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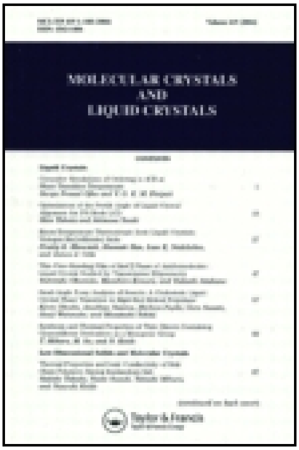

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Optical Memory by Novel Photoinduced Electrochromism

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Optical Memory by Novel Photoinduced Electrochromism

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The 4,4′-bipyridinium ions formed ion-pair charge-transfer (CT) complexes with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate in organic solutions, microcrystalline films, Langmuir-Blodgett films, and polymer films. Reversible colour changes between pale yellow and blue due to photoinduced electron transfer upon excitation of an ion-pair CT band and thermal reverse reactions were observed, which we call the photoinduced electrochromism. The rate of reverse reactions markedly depended on temperature and microenvironments. The blue-coloured state was formed very rapidly by pulsed laser excitation, which was stored without decay below 0°C in polymer films. Such photoinduced electrochromism may be applied to a new high-speed and high-density optical memory.

Keywords: 4,4′-bipyridinium ion, ion-pair charge-transfer complex, photoinduced electron transfer reactions, optical memory

INTRODUCTION

High-speed and high-density optical memory is expected to be one of the essential components in the future photonics. Conventional records have been almost completely replaced by audio Compact Disc (CD) in the last decade. CD-ROM (Compact Disc Read Only Memory), CD-R (Compact Disc Recordable) and WORM (Write Once Read Many) have been gradually increasing their market. Very recently EDRAW (Erasable Direct Read After Write) optical discs based on magneto-optical effect or reversible phase changes have become available as a high-density (128MB capacity with a 3.5 inch disc) rewritable information storage media for a personal computer. However, all these commercialized optical memories are so-called heat-mode recording systems. In other words, laser beam is focused and used as a heat source to form pits, bubbles, phase changes, or changes to the surface textures. 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 (ultra short pulse, focusing). In order to further increase the memory density in optical recording systems, so-called photon-mode optical memory employing photochemical reactions instead of thermal reactions should be developed.

Photochromic systems employing 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 of chemical bonds such as ring opening and closure in spiropyrans[1] or cis-trans isomerization in azobenzene.[2] 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 CT complexes with many ionic or neutral organic compounds and inorganic anions.[3,4] It also makes reversible redox reactions accompanying remarkable 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.[5-10] CT complexes of 4,4'-bipyridinium salts will be used for photon-mode optical memory if reverse reactions can be controlled. However, reverse electron transfer reactions are usually very rapid and no steady photoreduction of 4,4'-bipyridinium ions were observed upon excitation of a CT absorption band. A few reports have been made on accumulation of 4,4'-bipyridinium radical cations or generation of steady photocurrents via excitation of CT complexes employing sacrificial donor anions such as some carboxylate anions, dithioanion, or tetraphenylborate (abbreviated to TPB$^-$) in aqueous solutions.[11-15]

The "photomemory" of 4,4'-bipyridinium copolymers with *N*-vinyl-2-pyrrolidone has recently reported by Kamogawa *et al.*[16] Their system used UV irradiation for writing and oxygen for erasing. The former would accompany undesirable side reactions and the latter includes irreversible reactions.[17] Recently we have reported novel photochromism (photoinduced electrochromism) in organic solutions,[18,19] microcrystals,[20,21] LB films,[22-25] and polymer films[26,27] which was due only to the electron transfer via excited state of specific ion-pair charge-transfer (CT) complexes[28,29] of 4,4'-bipyridinium ions with tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate.[30] The photochemical colouring and thermal fading was highly reversible in all these systems.[18-27] The experimental results for possible application of novel photoinduced electrochromism to optical memory will be discussed.

