

# Ultrafast photon-mode recording and switching by photoinduced electron transfer

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**Abstract:** Ultrafast photon-mode recording and switching based on photoinduced electron transfer was proposed using ion-pair charge-transfer (IPCT) complexes of 4,4'-bipyridinium salts. Specific IPCT complexes were formed with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. Ultrafast colour changes (< 1 ps) were observed upon excitation of IPCT absorption. Such extremely fast colour changes were due to the fact that the IPCT absorption band is associated with the electronic transition from a partially charge-transferred ground state to an almost completely charge-separated excited state. The decay was controlled over a very wide range from ps to infinity by counter anions, the temperature, or the microenvironment. Molecular orientation of photogenerated radical cations and highly sensitive detection of colour changes even in a single monolayer film were also achieved.

## INTRODUCTION

Novel materials and systems are required for much faster recording or switching, and much higher storage density by the progress in the speed of computers and the rapidly expanding volume of information. Photon-mode recording or switching based on changes in absorption and/or refractive index by photoreactions is expected to have many advantages as compared with heat-mode recording, magnetic recording, or electro-optic switching. Various photochromic systems have recently attracted much interest in view of their promising applicability to high-speed and high-density photon-mode optical memory (1). The photochromism reported so far involves changes of chemical bonds such as ring opening and closing or cis-trans isomerization, which may limit the recording speed or the cycle number.

Recently we have reported novel photochromism, photoinduced electrochromism, in organic solutions (2-4), in microcrystals (5,6), in LB films (7-12), and in polymer films (12-15). It 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 (TFPB<sup>-</sup>) (18). The photochemical colouring due to the photoinduced electron transfer and the thermal fading due to the reverse electron transfer were highly reversible in deaerated atmosphere in all systems (2-15). In organic solutions reversible changes of IPCT fluorescence were also observed during repeated photoexcitation and storage in the dark (4). A schematic representation of photoinduced electrochromism in IPCT complexes of 4,4'-bipyridinium salts is shown in Fig. 1. The present paper will give a review of our studies on photoinduced electrochromism of IPCT complexes: (1) Very specific IPCT complex formation, (2) Control of reverse reactions by microenvironments and counter anions, (3) Ultrafast colour changes upon IPCT excitation, (4) Control of molecular orientation of photogenerated radical cations, (5) Highly sensitive detection of colour changes by the optical waveguide method, and (6) Possible applications to optical recording and switching.

## VERY SPECIFIC IPCT COMPLEX FORMATION

4,4'-Bipyridinium ions with various substituents and diquat (2,2'-bipyridinium) ion formed very specific IPCT complexes with TFPB<sup>-</sup> as a donor and showed characteristic IPCT absorption spectra yielding yellow to orange colour (16,17,19). The structures and abbreviations of compounds employed are shown in Fig. 2. It took very long time, 100 - 200 h, to reach the equilibrium of IPCT formation in solutions at 20°C, which was due to the extraordinary bulkiness of TFPB<sup>-</sup> (16,17,19). Fairly strong IPCT fluorescence with a peak at 520 - 525 nm was observed in these complexes, for the first time, in solutions at room temperature (16,19). The intensity of IPCT fluorescence also increased very gradually with IPCT complex formation. Diquat TFPB<sup>-</sup> salt further showed unusually well-resolved vibrational structure in IPCT absorption spectrum in solutions (19). These results strongly suggest that the structure of IPCT complexes is highly ordered just like a supramolecule owing to the space of a bulky TFPB<sup>-</sup> to incorporate or hold an almost planar diquat ion or a pyridinium ring of 4,4'-bipyridinium ion (16,17,19).

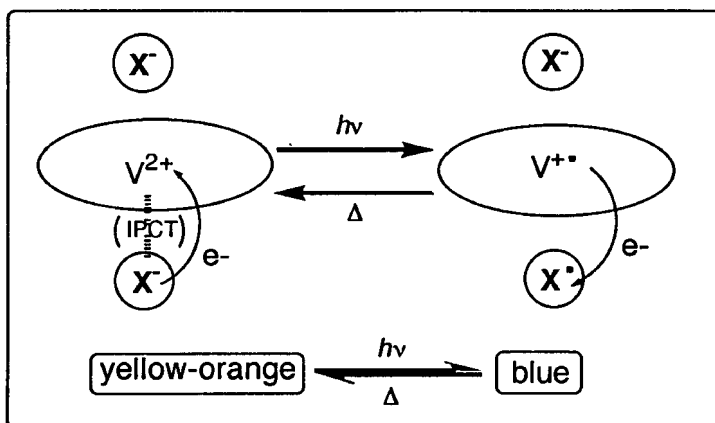


Fig. 1 A schematic representation of the photoinduced electrochromism using IPCT complexes of 4,4'-bipyridinium salts  $V^{2+}(X^-)_2$ .

