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ULTRAFAST COLOUR CHANGES IN ORGANIC THIN FILMS BASED ON PHOTOINDUCED ELECTRON TRANSFER REACTIONS

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Abstract Colour changes due to photoinduced electron transfer reaction were studied by picosecond pulsed laser in thin polymer films containing 4,4'-bipyridinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salts as part of the main chain at 98 - 300 °K. The transient absorption at about 600 nm appeared in less than 20 ps upon excitation of ion-pair charge-transfer absorption, which was controlled by the laser pulse width. The decay curve was analyzed by a fast component with a fraction of about 0.2 - 0.3 and lifetime of a few hundreds ps together with an extremely slow one corresponding to steady and reversible colour changes. The lifetime of the former slightly increased with decreasing temperatures. A reaction mechanism is proposed based on these results.

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].

Very recently we have reported novel photochromism (photoinduced electrochromism) in organic solutions[2,3], microcrystals[4,5], LB films[6-11], and polymer films[11-14] which was due only to the photoinduced electron transfer reaction via the

excited state of specific ion-pair charge-transfer (IPCT) complexes[15,16] of 4,4'-bipyridinium salts with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[17] (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[2-14]. The lifetime of coloured (blue) state depended markedly on the microenvironments and temperatures. For a polymer sample it was about 17 min in organic solutions and 72 h in cast films at 20°C[3,12,13]. From steady photolysis results it has been strongly suggested that 4,4'-bipyridinium radical cations escaped from the geminate reaction immediately after the photoinduced electron transfer became metastable owing to the bulk and chemical stability of $TFPB^-$, to the restriction of molecular motion by the microenvironment, and also probably to the very high exothermicity of the reverse reaction in the Marcus inverted region[18]. The quantum yield of 4,4'-bipyridinium radical cations upon IPCT excitation was estimated to be 0.0055 at 405 nm in solutions[2]. The blue state was stored stably below 0 °C in polymer films, which was shown to be closely related with the thermal transition of poly(tetrahydrofuran) units[12,13]. Appropriate coating of a protective layer on photoresponsive polymers made a stable colour change possible in air[14]. Very recently we have made a preliminary report that the colour changes occurred in less than 20 ps[19]. Highly sensitive detection of photoinduced electrochromism in ultra-thin polymer films has also been achieved [illegible] [illegible] redox sensors[20]. In the present paper transient absorption spectra upon ps laser excitation of polymer films will be reported.

EXPERIMENTAL

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 3.3 x 10^{-4} mol/g. Transparent and uniform films were obtained by casting 1,2-dimethoxyethane solutions of this polymer into a quartz plate. They were

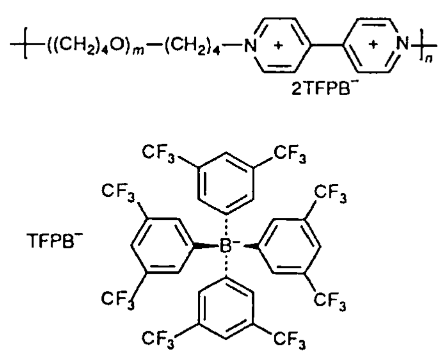

Fig. 1 The structure of a 4,4'-bipyridinium polymer and its counter ions.

polymer into a quartz plate. They were polymer and its counter ions.

thoroughly degassed in an Oxford Instruments DN1754 cryostat with an Oxford Instruments 3120 temperature controller. These samples were excited *in vacuo* at controlled temperature by the third harmonics (355 nm) of a ps Nd:YAG laser changing the position of irradiation at each laser shot with a linear optical stage, since a single shot of laser caused extremely long-lived species corresponding to steady and reversible colour changes.