EXPERIMENTAL

Several derivatives of 4,4'-bipyridinium ions were synthesized as shown in Figure 1. Two kinds of borate anions, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (abbreviated as TFPB$^-$) and tetraphenylborate (TPB$^-$) were used to form salts with these 4,4'-bipyridinium ions. The synthesis of an elastic polymer (PV^{2+}) containing 4,4'-bipyridinium salts as a part of the main chain was reported previously.[26,27] Transparent polymer films were obtained by casting 1,2-dimethoxyethane solutions of PV^{2+} salts on a quartz plate. Microcrystalline thin films of MV^{2+} or FV^{2+} salts were prepared from 1,2-dimethoxyethane solutions in a quartz cuvette. Amphipathic 4,4'-bipyridinium ions with symmetrical (HV^{2+}) and asymmetrical (AV^{2+}) long-alkyl substituents were also prepared to form LB films.[22-25] LB films of a 1:4 monolayer mixture of amphipathic 4,4'-bipyridinium salts and arachidic acid were deposited on a quartz plate from an aqueous subphase containing 0.25 mM $CdCl_2$ and 0.05 mM $NaHCO_3$ at 18°C and 20 mN·m^{-1}.

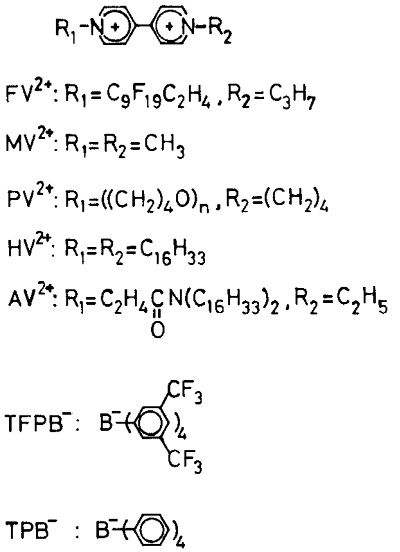

FIGURE 1 The structure of 4,4′-bipyridinium ions, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate and tetraphenylborate anions.

Polymer films were thoroughly degassed in an Oxford Instruments DN1754 cryostat with an Oxford 3120 temperature controller. LB films and microcrystalline thin films were thoroughly degassed in a quartz cuvette. LB films were rotated in vacuo around their deposition direction to change the incident angle for *p*-polarized light. These samples were irradiated in vacuo at controlled temperature by 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 to excite their CT absorption band alone. The photogeneration and decay processes of 4,4′-bipyridinium radical cations were observed by a UV/VIS spectrophotometer (JASCO UVIDEC-505) controlled by a microcomputer. The decay of absorbance was recorded with a digital memory for fast decay or with a microcomputer every one minute for slow decay. Laser flash photolysis experiments were made on this polymer films using the third harmonic (355 nm) of pulsed (10 ns) YAG laser as an excitation source and a He-Ne laser as a probe light. The transient signals were recorded with a Sony-Tektronix DSA601 Digitizing Signal Analyzer.

RESULTS AND DISCUSSION

$TFPB^-$ salts of 4,4′-bipyridinium ions showed ion-pair charge-transfer (CT) absorption above 350 nm in organic solution and in solid films as reported previously.[18-29] A 3,5-bis(trifluoromethyl)phenyl group of $TFPB^-$ as a donor and a pyridinium group of 4,4′-bipyridinium ion as an acceptor are expected to form a face-to-face CT complex in a similar manner as recently reported for a CT complex salt of $MV^{2+}(TPB^-)_2$ from the X-ray structural analysis of a single crystal.[31] These CT complexes of $TFPB^-$ salts showed very specific properties such as extremely slow formation and CT fluorescence in organic solutions at room temperature.[28,29] The extremely slow formation was attributed to the extraordinary bulkiness of TFPB$^-$.[29]

Small angle X-ray diffraction profiles are shown in Figure 2 for 60 monolayers of a mixture of $HV^{2+}(TFPB^-)_2$ and arachidic acid with a molar ratio of 1:4, which shows sharp diffractions up to the 7th order. The long spacing calculated from this result, 5.46 ± 0.06 nm, coincided with that of cadmium arachidate LB films within experimental error. LB films of $AV^{2+}(TFPB^-)_2$ gave similar results. It is strongly suggested from these results that well-defined Y-type LB films were formed from mixtures of amphipathic 4,4′-bipyridinium salts and arachidic acid.[24] A 4,4′-bipyridinium ion was presumed to be sandwiched by two TFPB$^-$ anions from the upper and lower sides as reported previously.[24]