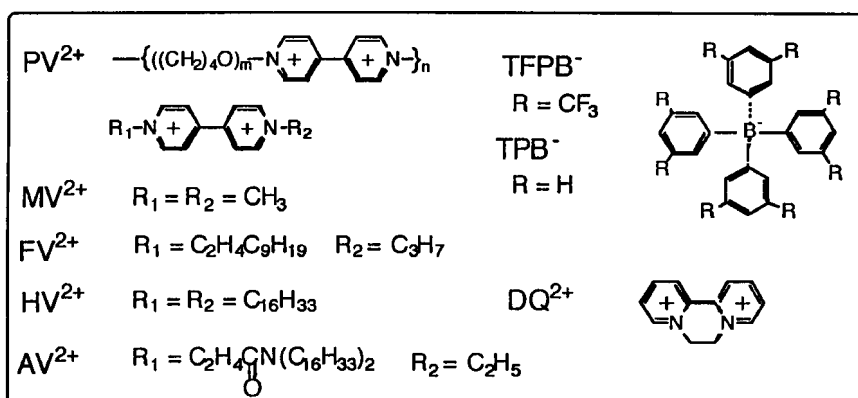


Fig. 2 The structure of bipyridinium salts employed in the present experiment.

### REVERSIBLE COLOUR CHANGES AND CONTROL OF REVERSE REACTIONS BY MICROENVIRONMENTS AND COUNTER ANIONS

Upon excitation of IPCT absorption by a Xe-Hg lamp above 365 nm in solutions or in solid films under degassed conditions, the colour of 4,4'-bipyridinium salts changed from pale yellow to blue due to the formation of 4,4'-bipyridinium radical cations. The blue colour decayed thermally and reversibly in TFPB<sup>-</sup> salts (2-15). The absorption spectrum of oxidized donor TFPB<sup>-</sup> with a peak at about 360 nm by pulse radiolysis (20) was not observed owing to the strong absorption of the parent ions and 4,4'-bipyridinium radical cations. Similar colour change from orange to blue was observed in usual tetraphenylborate (TPB<sup>-</sup>) salts. No decay was, however, observed due to the oxidative decomposition of TPB<sup>-</sup> (2). Upon dissolution with degassed solvents, photogenerated 4,4'-bipyridinium radicals in microcrystals disappeared in TFPB<sup>-</sup> salts, but did not decay at all in TPB<sup>-</sup> salts (6). No colour changes were observed in halide (Br<sup>-</sup>, I<sup>-</sup>) salts of 4,4'-bipyridinium in steady photolysis, although they showed fairly strong IPCT absorption. It was attributed to a very fast back electron transfer reaction as mentioned below. The lifetime of coloured (blue) state in TFPB<sup>-</sup> salts depended markedly on the microenvironments and temperatures. Fig. 3 shows the decay behavior of photogenerated 4,4'-bipyridinium radical cations at 20 °C for TFPB<sup>-</sup> salts in (a) polymer film of PV<sup>2+</sup>, (b) microcrystalline film of MV<sup>2+</sup>, (c) Langmuir-Blodgett film of HV<sup>2+</sup>, and (d) 1,2-dimethoxyethane (DME) solution of FV<sup>2+</sup>. For a polymer sample it was about 20 min in DME solutions and 72 h in cast films at 20 °C (3,13,14). The blue state was stored stably without decay below 0 °C in polymer films containing 4,4'-bipyridinium salts as part of the main chain, which was shown to be closely related with the thermal transition of poly(tetrahydrofuran) units in that polymer (13,14). Fast thermal decay was observed in polymer films at higher temperatures than 80 °C. Appropriate coating of a protective layer on such photoelectrochromic polymers made a stable colour change possible even in air (15). Diquat salts also showed reversible

colour changes between yellow and greenish yellow upon IPCT excitation and subsequent storage in the dark due to photoinduced electron transfer and reverse reactions. From steady photolysis results it has been indicated that 4,4'-bipyridinium radical cations escaped from the geminate recombination reaction immediately after the photoinduced electron transfer became metastable owing to the bulk and chemical stability of TFPB<sup>-</sup>, to the restriction of molecular motion, and also to the very high exothermicity of the reverse electron transfer reaction in the Marcus inverted region (21). 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 IPCT fluorescence intensity decreased upon IPCT excitation concomitantly with the photoinduced colour changes and increased gradually to the original value in accordance with the recovery of IPCT complexes in solutions (4). These colour and fluorescence changes were repeated reversibly for many times in TFPB<sup>-</sup> salts.

