

Reversible control of emission from ion-pair charge-transfer complex of 4,4'-bipyridinium with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion by electron transfer reaction

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Abstract

4,4'-Bipyridinium salts with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion (TFPB⁻) showed a charge-transfer (CT) absorption above 350 nm and broad structureless CT fluorescence with a maximum at 525 nm in 1,2-dimethoxyethane (DME). 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'-bipyridium TFPB⁻ salts can be applied to a photon-mode-type optical memory which can be read with either absorption or emission.

Keywords: Ion-pair charge-transfer complex; 4,4'-bipyridinium salt; CT fluorescence; Reversible photoreaction; Optical memory

1. Introduction

Very recently erasable direct read after write (ED-RAW) optical discs based on the magneto-optical effect or reversible phase changes have become available as high density rewritable information storage media for personal computers. However, all these commercialized optical memories are so-called heat-mode recording systems. In other words, the laser beam is focused and used as a heat source to change the physical properties of a recording layer. There will be limits to the much higher memory density in these heat-mode systems. Light has many superior properties such as wavelength, polarization and coherency (ultrashort pulse and focusing). In order to increase further the memory density, photon-mode recording systems employing photochemical reactions instead of thermal reactions should be developed. Photochromic systems in polymers or Langmuir–Blodgett (LB) films have recently attracted much

interest in view of their promising applicability to such purposes. The photochromism reported so far involves changes in chemical bonds such as ring opening and closure in spiropyrans or *cis-trans* isomerization in azobenzenes. These reactions might limit the thermal or cyclic stability and the response time for the optical recording especially in the solid states.

The 4,4'-bipyridinium ion is a good electron acceptor and forms charge-transfer (CT) complexes with many ionic or neutral organic compounds and inorganic anions [1,2]. It also makes reversible redox reactions accompanying colour changes. Ionic photodissociation from excited CT complexes of 4,4'-bipyridinium salts was observed by flash photolysis in polar solvents to form 4,4'-bipyridinium radical cations. However, reverse electron transfer reactions are usually very rapid. We have been reporting persistent and reversible colour changes using tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB⁻) as a counter-anion of 4,4'-bipyridinium salts in organic solutions [3,4], microcrystals [5,6], LB films [7–9], and polymer films [10–12] which were due only

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to electron transfer via the excited state of specific ion-pair CT complexes and the thermal reverse reactions. The colour change was irreversible if the counter-ion was exchanged with the usual tetraphenylborate [3,13].

In the present paper, the control of CT fluorescence intensity by persistent and reversible photoinduced electron transfer reactions will be discussed in connection with a potential means of reading the optical memory in addition to the absorption (or reflection) change.

2. Experimental details

2.1. Materials

The TPB^- and TFPB^- salts of N,N' -dimethyl-4,4'-bipyridinium (2 and 3 respectively) were obtained from sodium TPB^- and TFPB^- (Dojindo Laboratory) and the corresponding 4,4'-bipyridinium dichloride (1) [5]. The structure is shown in Fig. 1. The compound 2 and 3 were dissolved in 1,2-dimethoxyethane (DME) by sonication for about 5 min at various concentrations. The solutions were kept at 20 °C in the dark.

2.2. Measurements

The solutions for photoreaction were degassed by repeated freeze–pump–thaw methods. The light source for steady photolysis was a Hamamatsu 150 W Xe–Hg lamp equipped with a Toshiba L-39 cut-off filter ($\lambda > 365$ nm) and a 10 cm water filter. The photogeneration process of 4,4'-bipyridinium radical cations was observed by UV–visible spectrophotometer (JASCO Ubest-55) and fluorescence spectrophotometer (Shimadzu RF-5000) controlled by a microcomputer.

