MICROENVIRONMENTAL EFFECT ON CHARGE TRANSFER FLUORESCENCE IN ION-PAIR CT COMPLEXES OF 4,4'-BIPYRIDINIUM SALT

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Temperature dependence of charge transfer (CT) fluorescence were studied by time-resolved spectroscopies in thin polymer films containing 4,4'-bipyridinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salts as part of the main chain at 10-300 °K. The time-resolved fluorescence with peaks at 432 nm and 500 nm appeared upon excitation of ion-pair charge-transfer absorption at room temperature at about 360 and 390 nm, respectively. A shorter wavelength peak shifted from 432 nm to 402 nm with decreasing temperature from 300 °K to 10 °K. The fluorescence decay curve was analyzed by a fast ($\tau = 3-6$ ns) and a slow ($\tau = 15$ ns) component. The former corresponded to a shorter wavelength peak and the latter to that at ca. 500 nm for CT fluorescence spectra of 4,4'-bipyridinium salt. A reaction mechanism is proposed based on these results.

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 of 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 was due only to the photoinduced electron transfer reaction via the excited state of specific ion-pair charge-transfer (IPCT) complexes[16,17] of 4,4'-bipyridinium salts with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[18] (abbreviated to TFPB⁻). The photochemical colouring and the thermal fading due to the reverse electron transfer were highly reversible in deaerated atmosphere in all systems[2-

15]. The lifetime of coloured (blue) state depended markedly on the microenvironments and temperatures.

4,4'-Bipyridinium TFPB⁻ salts are known to show broad structureless with a maximum at 525 nm fluorescence from excited IPCT state in 1,2-dimethoxyethane solutions at room temperature[16]. The excitation of a CT band ($\lambda_{ex} = 475$ nm) in an oxygen-free atmosphere resulted in the quenching of CT fluorescence accompanied by a remarkable colour change from pale yellow to blue owing to the accumulation of 4,4'-bipyridinium radical cations. After disappearance of blue colour in about an hour at 20 °C, the CT absorbance and fluorescence intensity in DME recovered very gradually to the equilibrium values. The CT fluorescence and colour changes were repeated reversibly. These results demonstrated that 4,4'-bipyridinium TFPB⁻ salts can be applied to a photon-mode-type optical memory which can be read with either absorption or emission[19]. The observed ps fluorescence decay behavior did not correspond with the formation rate of transient absorption at about 600 nm which was much faster than the fluorescence decay. The ps time-resolved fluorescence spectra in 4,4'-bipyridinium polymer films have a broad and slow-decaying component with a peak at 490 nm and a less broad short-lived one with a peak at about 440 nm at room temperature[20]. In the present paper microenvironmental effects on charge transfer fluorescence in IPCT complexes of 4,4'-bipyridinium salts with TFPB⁻ in polymer films are discussed.

2. Experimental

Materials

The structure of a polymer containing 4,4'-bipyridinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB⁻) as part of the main chain is shown in Fig. 1. The content of 4,4'-bipyridinium ions is 2.3×10^{-4} mol/g. Transparent and uniform films were obtained by casting 1,2-dimethoxyethane solution of this polymer onto a glass plate.

Measurement

Polymer films were thoroughly degassed in a cryostat with Iwatani Plantech ultra-low-temperature cooling units. The fluorescence decay curve and the time-resolved fluorescence spectrum were measured on Horiba NAES-700F with a N₂ ns lamp NFL-700 in vacuo at controlled temperature. For time-resolved

Fig. 1 The structure of the elastic polymer PV²⁺(TFPB⁻)₂ containing bipyridinium ions and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion

Fig. 2 The transparent spectra of the band-pass and sharp-cut filters used in the present experiment.

emission spectrum measurements either U-340 and B-390 band-pass filters for 400-432 nm emission or B-390 band-pass filter for 500 nm emission were used to excite their CT absorption band alone. For time-resolved excitation spectrum either B-390 and L-42 filters or B-480 and Y-52 filters were used to monitor CT fluorescence at 400-432 nm as shown in Fig. 2.