The block diagram of a ps laser flash photolysis system to observe time-dependences of transient absorption by a streak camera (Hamamatsu Photonics C1587) is shown in Fig. 2. The laser source is a mode-locked Nd:YAG laser with a three-stage

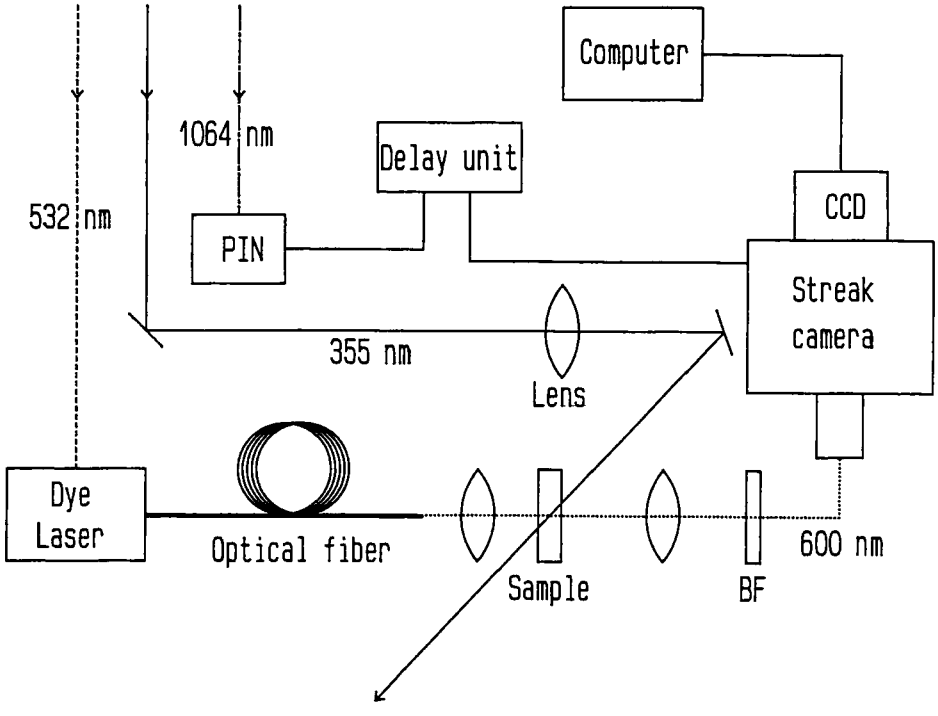

Fig. 2 The block diagram of a ps laser flash photolysis system.

YAG amplifiers (Matsui, YGM-500) delivering pulses with a FWHM of 30 ps, 10 Hz repetition, a maximum power of 80 mJ/pulse. A dye laser pulse at about 600 nm was generated by exciting Rhodamine B in ethanol with a second harmonic pulse of a ps Nd:YAG laser. A temporally broadened pulse of ca. 2 ns as shown in Fig. 3 was then obtained by introducing it into an optical fiber, a nearly flat part of which was used as a probe light to study the kinetics of colour changes in polymer films for about 1 ns time region upon excitation with the third harmonics of a ps Nd:YAG laser. A probe light with about 5 ns pulse duration was obtained by a bundle of several optical fibers

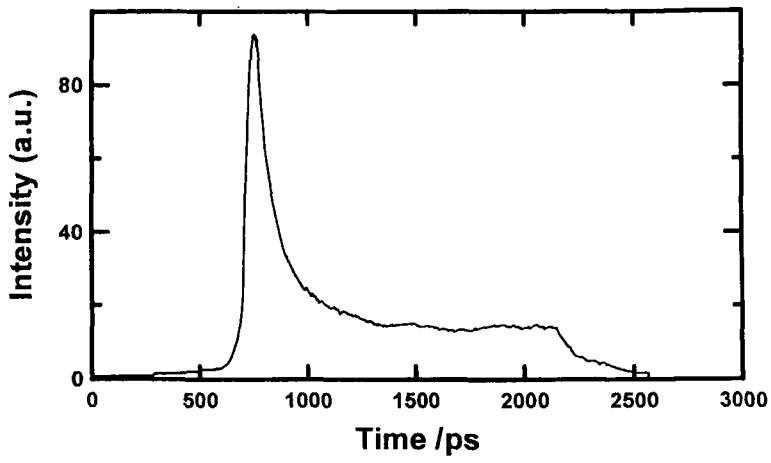

Fig. 3 Time profile of a temporally broadened dye laser pulse used for ps kinetics.

with different lengths, which was used to observe kinetics over about 3 ns with a streak camera. The transient absorption was calculated from accumulated probe intensities for several times without and with a pump pulse (355 nm). A continuum probe light with 10-50 ns duration was generated by focusing the fundamental (1064 nm) pulse onto the cathode of a high pressure Xe tube (Hamamatsu Photonics L2480)[22,23]. It was used as a probe light to observe transient absorption spectra by a streak camera.

