in Fig. 7(B). A clearer ‘‘rise’’ is found in the fluorescence excitation spec-

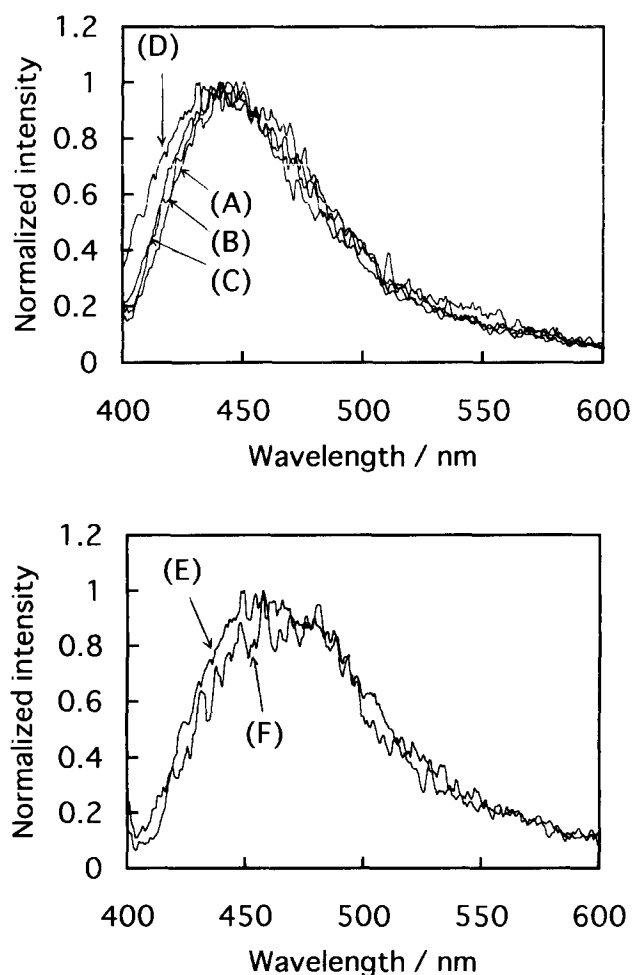


Fig. 4. Fluorescence spectra of $\text{PQ}^{2+}(\text{TFPB}^-)_2$, 2 ns after excitation at 350–400 nm, at: (A) 10 K; (B) 100 K; (C) 200 K; (D) 275 K on heating; (E) 275 K on cooling; (F) 300 K. The peak wavelengths in (A), (B), (C) and (D) are the same. The first three spectra are almost overlapped and (D) is slightly broadened.

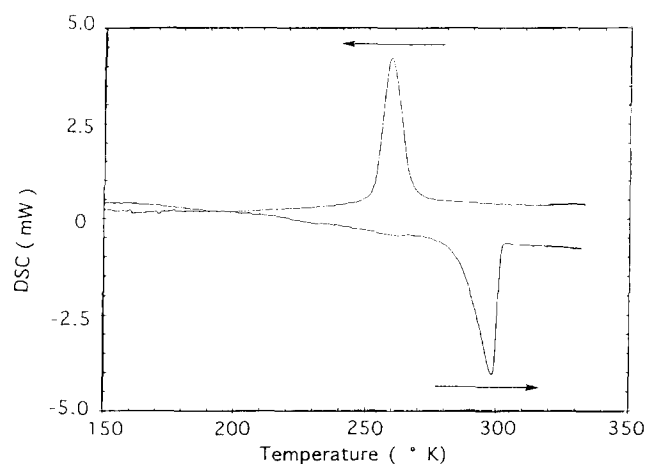


Fig. 5. DSC thermogram of $\text{PQ}^{2+}(\text{TFPB}^-)_2$ used in the experiment.

trum monitored at 500 nm for the $\text{PV}^{2+}(\text{TFPB}^-)_2$ film as reported previously [21]. The fluorescence excitation spectrum of $\text{PQ}^{2+}(\text{TFPB}^-)_2$ monitored at 500 nm is weaker and broader than that of $\text{PV}^{2+}(\text{TFPB}^-)_2$ [21]. In contrast with