Upon irradiation of a CT absorption band at $\lambda_{ex} > 365$ nm in vacuo the colour of all TFPB$^-$ salts of 4,4′-bipyridinium ions changed from pale yellow to blue in organic solutions[18,19] and in solid films.[20–27] The UV/VIS absorption spectra are shown in Figure 3 for polymer films (a) before and (b) after irradiation at 30°C as an example. Two absorption bands with peaks at about 400 and 600 nm were observed, which are characteristic to 4,4′-bipyridinium radical cations.[32] The absorption spectrum extended up to about 800 nm, which can be used for the non-

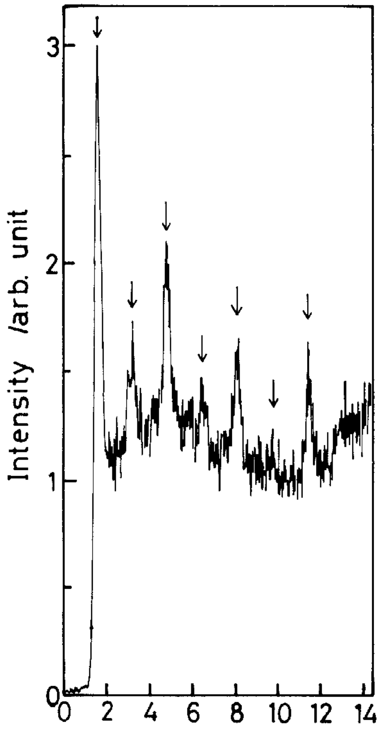

FIGURE 2 Small angle X-ray diffraction profiles for LB films of a 1:4 mixture of $HV^{2+}(TFPB^-)_2$ and arachidic acid.

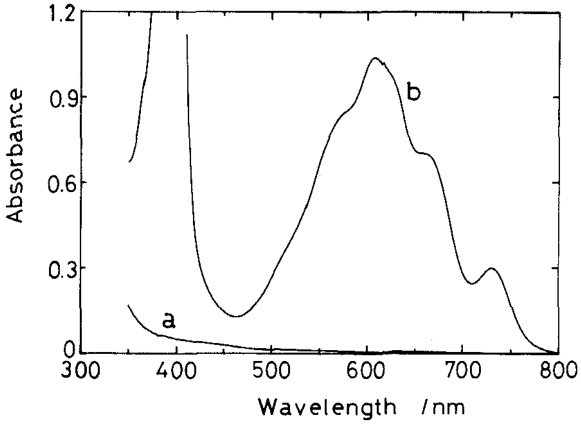

FIGURE 3 Absorption spectra of polymer films (a) before and (b) after irradiation in vacuo at 30°C for 45 min.

destructive reading with diode lasers. Similar absorption spectra were observed for all TFPB$^-$ salts of 4,4′-bipyridinium derivatives irradiated in solutions[18,19] or in solid films.[20–27] These results indicate that the photoreduction of 4,4′-bipyridinium ions via excited CT states caused colour changes. The absorption spectrum of oxidized TFPB$^-$ expected below about 350 nm was not resolved due to the strong absorption of parent ions as previously reported.[18]

Usual tetraphenylborate (TPB$^-$) salts of 4,4′-bipyridinium ions showed colour changes from orange to blue upon excitation of their CT bands. However, the colour change of these TPB$^-$ was irreversible in contrast with the reversible colour changes in TFPB$^-$ salts as mentioned below. The very rapid decomposition of usual TPB$^-$ after one electron oxidation caused such irreversible formation of 4,4′-bipyridinium radical cations.[18] The 4,4′-bipyridinium-TPB$^-$ salts can thus be applied to a photon-mode WORM optical memory.

The time-dependences of the absorbance at 605 nm for 4,4′-bipyridinium radical cations in 4,4′-bipyridinium-TFPB$^-$ salts in organic solutions and in solid films at 20°C are shown in Figure 4. Microcrystalline thin films and LB films showed almost identical lifetime ($\tau_{1/e}$ = 4 h), while the lifetime in polymer films and organic solutions was about 20 and 0.1 times of that in LB films, respectively. The blue colour was observed again upon excitation of a CT band and the colour change was repeated for many times in all solid films and organic solutions.[18–27] These results together with no decay of blue colour in TPB$^-$ salts mentioned above have led to two important features in colour changes of TFPB$^-$ salts. First, the thermal fading of blue colour in TFPB$^-$ salts was due to the reverse electron transfer reaction from reduced 4,4′-bipyridinium ion to oxidized TFPB$^-$. Secondly, microenvironments of 4,4′-bipyridinium radical cations markedly affected their decay. The lifetime of blue-coloured state in polymer films also depended on temperature as shown in Figure 5. No decay was observed even after 24 h below about 0°C. The initial yield of radicals after irradiation for a constant time was low at both lower and higher temperatures as shown in Figure 5. The blue-coloured state decayed rapidly at elevated temperatures. The absorption spectrum after thermal