The DSC thermogram was recorded by a MAC Science DSC 3100 Thermal Analysis Station from 150 °K to 340 °K with a heating rate of 5 °K/min.

3. Results

Fig. 3 shows the time-resolved fluorescence spectra of the polymer film excited at 350-400 nm at various temperatures. Fluorescence spectra were observed with a peak around 400-432 nm.

Fig. 3 The time-resolved fluorescence spectra of $PV^{2+}(TFPB^-)_2$ excited at 350-400 nm at (A) 10 °K, (B) 100 °K, (C) 200 °K and (D) 300 °K.

Another fluorescence peak at about 500 nm was observed upon excitation at 460 nm as shown in Fig. 4. The fluorescence band at 400-432 nm showed faster decay and shifted to longer wavelength with increasing temperature from 200 °K to 300 °K, whereas no temperature dependence was observed below 100 °K. The fluorescence band with a faster decay was broadened with increasing temperature as shown in Fig. 3. The fluorescence band at 500 nm showed slower decay and became predominant with increasing temperature.

Fig. 4 The time-resolved fluorescence spectra of $PV^{2+}(TFPB^{-})_2$ excited at 460 nm at room temperature.

Fig. 5 shows the time-resolved fluorescence excitation spectra of $PV^{2+}(TFPB^{-})_2$ at room temperature. The fluorescence excitation spectrum corresponded with the charge-transfer absorption spectrum except the shorter wavelength region than about 380 nm, where the fluorescence quantum yield was very low due to dissociation. The profile of fluorescence excitation spectra did not depend upon temperature. The fluorescence excitation spectrum monitored at 420 nm showed peaks at 350 nm, 375 nm, 400 nm as shown in Fig. 5(A). The fluorescence excitation spectrum monitored at 500 nm showed an additional peak around 460 nm as shown in Fig. 5(B). For the emission band at 500 nm the time resolved fluorescence excitation spectra showed a "rise" as shown in Fig. 5(D).

Fig. 6 shows the fluorescence decay curves of $PV^{2+}(TFPB^{-})_2$ at room temperature at (A) 420 nm and (B) 500 nm. The fluorescence decay curves were fitted with triple-exponential with lifetimes of 3 ns, 6 ns and 10-30 ns. The fluorescence band at a shorter wavelength had faster decay and the longer band had slower.

Fig. 7 shows the fluorescence lifetime versus temperature between 10 °K and 300 °K. A fastest component at 400 nm emission was independent of temperature. The second one depended on temperatures and showed a considerable change at 175 °K and 275 °K. Such temperatures corresponded to the glass transition temperature and the melting temperature of microcrystals of tetrahydrofuran units as shown in Fig. 8 [13]. The slow component decreased gradually above 150 °K as shown in Fig. 7.

Fig. 8 shows the DSC thermogram of $PV^{2+}(TFPB^{-})_2$ from 150 °K to 340 °K. The transition temperatures were observed at 165, 255 and 290 °K corresponding to the glassy transition temperature, the crystallization temperature and the melting temperature of microcrystals of tetrahydrofuran units respectively.

Fig. 5 The time-resolved fluorescence excitation spectra of $PV^{2+}(TFPB^-)_2$ at room temperature monitored at (A),(C) 420 nm (A),(C) and 500 nm (B),(D) emission. The time in (C) and (D) is the delay from the excitation pulse.

Fig. 6 The fluorescence decay curves of $PV^{2+}(TFPB^-)_2$ at room temperature at (A) 420 nm and (B) 500 nm.

Fig. 7 The fluorescence lifetime versus temperature of $PV^{2+}(TFPB^-)_2$ excited at 350–400 nm.

Fig. 8 The DSC thermogram of $PV^{2+}(TFPB^-)_2$ used in the present experiment.