3. Results and discussion

The absorption spectra for a DME solution (2 mM) of 3 are shown in Fig. 2 at various stages of storage in the dark at 20 °C. Only a weak extended tail absorption

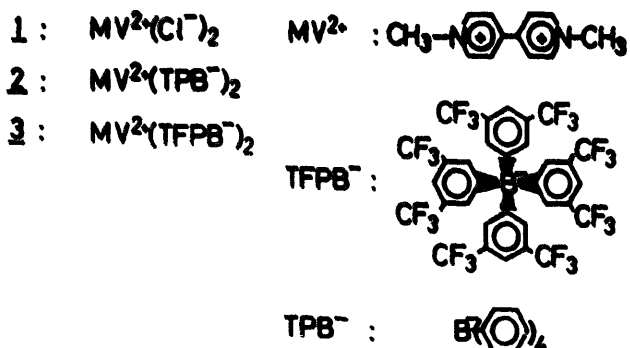


Fig. 1. Structure and abbreviation of 4,4'-bipyridinium salts.

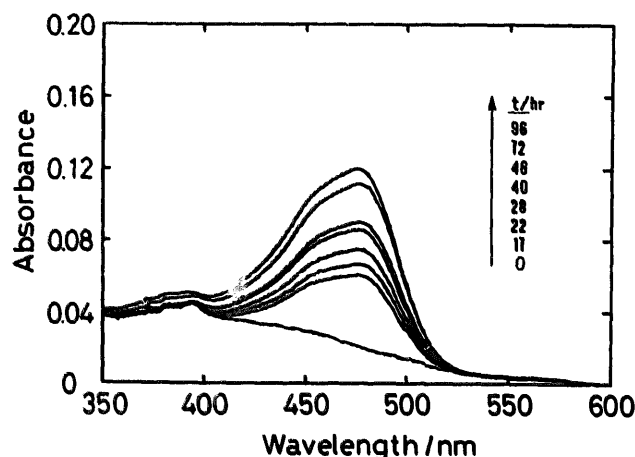


Fig. 2. Variation in UV–visible absorption spectra with time for a 2 mM solution of 3 in DME at 20 °C.

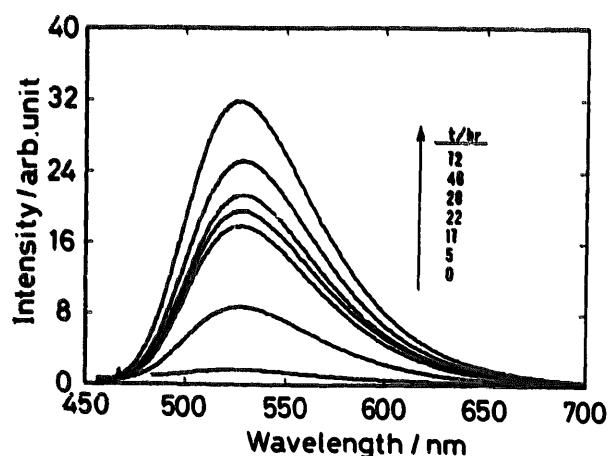


Fig. 3. Variation in fluorescence spectra with time for a 2 mM solution of 3 in DME at 20 °C.

was observed immediately after dissolution. The new absorption with a maximum around 475 nm grew very gradually. 4,4'-Bipyridinium dichloride (1) and sodium TFPB^- showed no absorption above 350 nm. A TPB^- salt 2 in DME showed a fairly strong new absorption above 350 nm without a discrete peak immediately after dissolution and showed an increase in absorption by only 20% of the initial absorbance at the equilibrium which was reached much more rapidly than a TFPB^- salt (after about 20 h). These new absorption spectra were ascribed to ion-pair CT complexes between 4,4'-bipyridinium ion as an acceptor and TFPB^- or TPB^- as a donor [4].

The emission spectra of a DME solution (2 mM) of 3 at $\lambda_{\text{ex}} = 475$ nm are shown in Fig. 3 during storage at 20 °C (stage 1), which is almost a mirror image of CT absorption spectra. The fluorescence excitation spectrum monitored at 525 nm corresponded well to the CT absorption. The emission with a peak at 525 nm in DME also increased very gradually. We have attributed such emission to the CT fluorescence due to

ion pair complexes with borate anion as a donor and 4,4'-bipyridinium ion as an acceptor [14]. A 3,5-bis(trifluoromethyl)phenyl group of TFPB⁻ and a pyridinium group of 4,4'-bipyridinium ion are expected to form a face-to-face CT complex in a similar manner as reported for a CT complex of **2** from the X-ray structural analysis of a single crystal [15]. Such face-to-face orientation in a CT complex between a 4,4'-bipyridinium and TFPB⁻ with very bulky and crowded structure is presumed to contribute rather unusually strong CT fluorescence with $\phi_F=0.32$ in solutions at room temperature [14].