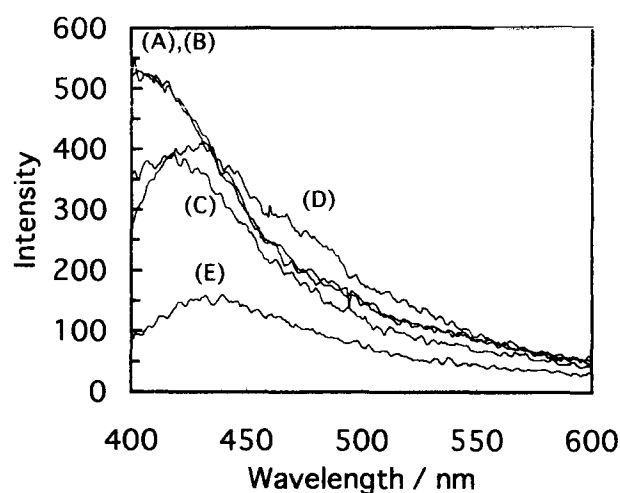


Fig. 6. Fluorescence spectra of $\text{PV}^{2+}(\text{TFPB}^-)_2$, 2 ns after excitation at 350–400 nm, at: (A) 10 K; (B) 100 K; (C) 200 K; (D) 275 K; (E) 300 K. Spectra (A) and (B) are overlapped.

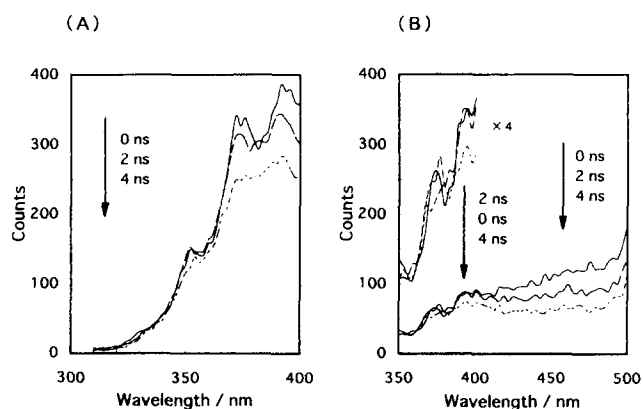


Fig. 7. Time-resolved fluorescence excitation spectra of $\text{PQ}^{2+}(\text{TFPB}^-)_2$ at room temperature monitored at 460 nm (A) and 500 nm (B). The time is the delay from the excitation pulse.

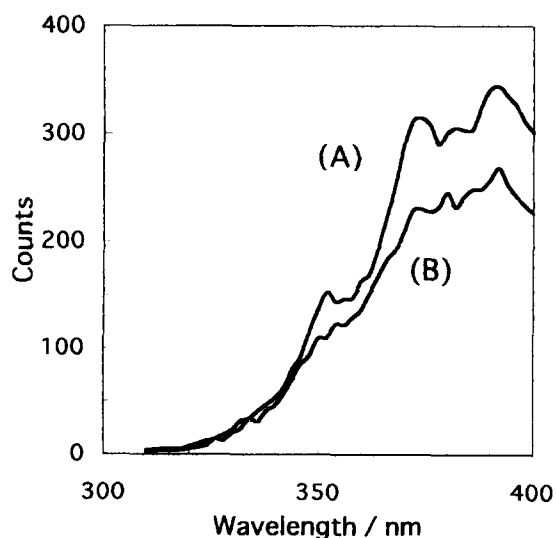


Fig. 8. Time-resolved fluorescence excitation spectra of $\text{PQ}^{2+}(\text{TFPB}^-)_2$, 2 ns after excitation, at 10 K (A) and 300 K (B) monitored at 440–460 nm.