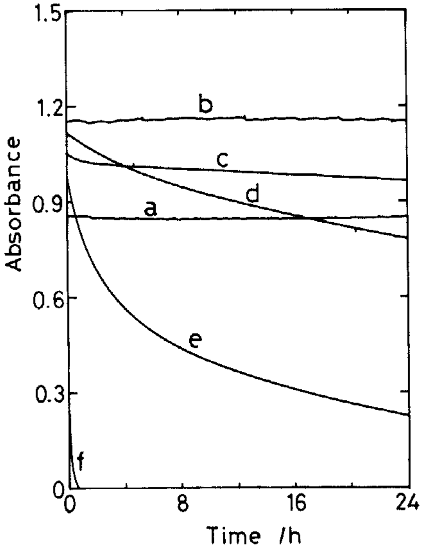

FIGURE 4 Time-dependence of absorbance at 605 nm in the dark for polymer films irradiated (λ_{ex} > 365 nm) in vacuo for 45 min at (a) −20, (b) 0, (c) 10, (d) 20, (e) 30, and (f) 80°C.

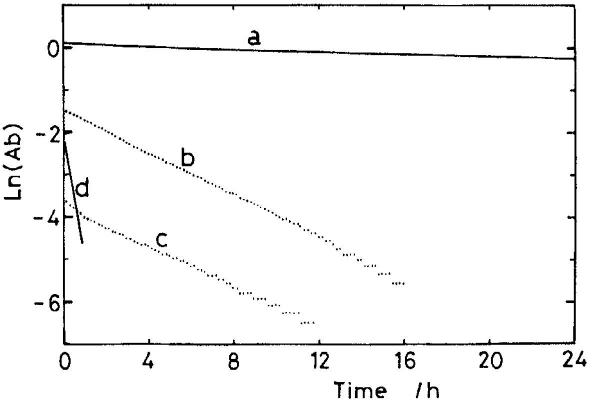

FIGURE 5 Logarithmic plots of thermal decay of 4,4′-bipyridinium radical cations monitored at 605 nm for TFPB$^-$ salts of various 4,4′-bipyridinium ions; (a) polymer film of PV^{2+}, (b) microcrystalline film of MV^{2+}, (c) LB film of HV^{2+}, and (d) 1,2-dimethoxyethane solution of FV^{2+}.

decay of 4,4′-bipyridinium radical cations was similar to that of the original polymer films. The 4,4′-bipyridinium radical cations were formed again upon excitation of the CT band at each temperature in vacuo.

We have shown that 4,4′-bipyridinium radical cations escaping from the germinate reaction immediately after the photoinduced electron transfer reactions via conformational changes (distance and/or orientation) became metastable owing to the bulk and chemical stability of TFPB$^-$ and also to the restriction of molecular motion by the microenvironment.[20–27,30] The much increased lifetime in polymer films compared with that in microcrystals or LB films strongly suggests that the microenvironment in highly elastic polymers facilitated the change of mutual orientation and/or distance of charge-separated species and also restricted the molecular motions leading to the reverse reaction.[26,27] Persistent storage of optically written data below about 0°C is most probably related to the endotherm observed at about −6°C ~ 40°C in a DSC thermogram which was attributed to the melting of poly(tetrahydrofuran) microcrystals.[27] Crystalline poly(tetrahydrofuran) units seemed to restrict markedly the reorientation of 4,4′-bipyridinium radical cations. The lower yield of radicals at higher irradiation temperatures was caused by the thermal decay. The decrease of radical yield at lower temperatures, on the other hand, was most probably attributed to the increase of geminate reactions due to higher restriction of molecular motions.