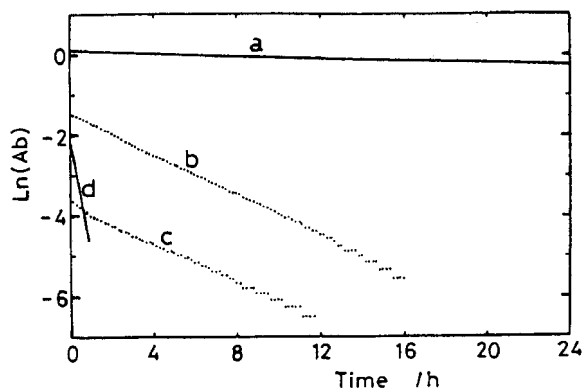


Fig. 3 Logarithmic plots of absorbance at 605 nm for TFPB<sup>-</sup> salts of various 4,4'-bipyridinium ions, (a) polymer film of PV<sup>2+</sup>, (b) microcrystalline film of MV<sup>2+</sup>, (c) Langmuir-Blodgett film of HV<sup>2+</sup>, and (d) 1,2-dimethoxyethane solution of FV<sup>2+</sup> at 20 °C.

### ULTRAFAST COLOUR CHANGES UPON IPCT EXCITATION

Upon picosecond (ps) laser excitation of PV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub> film at 355 nm, transient absorption spectrum with peaks at about 600 and 400 nm was observed, which is characteristic to 4,4'-bipyridinium radical cations indicating photoinduced electron transfer reaction via excited IPCT complexes. The transient absorption at 600 nm appeared in less than 20 ps in solid polymer films, which was controlled by the pulse width of a ps laser as shown in Fig. 4. From these results it was confirmed that the colour changes from pale yellow to blue in the polymer film due to photoinduced electron transfer reaction upon IPCT excitation occurred within the ps laser pulse (22,23). About 20% of photogenerated radical cations decayed with a lifetime of 280 ps at 20°C. The rest did not decay in the ns-ms region and is thought to correspond to the colour changes in steady photolysis. The lifetime of the fast component gradually increased with lowering temperatures, to about 650 ps at 98 °K. The rate constant of the fast component showed a linear relationship against 1/T, from which the activation energy of 0.50 kJ/mol was estimated (23). The value of -ΔG<sup>0</sup> for reverse electron transfer in the present system is expected to exceed 3.2 eV, since the oxidation potential of TFPB<sup>-</sup> is higher than 3 V vs. NHE and the reduction potential of 4,4'-bipyridinium ions is 0.19 V vs. NHE in acetonitrile (2). The rate constants in the inverted region were reported to show almost no temperature dependence in disagreement with the expectations of the classical Marcus theory (24). It was explained by theories that include quantum-mechanical treatments of high-frequency molecular vibrations of the donor and acceptor groups (25). The very small activation energy in the present system would suggest that such effects hold for the fast decaying component in reduced 4,4'-bipyridinium and oxidized TFPB<sup>-</sup>. Owing to the excess energy upon IPCT excitation, some parts of charge-separated species photogenerated will be escaped from the very fast geminate reaction and will change mutual distance and/or orientation as compared with the original configuration of IPCT complexes before excitation. Then the rate of reverse electron transfer reaction by tunneling becomes extremely small and will be controlled by the molecular motions of the surrounding media as mentioned in the previous section.