RESULTS AND DISCUSSION

Transient absorption spectrum at 0-5 ns after excitation is shown in Fig. 4, which showed absorption at about 600 and 400 nm characteristic to 4,4'-bipyridinium radical cations. This result indicates that photoinduced electron transfer reactions occurred in polymer films upon ps laser excitation. The time-dependence of logarithmic transient absorption at about 600 nm is shown in Fig. 5 together with logarithmic intensity of the second harmonics of a ps laser. Since the second and the third harmonic pulses were generated from the ps fundamental pulse by KD*P crystals, the time profile of a ps laser (532 nm) shown in Fig. 5 is expected to be the same as that of the excitation

pulse itself (355 nm), though it was not measured due to the limited sensitivity of the detection system. The rise time of transient absorption at about 600 nm, 20 ps, was found to be smaller than the pulse width (30 ps) of a ps laser as shown in Fig. 5. This result clearly indicated that the colour changes, which were seen by naked eyes upon a

single shot of a ps laser, occurred in less than 20 ps. This is the fastest response of

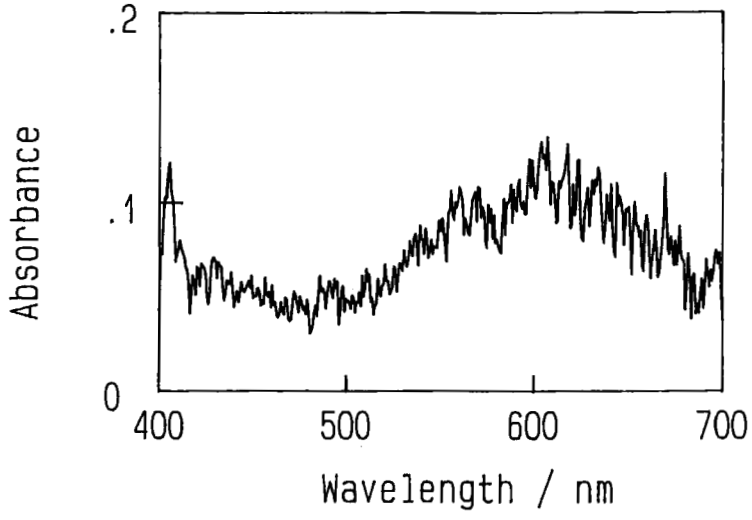

Fig. 4 Transient absorption spectrum of a polymer film at 0-5 ns upon excitation with a 355 nm ps laser.

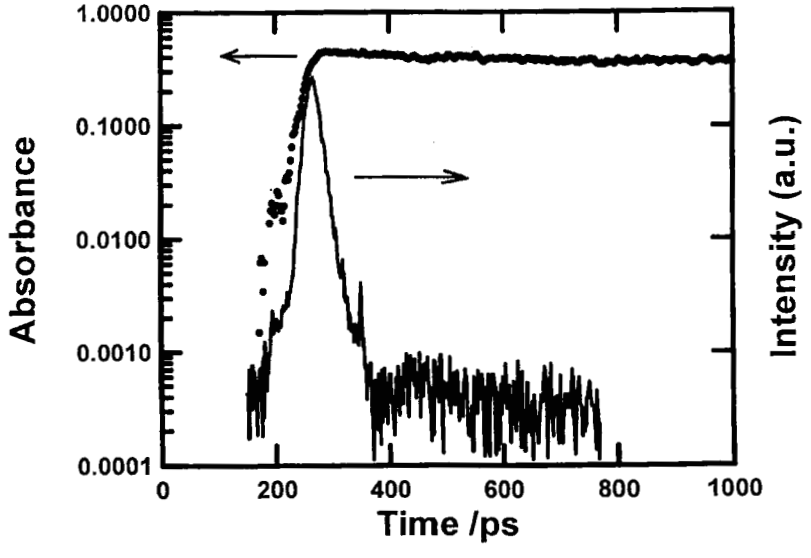

Fig. 5 Logarithmic plots of transient absorbance at about 600 nm (dots) and the intensity of a ps laser pulse (532 nm, solid lines).

steady photochromism reported so far. Wasielewski et al.[24] recently reported picosecond optical switch based on transient absorption due to photoinduced electron transfer with 5 and 178 ps switching on and off times, respectively.