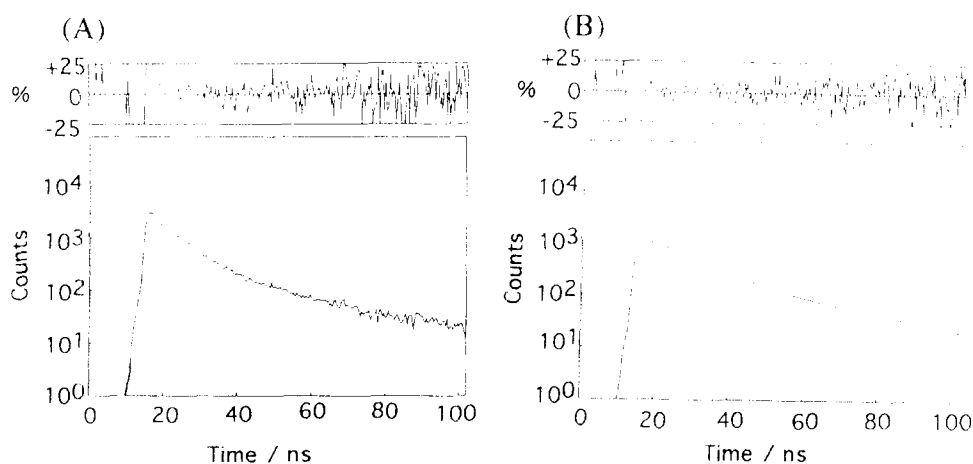


Fig. 9. Fluorescence decay curves of $\text{PQ}^{2+}(\text{TFPB}^-)_2$ film at room temperature at 460 nm (A) and 510 nm (B).

the fluorescence spectra, the profile of the fluorescence excitation spectra is not dependent on temperature for polymer films of $\text{PV}^{2+}(\text{TFPB}^-)_2$ [21] and $\text{PQ}^{2+}(\text{TFPB}^-)_2$ (shown in Fig. 8 for $\text{PQ}^{2+}(\text{TFPB}^-)_2$ at 10 and 300 K).

The fluorescence decay curves of $\text{PQ}^{2+}(\text{TFPB}^-)_2$ were fitted with a triple exponential with lifetimes of 2, 7 and 21 ns as shown in Fig. 9 for fluorescence at 460 and 510 nm. $\text{PV}^{2+}(\text{TFPB}^-)_2$, $\text{MV}^{2+}(\text{TFPB}^-)_2$ and $\text{DQ}^{2+}(\text{TFPB}^-)_2$ show similar triple-exponential decay. The fluorescence lifetimes of these IPCT complexes are summarized in Table 1. The fluorescence band at shorter wavelength shows a faster decay and the longer wavelength band shows a slower decay, similar to that reported for $\text{PV}^{2+}(\text{TFPB}^-)_2$ [21].

Fig. 10 shows the fluorescence lifetime plotted against the temperature (between 10 and 300 K) for $\text{PV}^{2+}(\text{TFPB}^-)_2$ (A) and $\text{MV}^{2+}(\text{TFPB}^-)_2$ (B). The fluorescence lifetimes of all the components in $\text{MV}^{2+}(\text{TFPB}^-)_2$ microcrystals exhibit no temperature dependence as shown in Fig. 10(B). The first component in $\text{PV}^{2+}(\text{TFPB}^-)_2$ polymer films, with the shortest lifetime, is hardly dependent on temperature. The second component in $\text{PV}^{2+}(\text{TFPB}^-)_2$ is observed above T_g and exhibits a considerable change at 175 and 275 K as shown in Fig. 10(A). These temperatures in $\text{PV}^{2+}(\text{TFPB}^-)_2$ films correspond to the glass transition temperature (165 K) and the melting temperature of microcrystals of tetrahydrofuran units (255 K and 290 K), as shown by the DSC thermogram reported previously [13,21]. The third component with the longest lifetime shows a similar temperature dependence to

the second component. Similar tendencies, although more scattered due to very weak intensities, are observed in the corresponding components for $\text{PQ}^{2+}(\text{TFPB}^-)_2$ and $\text{DQ}^{2+}(\text{TFPB}^-)_2$.

Fig. 11 shows the temperature dependence of the total fluorescence intensity between 10 and 300 K for $\text{PV}^{2+}(\text{TFPB}^-)_2$ (A), $\text{MV}^{2+}(\text{TFPB}^-)_2$ (B), $\text{PQ}^{2+}(\text{TFPB}^-)_2$ (C) and $\text{DQ}^{2+}(\text{TFPB}^-)_2$ (D). The fluorescence intensity of both $\text{MV}^{2+}(\text{TFPB}^-)_2$ and $\text{DQ}^{2+}(\text{TFPB}^-)_2$ in microcrystals is not dependent on the temperature as shown in Figs. 11(B) and 11(D). On the other hand, the fluorescence intensity of both $\text{PV}^{2+}(\text{TFPB}^-)_2$ and $\text{PQ}^{2+}(\text{TFPB}^-)_2$ in polymer films decreases gradually above the glass transition temperature, as shown in Figs. 11(A) and 11(C).