Upon irradiation of a CT absorption band in an oxygen-free atmosphere the colour of **3** changed from pale yellow to blue in DME solution. The UV-visible absorption spectra are shown in Fig. 4 before ($t=0$) and during irradiation (full curves) at 20 °C. Two absorption bands with peaks at 395 and 605 nm were observed, which are characteristic of 4,4'-bipyridinium radical cations. The time dependence of absorbances (605 nm) (open circles) and fluorescence intensity (525 nm) (full circles) are shown in Fig. 5 for successive photoirradiation and storage in the dark. The fluorescence intensity decreased during photoirradiation corresponding to the formation of 4,4'-bipyridinium radical cations. It recovered very gradually and reversibly after irradiation while radicals decayed rapidly in the dark (stage 2 to stage 5). The photogenerated 4,4'-bipyridinium radical cations of **3** decayed thermally with a lifetime $1/e$ of about 26 min at 20 °C. The recovery of the CT fluorescence was much slower than the decay of 4,4'-bipyridinium radical cations, as shown in Fig. 5. During storage in the dark no absorption other than the original CT spectrum was observed as shown in Fig. 4 (dotted curve) for 1 h after irradiation. The time dependence of the CT fluorescence recovery was almost the same as that of corresponding CT absorption growth

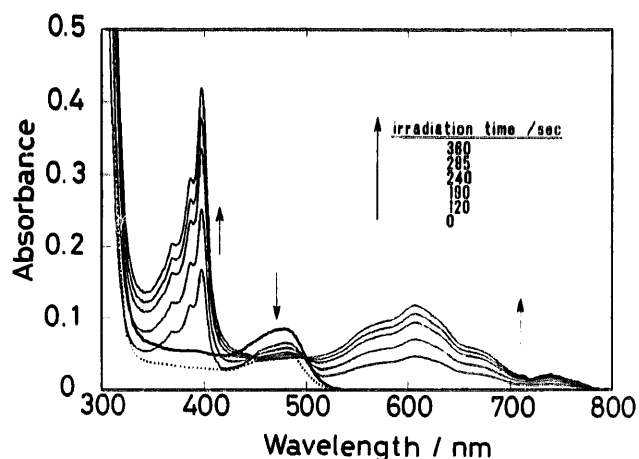


Fig. 4. Variation in absorption spectra before (—) and during irradiation (—) and 1 h after irradiation (···) for a 2 mM solution of **3** in DME.

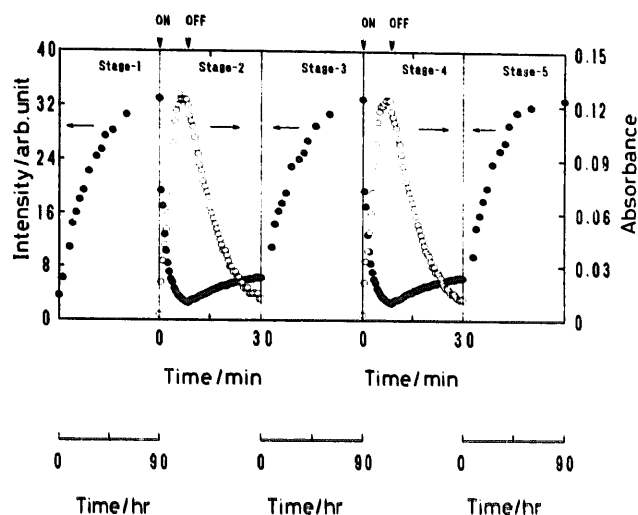


Fig. 5. The time dependence of fluorescence intensity at 525 nm for a 2 mM DME solution of **3** at 20 °C in an oxygen-free atmosphere in the dark (stage 1), repeated absorbance (at 605 nm) (○) and fluorescence intensity (●) changes (stage 2 to stage 5). The sample was irradiated repeatedly for 8 min (between ON and OFF) and was kept in the dark after each irradiation.