Femtosecond (fs) laser flash photolysis has very recently been studied in DME solutions of PV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub> and in dimethylsulfoxide (DMSO) solutions of N,N'-dimethyl-4,4'-bipyridinium (MV<sup>2+</sup>) diiodides (I<sup>-</sup>). These sample solutions in a 2-4 mm cell were excited in air at room temperature by the second harmonics (400 nm) of a fs Ti:sapphire laser with a regenerative Ti:sapphire amplifier. Amplified Ti:sapphire laser delivered pulses with a FWHM of 200-250 fs, 10 Hz repetition, a maximum power of 6 mJ/pulse at 800 nm. A probe white light was obtained by focusing the residual 800 nm light into a cell containing D<sub>2</sub>O/H<sub>2</sub>O (2:1) mixture after passing through a BBO crystal to obtain the second harmonics. Transient absorption with a peak at about 600 nm, characteristic of 4,4'-bipyridinium radical cations, was observed in both salts immediately upon excitation of an IPCT band with a fs laser at 400 nm. 4,4'-Bipyridinium radical cations were thus formed in a fs time scale by the photoinduced electron transfer from a donor (TFPB<sup>-</sup> or I<sup>-</sup>) to an acceptor (4,4'-bipyridinium) upon IPCT excitation. The time profile of transient absorption at 600 nm is shown in Fig. 5 for MV<sup>2+</sup>(I<sup>-</sup>)<sub>2</sub> in DMSO. It showed very rapid rise in about 0.3 picosecond (ps), which was almost the same as the time resolution of our amplified Ti:sapphire laser system. The decay curve was composed of a major fast (τ = about 2 ps) component and a minor slow (τ > 1.3 ns) one. The latter ascribed to cage-escaped species in solutions will be minimized in solid films. Photogenerated 4,4'-bipyridinium

radical cations disappeared completely in the case of  $MV^{2+}(I^-)_2$  during 10 Hz laser irradiation, which corresponded well with the fact that no steady colour changes were observed upon IPCT excitation as mentioned above.  $TFPB^-$  salts of  $PV^{2+}$ , which showed steady and reversible colour changes in films and solutions, also showed a very rapid rise of transient absorption at 600 nm in about 0.3-0.5 ps upon IPCT excitation. The decay behavior was totally different from that of  $MV^{2+}(I^-)_2$  in DMSO and no decay was observed in a similar time region shown in Fig. 5. About a half of photogenerated 4,4'-bipyridinium radical cations decayed much more slowly ( $\tau = 80$  ps). The rest survived for an extremely long time corresponding to the reversible and persistent colour changes observed by steady photolysis (4,14,15).

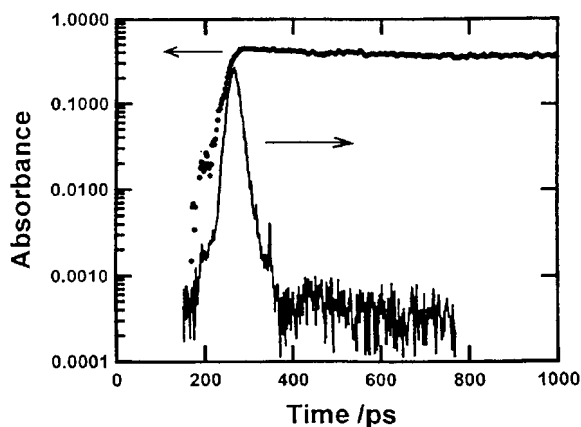


Fig. 4 Logarithmic plots of transient absorption at 600 nm in a  $PV^{2+}(TFPB^-)_2$  film and the intensity of a ps laser pulse (532 nm).

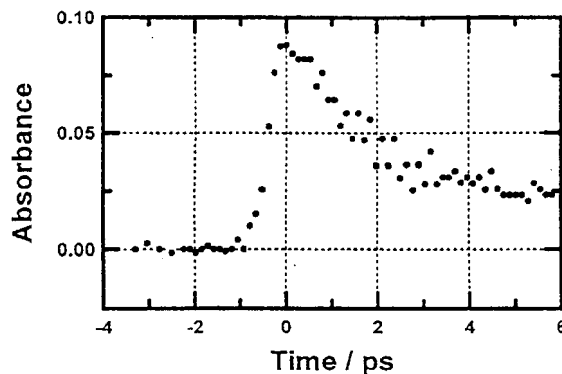


Fig. 5 A time profile of transient absorption at 600 nm for  $MV^{2+}(I^-)_2$  in DMSO upon excitation with a 400 nm fs laser.