4. Discussion

Since the observed fluorescence spectra are due to the excited IPCT complexes, many factors will affect the fluorescence wavelength and lifetime. Firstly, the peak shift of the shorter wavelength fluorescence, showing a faster decay, with temperature in polymer films will be considered. Such a peak shift may be caused by microenvironmental polarity changes below and above the glass transition temperature (T_g). The fluorescence excitation spectra of IPCT complexes of $\text{MV}^{2+}(\text{TFPB}^-)_2$ and $\text{DQ}^{2+}(\text{TFPB}^-)_2$ have been reported to correspond to the IPCT absorption spectra, except in the shorter wavelength region below about 400 nm [16,22]. Fig. 12 shows the fluorescence and fluorescence excitation spectra of $\text{PV}^{2+}(\text{TFPB}^-)_2$ in DME solution. The excitation spectrum corresponds well to the IPCT absorption spectrum of $\text{PV}^{2+}(\text{TFPB}^-)_2$ in DME solution, except in the shorter wavelength region [3]. If the fluorescence peak shift is caused by microenvironmental polarity changes, the fluorescence excitation spectrum should show similar changes. However, the fluorescence excitation spectrum shows no temperature dependence as mentioned above. These results

Table 1
Fluorescence lifetime of IPCT complexes at room temperature

Sample	Fluorescence lifetime (ns)		
	First component	Second component	Third component
$\text{PV}^{2+}(\text{TFPB}^-)_2$	3	6	12
$\text{MV}^{2+}(\text{TFPB}^-)_2$	0.3	3	34
$\text{PQ}^{2+}(\text{TFPB}^-)_2$	2	7	21
$\text{DQ}^{2+}(\text{TFPB}^-)_2$	3	5	29

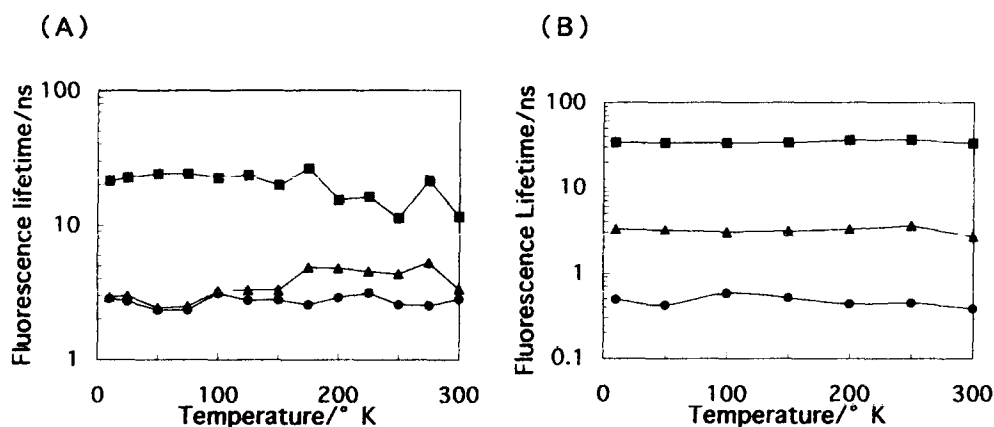


Fig. 10. Fluorescence lifetime plotted against temperature for bipyridinium salts in microcrystals and polymer films excited at 350–400 nm: (A) $PV^{2+}(TFPB^-)_2$; (B) $MV^{2+}(TFPB^-)_2$.