4. Discussion

First, the peak shift of the shorter wavelength fluorescence showing a faster decay with temperatures will be considered. Such a peak shift might be caused by microenvironmental polarity changes below and above glass transition temperature (T_g). The fluorescence excitation spectra showed no temperature dependence. The fluorescence excitation spectra of IPCT complexes of 4,4'-bipyridinium $TFPB^-$ salts have been reported to correspond with the IPCT absorption spectra except at the shorter wavelength region below about 400 nm[16]. If the fluorescence peak shift was caused by the microenvironmental polarity changes, the fluorescence excitation spectrum should show similar changes. These results excluded the possibility of microenvironmental polarity changes.

The fluorescence spectra with a faster decay were then assumed to consist of two fluorescence bands having peaks at 400 nm and 432 nm. With increasing temperature above T_g , the fluorescence band became more broadened in addition to the peak shift from 402 to 432 nm as shown in Fig. 3. The cooling experiment from room temperature to 10 °K gave a spectral shift from 432 to 402 nm and the sharpening of the fluorescence spectra.

The time-resolved IPCT fluorescence spectra and their temperature dependence in this $PV^{2+}(TFPB^-)_2$ system can be explained by potential surfaces as shown in Fig. 9. The ground state will be represented by two potential curves for $(D^+A^+)_s$ and $(D^+A^+)_l$ corresponding to the different configuration of IPCT complexes. The subscript s or l stands for shorter or longer wavelength fluorescence, respectively. $(D^+A^+)_s$ excited at 350–400 nm will become $(D^+A^+)_s^*$. The potential surface of $(D^+A^+)_s^*$ is assumed to have two local minima as shown in Fig. 9. The fluorescence from the upper local minimum will have a peak at 402 nm. If the potential barrier of $(D^+A^+)_s^*$ will be crossed over thermally at higher temperatures than T_g , the fluorescence at 432 nm will also be observed. The glass transition temperature and the melting temperature (T_m) affected

the fluorescence lifetime as shown in Fig. 7. A second component with the intermediate lifetime appeared above T_g as shown in Fig. 7.

Fig. 9 Proposed potential surfaces for IPCT complexes of $PV^{2+}(TFPB^-)_2$.

The longer wavelength fluorescence with a peak at 500 nm was observed at all temperatures and excitation wavelength. $(D-A^+)_l$ will be excited either directly by longer wavelength excitation as shown in Fig.4 or by the energy transfer from $(D-A^+)_s^*$ formed upon shorter wavelength excitation. The fluorescence from $(D-A^+)_l^*$ will have a peak around 500 nm and a slower decay. The time-resolved fluorescence excitation spectra monitored at 500 nm showed the "rise" as shown in Fig. 5(D) strongly suggesting the energy transfer from $(D-A^+)_s^*$. The fluorescence lifetime of the third component at 500 nm decreased around T_g and T_m as shown in Fig.7 most probably due to the increase of non-radiative process.

We then consider how each fluorescence component will be influenced by microenvironmental effects of IPCT complex. The $(D-A^+)_s$ complex which showed the fluorescence band predominantly at 402 nm below T_g and the fastest decay most probably have a structure that a donor and an acceptor are rigidly held in a face-to-face sandwich manner. The second local minimum in $(D-A^+)_s^*$ with the fluorescence band at 432 nm will correspond to a configuration with larger mutual distance and/or orientation between a donor and an acceptor. The $(D-A^+)_l$ complex which showed the fluorescence peak at 500 nm and longer lifetime would have a structure that a donor and an acceptor are partially overlapped.

5. Conclusion

The time-resolved fluorescence spectra of ion-pair charge-transfer complexes of $PV^{2+}(TFPB^-)_2$ depended on temperature, which was reversible during cooling and heating processes between 300 °K and 10 °K. The fluorescence band at 400 nm shifted to 432 nm with

temperature above T_g . In addition to them the fluorescence spectra with a peak around 500 nm a slower decay were observed.

The observed IPCT fluorescence behavior was explained by considering two kinds of IPCT complexes which correspond to the different configuration of the donor and the acceptor. The potential surface of the excited state for one of them was assumed to have two local minima and contributed to the fluorescence spectral shift with temperatures, whereas no temperature dependence was observed for the fluorescence excitation spectra.

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