The present result of colour change in about 0.3 ps with  $PV^{2+}(TFPB^-)_2$  is the fastest response reported so far among materials which show steady photochromism. In relation to the results with  $MV^{2+}(I^-)_2$ , Wasielewski et al. (26) recently reported picosecond optical switch based on transient absorption due to the photoinduced electron transfer with 5 and 178 ps switching on and off times, respectively. The electrons correlated with a CT band are transferred partially at the ground state and completely at the excited state. 4,4'-Bipyridinium radical cations showing blue colour is thus expected to be formed immediately from the Franck-Condon excited state upon IPCT excitation. Such a situation is very different from usual photochromism which is caused by various changes of chemical bonds via the excited state. The difference in decay behavior of  $PV^{2+}(TFPB^-)_2$  and  $MV^{2+}(I^-)_2$  can be explained by the redox potentials and structures of two anions. The faster decay of 4,4'-bipyridinium radical cations in  $MV^{2+}(I^-)_2$  is most probably due to the lower exothermicity, since the oxidation potential for  $I^-$  in methanol is +0.36 V vs. NHE (27), which is much smaller than that of  $TFPB^-$  mentioned above. These results strongly suggest that  $PV^{2+}(TFPB^-)_2$  and  $MV^{2+}(I^-)_2$  may be applied to novel ultrafast photon-mode recording and ultrafast optical switching, respectively. We can control the photoresponses of IPCT complexes by choosing appropriate pairs from many other possible combinations of donors and acceptors and by controlling the microenvironment.

The time-resolved fluorescence studies revealed that the 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 (23). It is thus indicated that the excited states showing fluorescence did not participate in the photoinduced electron transfer reaction. The reaction mechanism was proposed for photoresponses of  $PV^{2+}(TFPB^-)_2$  in solutions and in solid films based on fs and ps laser flash photolysis and steady photolysis as shown in Fig. 6, where  $PV^{2+}$ ,  $PV^+$ , and  $TFPB^-$  stand for polymeric 4,4'-bipyridinium ion, its one-electron reduced form and oxidized  $TFPB^-$ . 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  $PV^+ \cdot (TFPB^-) \cdots (TFPB^-)$  by path b while most of them revert to the original IPCT state via back electron transfer (path c). Metastable charge-separated species go back to the initial ion pairs by path d, which will then form IPCT complexes very gradually (4). Path e shows radiative and nonradiative processes.

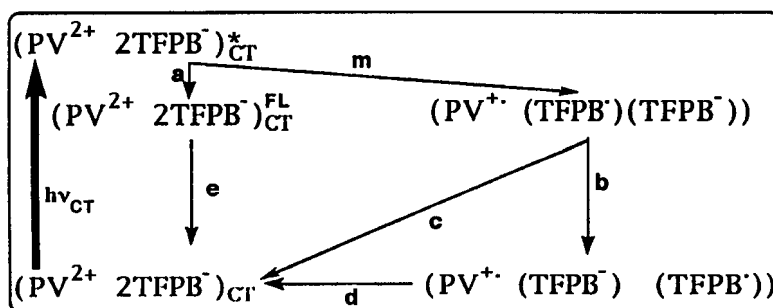


Fig. 6 A schematic representation of the reaction mechanism for the colour and fluorescence changes observed in the steady photolysis and ultrafast laser flash photolysis experiments.

### CONTROL OF MOLECULAR ORIENTATION AND HIGHLY SENSITIVE DETECTION OF PHOTOGENERATED RADICAL CATIONS

TFPB<sup>-</sup> salts of 4,4'-bipyridinium ions containing long alkyl chains, HV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub> and AV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub>, in several mixtures with arachidic acid (AA) gave Y-type LB films with good quality (7-12). Polarized absorption spectra of photogenerated 4,4'-bipyridinium radical cations were measured in vacuo for these LB films composed of 120 monolayers as a function of polarization angle and incident angle (10,11). The thermal decay of radicals during measurements of polarized absorption spectra was corrected by their lifetime. The different optical path length in the incident angle dependence measurements was also corrected from an apparent incident angle dependence of s-polarized absorption in a similar way as reported for amphipathic porphyrin (28). No polarization angle dependence was observed at normal incidence in both LB films. The p-polarized absorption of 4,4'-bipyridinium radical cations at 400 nm, which corresponds to a short-axis transition, showed a minimum absorbance in HV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub>/AA and a maximum in AV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub>/AA at normal incidence. Similar incident angle dependencies were observed at 614 nm which is due to a long-axis transition of 4,4'-bipyridinium radical cations. From the least square calculations of the observed results, taking the angle distribution of the transition dipole moments with respect to the surface normal into account, it was shown that both the long and short axes of 4,4'-bipyridinium radical cations lay almost flat in LB films of AV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub>/AA and inclined by about 46° to the substrate surface in LB films of HV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub>/AA (10,11). These results demonstrated the molecular control of orientation of photoelectrochromic groups in LB films which will be useful in multiple photon-mode recording based on polarization.