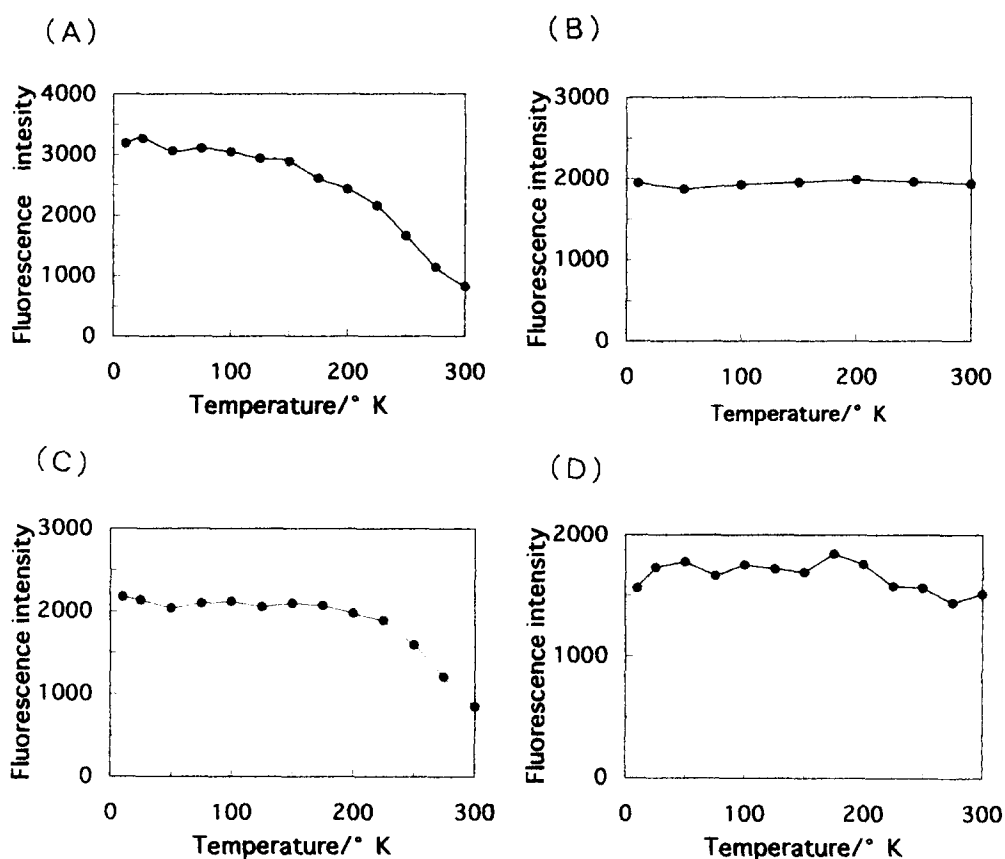


Fig. 11. Fluorescence intensity plotted against temperature for bipyridinium salts in microcrystals and polymer films excited at 350–400 nm: (A) $PV^{2+}(TFPB^-)_2$; (B) $MV^{2+}(TFPB^-)_2$; (C) $PQ^{2+}(TFPB^-)_2$; (D) $DQ^{2+}(TFPB^-)_2$.

exclude the possibility of microenvironmental polarity changes being responsible for the peak shift.

The temperature dependence of the shorter wavelength fluorescence (with a faster decay) in $PV^{2+}(TFPB^-)_2$ may be due to the different contributions of two fluorescence bands with peaks at 402 nm and 432 nm. If this is the case, the fluorescence spectrum should exhibit continuous changes with temperature, showing a peak and a shoulder as a result

of the overlapping of two bands. However, this is not observed, as shown in Fig. 6; a peak is observed at 420 nm, but no shoulders at either 402 nm or 432 nm, in the temperature range 175–250 K.

The fluorescence spectra in polymer films exhibit a red shift with increasing temperature, as shown in Table 2, but no shift is observed in the fluorescence excitation spectra; this strongly suggests that the excited state of IPCT com-

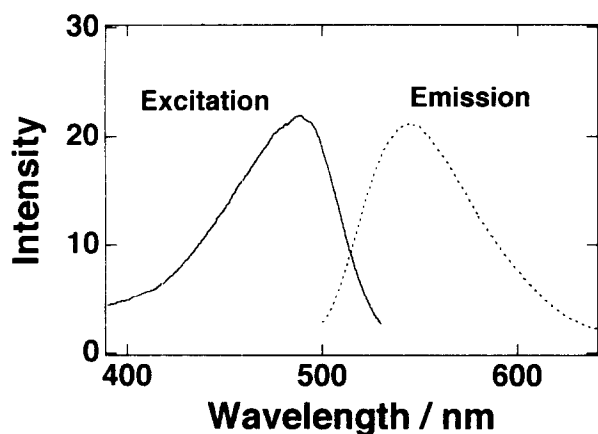


Fig. 12. Fluorescence ($\lambda_{\text{ex}}=485$ nm) and fluorescence excitation ($\lambda_{\text{em}}=540$ nm) spectra of $\text{PV}^{2+}(\text{TFPB}^-)_2$ in DME (1 mM).