The decay curves consisted of two components; a fast and an extremely long one. The latter did not decay even in a μs time region and corresponded to steady and reversible colour changes which were supposedly caused by cage-escaped 4,4'-bipyridinium radical cations. The temperature dependences of decay behavior were studied over 98 - 300 °K. The average absorbance of last 30 points in a linear region of a streak camera trace at 5 ns time window, corresponding to about 2.25 - 2.40 ns, was subtracted from the observed data at all temperatures studied as the absorbance of an extremely long component. It was confirmed from the measurement at 10 ns time window that no absorbance changes were observed after that. The observed absorbance and a fast component evaluated in such a way are plotted in Figs. 6 and 7 for 258 and 98 °K, respectively. The lifetime τ of a fast component slightly increased from about 470 ps at 258 °K to about 650 ps at 98 °K. The fraction of a fast component was also gradually increased from 0.24 at 258 °K to 0.31 at 98 °K. The rate constants (k= 1/τ) plotted

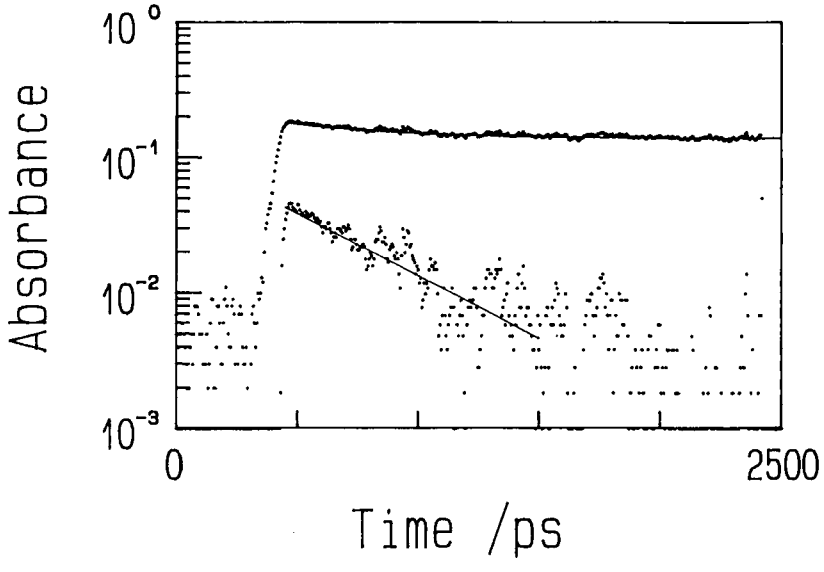

Fig. 6 Logarithmic plot of transient absorbance at 258°K upon excitation with a ps laser at 355 nm.

against 1/T gave a linear relationship as shown in Fig. 8, from which the activation energy of 0.50 kJ/mol was estimated.

Since the CT absorption band is ascribed to the electronic transition from a partially charge-transferred ground state to an almost completely charge-separated excited state, the Franck-Condon state will be mostly converted to the charge-separated state upon CT excitation. Very fast geminate recombination will then occur unless