It is very interesting and important to observe absorption changes in LB films composed of a single or a few monolayers from viewpoints of basic science and applications of photoresponsive ultrathin films. We have applied an optical waveguide (OWG) method for such purposes (29,30). The electric fields of light propagating through the OWG layer have an exponentially decreasing value as evanescent waves beyond both surface of the OWG to the order of its wavelength. Evanescent waves have been used to sensitively detect and characterize adsorbates and thin films on the OWG. Thin films deposited on the surface of OWG were degassed by a rotary pump in a small chamber and irradiated with a Xe-Hg lamp through appropriate filters (> 365 nm). A linearly polarized He-Ne laser (632.8 nm) was used as a monitor light. A 150-fold sensitivity of the OWG method as compared with the conventional method was demonstrated from the colour change measurement in about 180 nm thick film of PV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub> (29). The absorbances calculated from the changes of OWG signal for PV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub> thin films of various thickness from 10 to 180 nm increased linearly with irradiation time. The rate of absorbance changes was proportional to the film thickness in the range studied. These results strongly suggested PV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub> thin films of various thickness are homogeneous and that 4,4'-bipyridinium groups are distributed randomly throughout the polymer films as schematically shown in Fig. 7.

Photoinduced colour change in a single monolayer LB film of HV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub>/AA or AV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub>/AA was successfully detected by the OWG. The absorbance changes increased with the number of monolayers deposited. In contrast to the almost linear increase in absorbance of polymer films with irradiation time, the absorbances in LB films tended to saturate at longer irradiation times. The "saturated" absorbances increased almost proportional with the number of monolayers. In LB films the 4,4'-bipyridinium ions are not distributed randomly but are confined to and aligned in a layer of a few ångströms thick periodically distributed in the direction of the surface normal as schematically shown in Fig. 7. The long spacing of LB films of HV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub>/AA was evaluated as 5.5 nm by X-ray scattering (7,12). Such structural properties and much smaller thickness of LB films most probably contributed to the "saturation" tendency observed.

4,4'-Bipyridinium radical cations photogenerated in polymer thin films showed the same absorbance for polarized OWG measurements with both transverse electric (TE) and transverse magnetic (TM) modes. This result corresponded with the random orientation of radical cations in consistent with the linear time dependence of photogeneration mentioned above indicating the random distribution of 4,4'-bipyridinium groups throughout the polymer films. In LB films of HV<sup>2+</sup>(TFPB<sup>-</sup>)<sub>2</sub>/AA with a single to six monolayers

the OWG signals after photoexcitation displayed anisotropic absorption for TE and TM modes. Both the substituents of the 4,4'-bipyridinium ions and the nature of the substrate surface were found to affect the anisotropic absorption in LB films by the OWG method.

From fs laser flash photolysis extremely fast colour changes due to the photoinduced electron transfer reaction in 4,4'-bipyridinium IPCT complexes with TFPB<sup>-</sup> and I<sup>-</sup> were confirmed. The reverse reaction was controlled from ps to persistent by counter anions and microenvironments. The control of molecular orientation of chromophores and highly sensitive detection of photoresponses became possible. These results are important not only to elucidate the very specific characteristics of excited IPCT complexes, but also to develop new materials for ultrafast photon-mode optical memory or optical switching.

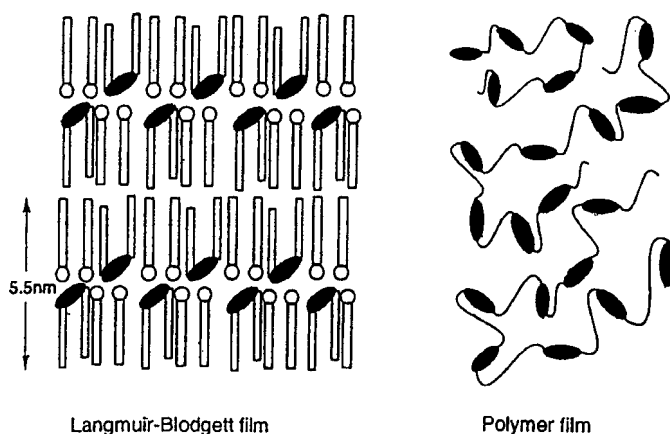


Fig. 7 Schematic representations of 4,4'-bipyridinium chromophores (closed ellipses) in mixed LB films of  $HV^{2+}(TFPB^-)_2/AA$  and in polymer films. Counter anions are not shown for simplicity.

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