Table 2

Fluorescence peaks in various microenvironments for $\text{PV}^{2+}(\text{TFPB}^-)_2$ and $\text{PQ}^{2+}(\text{TFPB}^-)_2$

Sample	IPCT fluorescence peak in various microenvironments (nm)		
	Glassy state	Rubbery state	Molten state
$\text{PV}^{2+}(\text{TFPB}^-)_2$	402	420	432
$\text{PQ}^{2+}(\text{TFPB}^-)_2$	440	440	460

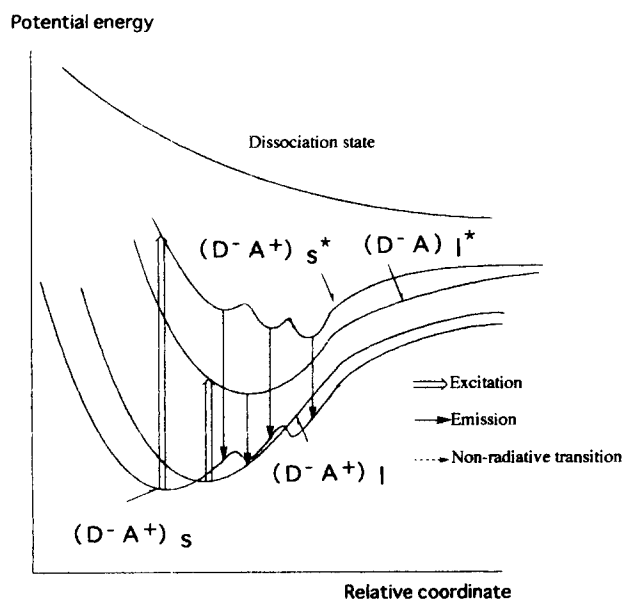


Fig. 13. Proposed potential surfaces for IPCT complexes $((\text{A}^+\text{D}^-)_s$ and $((\text{A}^+\text{D}^-)_l)$ of $\text{PV}^{2+}(\text{TFPB}^-)_2$.

plexes is more ‘‘stabilized’’ in polymer films with increasing temperature. The extent of the molecular motions of IPCT complexes of 4,4'-bipyridinium and 2,2'-bipyridinium TFPB^- salts in polymer films will be increased with temperature depending on the characteristic transition. The larger the mobility of the IPCT complexes of 4,4'-bipyridinium and 2,2'-bipyridinium TFPB^- salts in polymer films, the more

stable will be the configuration of the IPCT complexes. $\text{PQ}^{2+}(\text{TFPB}^-)_2$ shows fluorescence at longer wavelengths in all states, from glassy to molten, compared with $\text{PV}^{2+}(\text{TFPB}^-)_2$ and also shows the same fluorescence peak in glassy and rubbery states. These results strongly suggest a larger freedom of motion around IPCT complexes in $\text{PQ}^{2+}(\text{TFPB}^-)_2$. The fluorescence of $\text{PV}^{2+}(\text{TFPB}^-)_2$ is observed at 540 nm in less polar DME solutions as shown in Fig. 12; this is red shifted by 108 nm relative to that observed in the molten state (shown in Table 2). However, the fluorescence excitation spectrum of $\text{PV}^{2+}(\text{TFPB}^-)_2$ in DME solution is red shifted by only about 25 nm relative to that in its molten state. An excited state of IPCT complexes with non-ionic character will be more strongly affected by molecular motion than a ground state with strong ionic character, which most probably explains the observed fluorescence shift with temperature in polymer films. 2,2'-Bipyridinium TFPB^- salts also show a similar dependence on temperature.