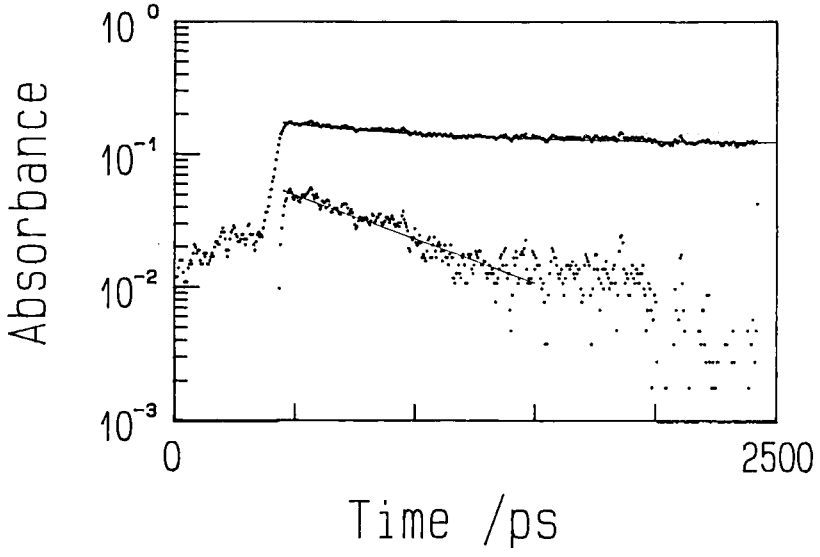

Fig. 7 Logarithmic plot of transient absorbance at 98°K upon excitation with a ps laser at 355 nm.

charge-separated species make some rearrangements to facilitate the cage escape. Ebbesen et al.[25] reported that a quantum yield of charge-separated species upon CT excitation of dithiocyanate complexes of N,N'-dimethyl-4,4'-bipyridinium ions decreased from 0.30 with a ps laser excitation to 0.16 with a ns laser due to fast geminate recombination.

The fast component of transient absorptions at 600 nm decayed with rate constants about 1.5 - 2.5 (x10^9 s^{-1}),

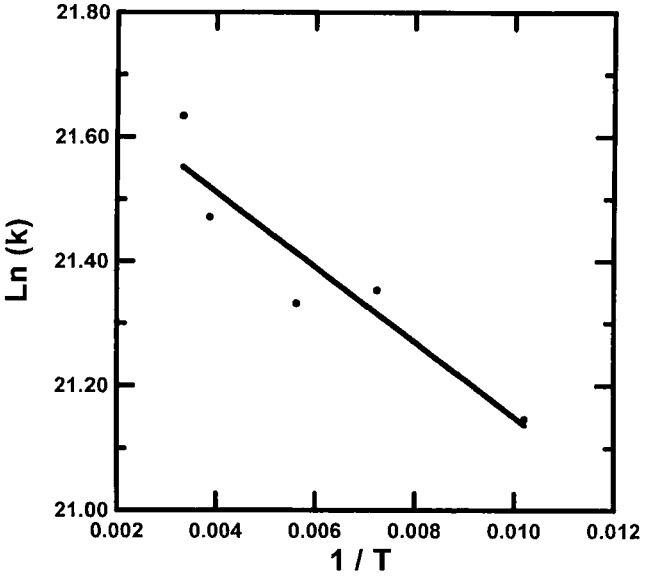

Fig. 8 Arrhenius plot of the rate constant of a fast component of transient absorption.

which are comparable with that reported by Ebessen et al.[25] with ps photolysis. The fraction of the fast component was only about 0.2 - 0.3 as mentioned above, which indicated that about 70 - 80 % of photogenerated radicals would become metastable if there is no decay during a ps laser pulse. This is not consistent with the quantum yield of 4,4'-bipyridinium radical cations by steady photolysis[2] (0.0055) and strongly suggests that there is an extremely fast recombination process. The back electron transfer in less than 1 ps is possible by a tunneling mechanism for donor and acceptor separated by about 0.33 nm and oriented face-to-face as reported for a single crystal of similar N,N'-dimethyl-4,4'-bipyridinium tetraphenylborate IPCT complexes[26]. The subpicosecond laser flash photolysis is needed to elucidate the mechanism and kinetics of such extremely fast reactions.