The incident angle dependences of *p*-polarized absorption at 400 nm for irradiated two 4,4′-bipyridinium LB films prepared from a 1:4 mixture of amphipathic 4,4′-bipyridinium-TFPB$^-$ salts with arachidic acid (AA) are shown in Figure 6, where HV and AV stand for $HV^{2+}(TFPB^-)_2$ and $AV^{2+}(TFPB^-)_2$, respectively. No polarization angle dependences were observed at normal incidence for both LB films. As shown in Figure 6, AV/AA and HV/AA LB films showed the maximum and the minimum, respectively, at normal incidence. The solid lines in Figure 6 are the calculated dependences from a least square method using the observed data corrected for the optical path length and thermal decay, and an equation derived for the orientational distribution of transition moments in the direction normal to the

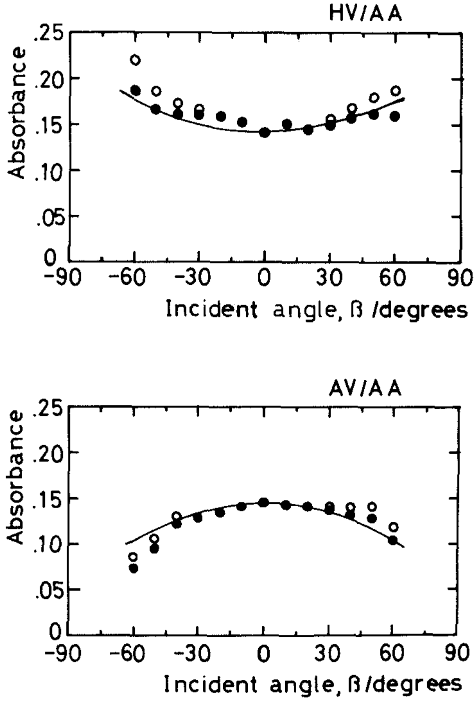

FIGURE 6 The incident angle dependences of *p*-polarized absorption at 400 nm for radical cations in HV/AA and AV/AA LB films. ○: observed data corrected for thermal decay during measurements, ●: after correction for the optical path length. Solid lines show calculated dependences. See text for details.

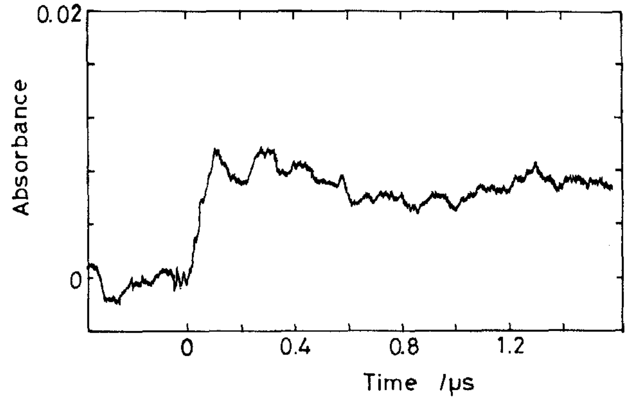

FIGURE 7 Transient absorption monitored by a He-Ne laser (632.8 nm) during laser flash photolysis for polymer cast films of $PV^{2+}(TFPB^-)_2$ excited at 355 nm.

substrate surface.[25] From these results, it is indicated that 4,4′-bipyridinium radical cations in HV/AA and AV/AA LB films obliqued by about 45° and lay almost parallel to the substrate, respectively. This result indicates that the orientation of chromophores can be controlled by their substituents and may be used to increase the memory density by using the polarized light.

An example of transient absorption monitored by a He-Ne laser during ns laser flash photolysis is shown in Figure 7. The fast rise of absorption at 632.8 nm controlled by the pulse width of a pumping ns laser is indicated in Figure 7.[33] The very high-speed optical writing in the present polymer was thus demonstrated. Further studies are under way using a ps laser photolysis. These results indicate that the data can be written optically with short pulsed lasers and can be stored in polymer films. These data can be read with diode lasers and can be erased thermally as mentioned above.

CONCLUSIONS

Reversible colour changes between pale yellow and blue due to photoinduced electron transfer and thermal reverse reactions were observed in ion-pair charge-transfer complexes of 4,4′-bipyridinium salts with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate in various microenvironments. The lifetime of blue-coloured 4,4′-bipyridinium radical cations generated very rapidly was controlled by microenvironments and temperature. The molecular orientation of blue species was controlled in LB films. Such photoinduced electrochromism is expected to be applied to a new photon-mode optical memory.

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