The temperature-dependent spectral shift of the time-resolved IPCT fluorescence in $\text{PV}^{2+}(\text{TFPB}^-)_2$ can be explained by the potential surfaces shown schematically in Fig. 13. The ground state is represented by two potential curves for $(\text{D}^-\text{A}^+)_s$ and $(\text{D}^-\text{A}^+)_l$ corresponding to the different configurations of the IPCT complexes. The subscripts s and l denote shorter and longer wavelength fluorescence respectively. $(\text{D}^-\text{A}^+)_s$ excited at 350–400 nm will result in $(\text{D}^-\text{A}^+)_s^*$. The potential surface of $(\text{D}^-\text{A}^+)_s^*$ is assumed to have three local minima as shown in Fig. 13, reflecting three different states of the polymer chains. The fluorescence from the upper local minimum has a peak at 402 nm. If the potential barrier of $(\text{D}^-\text{A}^+)_s^*$ is crossed over thermally at temperatures higher than the glass transition temperature (T_g), fluorescence at 420 nm will be observed. If the potential barrier of $(\text{D}^-\text{A}^+)_s^*$ is crossed over thermally at temperatures higher than the melting temperature (T_m), fluorescence at 432 nm will be observed. T_g and T_m affect the fluorescence lifetime of the IPCT complexes in polymer films as shown in Fig. 10 and reported previously [21]. A second component with an intermediate lifetime appears in $\text{PV}^{2+}(\text{TFPB}^-)_2$ above T_g [21]. The coexistence of IPCT complexes with three different configurations in the ground state dependent on temperature would lead to the observation of temperature-dependent fluorescence in polymers. In such a case, the fluorescence excitation spectra should also be dependent on the temperature. However, no temperature dependence is observed for the fluorescence excitation spectra of films of $\text{PV}^{2+}(\text{TFPB}^-)_2$ and $\text{PQ}^{2+}(\text{TFPB}^-)_2$ as mentioned above. Therefore the potential curve shown in Fig. 13 is the most probable explanation for the temperature dependence of the fluorescence spectra of $\text{PV}^{2+}(\text{TFPB}^-)_2$ films. In the case of $\text{PQ}^{2+}(\text{TFPB}^-)_2$, the height of the first barrier will be negligibly small, since the same fluorescence spectra are observed in both the glassy and rubbery states.

The longer wavelength fluorescence with a peak at 500 nm is observed at all temperatures and excitation wavelengths

studied. $(D^-A^+)_1$ will be excited either directly by longer wavelength excitation, as shown in Fig. 13, or by energy transfer from $(D^-A^+)_s^*$ formed on shorter wavelength excitation. The fluorescence from $(D^-A^+)_1^*$ will have a peak around 500 nm and a slower decay. The time-resolved fluorescence excitation spectrum monitored at 500 nm exhibits a "rise" at 350–400 nm as shown in Fig. 7(B), strongly suggesting energy transfer from $(D^-A^+)_s^*$. A similar and clearer "rise" is observed at 350–420 nm in the fluorescence excitation spectrum monitored at 500 nm of $PV^{2+}(TFPB^-)_2$ as reported previously [21]. The fluorescence lifetime of the third component at 500 nm decreases around T_g and T_m as shown in Fig. 10(A), most probably due to the increase in non-radiative processes. Similarly, the decrease in the fluorescence intensity in polymer films of $PV^{2+}(TFPB^-)_2$ and $PQ^{2+}(TFPB^-)_2$ above T_g , shown in Fig. 11, can be explained by an increase in non-radiative processes.

5. Conclusions

The time-resolved fluorescence spectra of IPCT complexes of 4,4'-bipyridinium and 2,2'-bipyridinium $TFPB^-$ salts in polymer films are dependent on temperature; the changes are reversible during cooling and heating processes between 300 and 10 K. The fluorescence band with a faster fluorescence decay shifts to longer wavelength with increasing temperature above T_g . A relatively weak fluorescence band with a peak around 500 nm and a slower decay is also observed at all temperatures and excitation wavelengths.

The observed IPCT fluorescence behaviour can be explained by changes in the configurations of the IPCT complexes, which are dependent on the molecular motions caused by increasing temperature. The potential surface of the excited IPCT state is assumed to contain three local minima and contributes to the fluorescence spectral shift with temperature, whereas no temperature dependence is observed for the fluorescence excitation spectra.

The fluorescence intensity in polymer films gradually decreases with increasing temperature above T_g due to the increased non-radiative component of the IPCT complexes

caused by the thermal relaxation of the poly(tetrahydrofuran) units in the polymer chain.

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