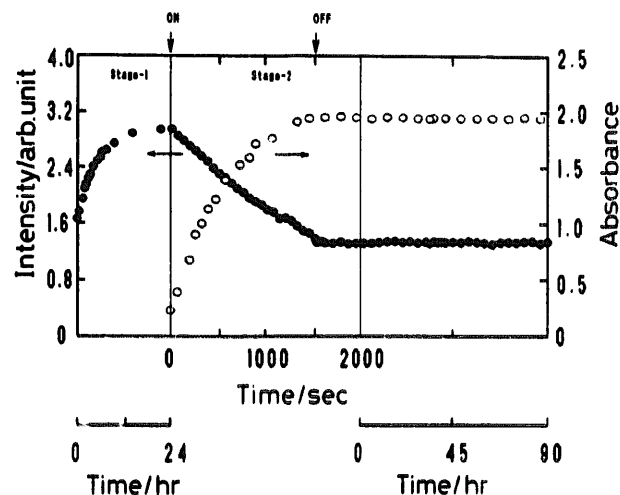


Fig. 6. The time dependence of fluorescence intensity (●) at 525 nm for 1 mM DME solution of **2** in an oxygen-free atmosphere at 20 °C during CT complex formation (stage 1) and subsequent irradiation and storage in the dark (stage 2) together with the time dependence of absorbance (○) at 605 nm of photogenerated radicals.

at 475 nm shown in Fig. 2. This photogeneration and the thermal decay of 4,4'-bipyridinium radical cations, and the decay and recovery of the CT fluorescence intensity, were repeated reversibly many times as shown in Fig. 5, e.g. for the successive two photoreaction processes. For the TPB⁻ salt **2**, irreversible colour changes and decay in the CT fluorescence upon similar irradiation were observed as shown in Fig. 6. This result indicated that TPB⁻ worked as a sacrificial electron donor owing to its oxidative decomposition [6]. These results clearly indicated that photogenerated 4,4'-bipyridinium radical cations in TFPB⁻ salts **3** de-

cayed by a reverse electron transfer reaction to oxidized TFPB⁻ and that ion-pair CT complexes were formed again by the process mentioned below.

It took more than 90 h for full recovery of the CT fluorescence. Its time dependence did not correspond to the decay of photogenerated radicals as shown in Fig. 5 and in Fig. 7. Fig. 7 shows a logarithmic plot of absorbance and observed fluorescence intensity for stage 2 in Fig. 5 and also the calculated fluorescence intensity as mentioned below. The photogenerated radical cations decayed almost exponentially and disappeared completely within 1 h after irradiation. Then the reverse electron transfer and reformation of the ion-pair CT complexes can be treated almost independently. These results can be explained as follows. Almost the same kinetics of CT fluorescence during the initial stage and after disappearance of photogenerated radical cations strongly suggested that the reverse electron transfer reactions from 4,4'-bipyridinium radical cation to oxidized TFPB⁻ resulted not in well-ordered ion-pair CT complexes but in rather separated or almost free-ion pairs, as schematically shown in Fig. 8. The 1:1 ion-pair CT complex was reported previously to be formed between MV²⁺ and

TFPB⁻ [14]. Another TFPB⁻ ion is shown in Fig. 8 to satisfy the balance of charges; this does not participate in the CT complex but stays in the vicinity of MV²⁺ only as a counter-ion. Then the following rate equation is derived from the formation and dissociation of 1:1 CT complexes between the almost free 4,4'-bipyridinium ion (MV²⁺) and the TFPB⁻ ion formed by the reverse electron transfer reaction from charge-separated species [MV^{•+} (TFPB⁻) ··· (TFPB⁻)];

$$\begin{aligned} \frac{d[I_F^{CT}]}{dt} &= k_1[MV^{2+}][TFPB^-] - k_2[CT] \\ &= k_1([MV^{2+}]_0 - [CT])([TFPB^-]_0 \\ &\quad - [CT]) - k_2[CT] \end{aligned} \quad (1)$$