The prediction of the classical Marcus theory[18] that rate constants of highly exothermic electron transfer (inverted region) would decrease if the driving force, $-\Delta G°$, became greater than the reorganization energy of the reactants and the surrounding solvents was confirmed by Miller et al.[27-29] for intramolecular electron transfer reactions between donor and acceptor at fixed distance with $-\Delta G° < 2.3$ eV. The value of $-\Delta G°$ for the present system is expected to exceed 3.2 eV since the oxidation potential of $TFPB^-$ is higher than 3 V vs. NHE and the reduction potential of 4,4'-bipyridinium ions is 0.19 V vs. NHE in acetonitrile as reported previously[2]. A drastic decrease of the back electron transfer rate constant could be expected at such high exothermicity. Miller et al. further clarified that the rate constants in the inverted region showed almost no temperature dependences in disagreement with the expectations of the classical Marcus theory[30]. It was explained by theories which include quantum-mechanical treatments of high-frequency molecular vibrations of the donor and acceptor groups[31]. The present result gave a very small activation energy and would suggest that such effects hold for the fast decaying component in our system. Once charge-separated species photogenerated are escaped from the very fast geminate reaction owing to the excess vibrational energy upon CT excitation, the rate of back electron transfer reaction controlled by tunneling becomes extremely small and may be controlled also by the molecular motions of the surrounding media.

4,4'-Bipyridinium $TFPB^-$ salts are known to show unusually fluorescence from excited IPCT states in solutions at room temperature[15]. 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. It is thus indicated that the excited states showing fluorescence did not participate in the photoinduced electron transfer reaction. The ps fluorescence dynamics will be reported elsewhere in details. The reaction mechanism shown in Fig. 9 is proposed for colour changes in

4,4'-bipyridinium $TFPB^-$ polymer films upon IPCT excitation on the basis of the present

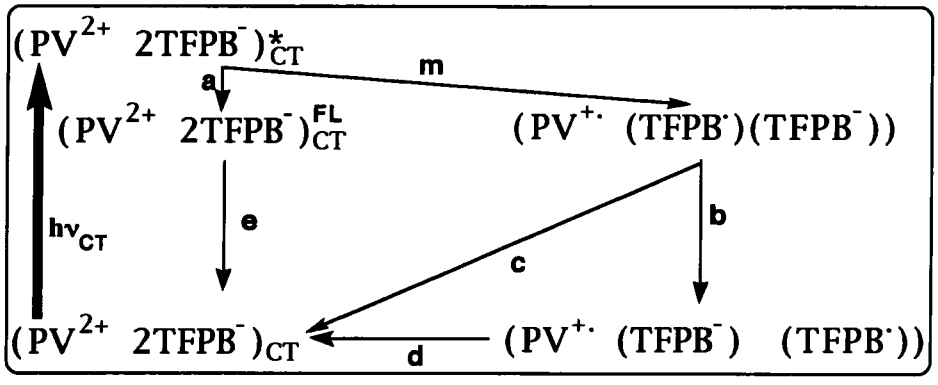

Fig. 9 A schematic representation of the electron transfer reaction proposed for the colour changes observed in the steady and ps laser flash photolysis experiments.

ps laser flash photolysis and the previous steady photolysis, where PV^{2+}, $PV^{+\cdot}$, and $TFPB^{\cdot}$ stand for polymeric 4,4'-bipyridinium ion, its one-electron reduced form and oxidized $TFPB^-$. The previously proposed reaction scheme[12,13] based on steady photolysis was revised according to the present result. The Franck-Condon state $(PV^{2+}\ 2TFPB^-)^*_{CT}$ will be converted extremely fast to geminate pairs by path **m** and to an electronically excited (fluorescent) state by path **a**. A small fraction of geminate pairs will form metastable charge-separated species $PV^{+\cdot}(TFPB^-)\cdots(TFPB^{\cdot})$ by path **b** while most of them revert to the original IPCT state via back electron transfer (path **c**). Metastable charge-separated species revert to the original IPCT state thermally (path **d**). Path **e** shows radiative and nonradiative processes. Subpicosecond laser photolysis experiments are under way to measure the real response time of colour changes which is expected to be much faster than the presently observed value and also to elucidate the deactivation mechanism of excited IPCT states.

CONCLUSIONS

From ps laser flash photolysis it was found that the colour changes in polymer films containing 4,4'-bipyridinium $TFPB^-$ salts occurred in less than 20 ps. The short-lived species formed upon ps laser excitation was rather a minor component and showed a very small temperature dependence. CT fluorescence showed much slower decay as compared with the rise of transient absorption. These results together with those from subpicosecond experiments under way are important not only to elucidate the very specific characteristics of excited IPCT complexes but also to construct ultrafast photon-mode optical memory.

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