where [MV²⁺]₀ and [TFPB⁻]₀ are the initial concentrations of 4,4'-bipyridinium ions and TFPB⁻ respectively. The forward reaction rate constant k_1 and reverse reaction rate constant k_2 were determined by a least-squares method from the fluorescence intensity data of stage 1 and the integration of Eq. (1) as $k_1 = 3.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = 1.4 \times 10^{-6} \text{ s}^{-1}$ at 20 °C. These values agreed with those reported previously for time-dependent CT absorption [4]. The calculated time dependence of CT fluorescence of stage 2 based on these values is shown by a dotted curve in Fig. 7. Excellent agreement between the observed and the calculated values of fluorescence intensity was obtained over the whole time region studied. This result supported the CT mechanism mentioned above for the very slow recovery of fluorescence. The unusually slow formation of ion-pair CT complexes of 4,4'-bipyridinium TFPB⁻ in solutions was attributed to the exceptionally small pre-exponential factor [4]. The activation energy and pre-exponential factor for the CT formation were evaluated in a previous paper [4] from the Arrhenius plot of k_1 to be 23 kJ mol⁻¹ and 50 M⁻¹ s⁻¹ respectively. The probability of face-to-face orientation appropriate for a CT complex formation between a 4,4'-bipyridinium group and 3,5-bis(trifluoromethyl)phenyl group of TFPB⁻ in a similar manner as a phenyl group of TPB⁻ and a pyridinium ring of MV²⁺ reported for a single crystal of 2 [15] will be extremely low owing to the very bulky and crowded structure of TFPB⁻.

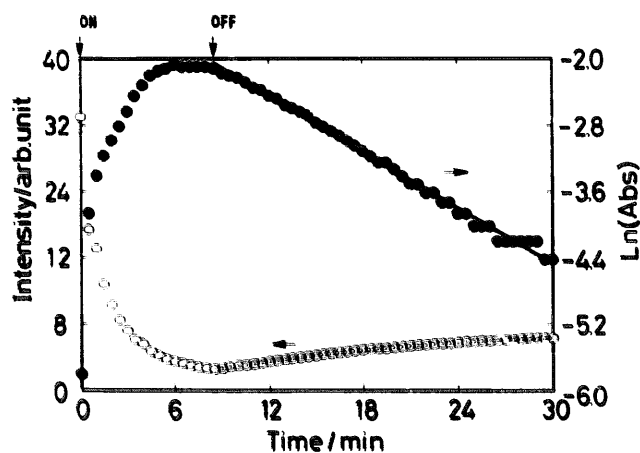


Fig. 7. The decay of absorbance (●) at 605 nm and the recovery of fluorescence intensity (○) at 525 nm for a 2 mM solution of 3 in DME (stage 2); ····, calculated time dependence. See text for details.

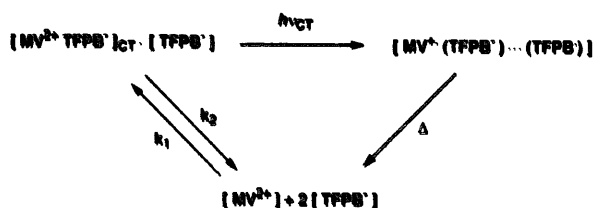


Fig. 8. A schematic representation of the electron-transfer reaction responsible for the colour and fluorescence intensity changes observed. MV²⁺, MV^{•+} and TFPB⁻ are the *N,N*-dimethyl-4,4'-bipyridinium ion, its reduced form and oxidized TFPB⁻ respectively. See text for details.

4. Conclusion

4,4'-Bipyridinium salts with TFPB⁻ showed a CT absorption and CT fluorescence. The excitation of a CT band in an oxygen-free atmosphere resulted in the quenching of CT fluorescence accompanied by a marked colour change due to the accumulation of 4,4'-bipyridinium radical cations. The CT absorption and fluorescence intensity recovered very gradually to the equilibrium values. The changes in colour and fluorescence

intensity were repeated reversibly. The observed very slow recovery of CT absorption and fluorescence were well explained by the time-dependent formation of CT complexes between ion pairs once dissociated after the reverse electron transfer reaction.

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