

## Novel Photochromism in 4,4'-Bipyridinium Monolayer Assemblies *via* Excitation of Ion-pair Charge-transfer Complexes

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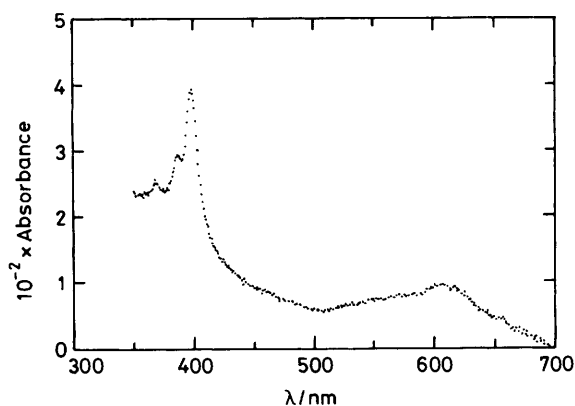
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*N,N'*-Dihexadecyl-4,4'-bipyridinium salts with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate in mixed monolayer assemblies with arachidic acid showed photochromism due to the electron transfer reaction *via* excitation of an ion-pair charge-transfer band ( $\lambda_{\text{ex.}} > 365 \text{ nm}$ ).

4,4'-Bipyridinium ion undergoes reversible redox reactions accompanied by marked colour changes (electrochromism) and also forms charge-transfer (C.T.) complexes as a good electron acceptor with many organic compounds and inorganic anions. Ionic photodissociation from excited C.T. complexes of 4,4'-bipyridinium salts was observed by flash photolysis in polar solvents to lead to 4,4'-bipyridinium cation radicals. However, reverse electron-transfer reactions are usually very rapid and no steady photoreduction of 4,4'-

bipyridinium ions has been observed upon excitation of a C.T. absorption band without employing sacrificial donor anions.

Recently we have reported that excitation of an ion-pair C.T. complex<sup>1-3</sup> of 4,4'-bipyridinium salts with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion (TFPB<sup>-</sup>)<sup>4</sup> in microcrystals<sup>1</sup> or in organic solutions<sup>5</sup> *in vacuo* or in Ar resulted in the accumulation of 4,4'-bipyridinium cation radicals which disappeared thermally. The photochemical colouring and thermal fading was highly reversible in both systems.<sup>1,5</sup>



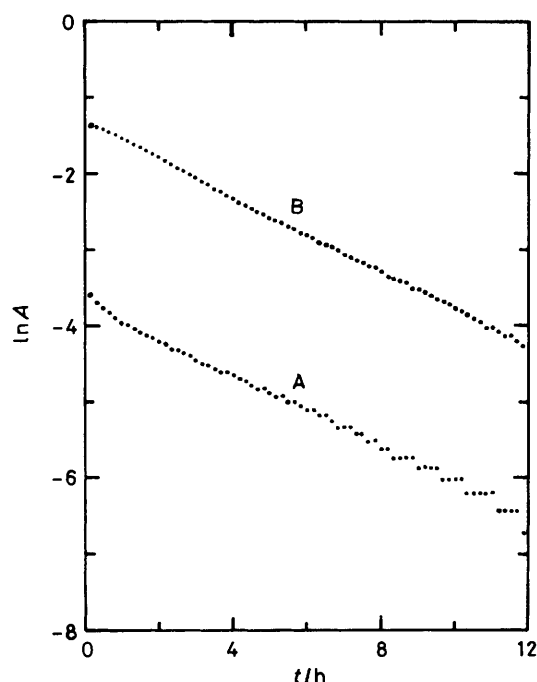
**Figure 1.** Absorption spectrum of mixed monolayers ( $2 \times 60$ ) of HV and AA (1:4) after excitation ( $>365$  nm) *in vacuo* at  $20^\circ\text{C}$  for 10 min. A sample of non-irradiated monolayers was used as a reference.

Photochromic systems employing monolayer assemblies have recently attracted much interest in view of their promising applicability in high-density optical memories. The photochromism in all compounds reported so far involves changes of chemical bonds such as heterolytic cleavage of a pyran ring in spiropyrans or *cis-trans* isomerization in azobenzenes.<sup>6</sup> These reactions might limit the thermal or cyclic stability and the response time for the photochromism. Excitation of solid 4,4'-bipyridinium salts by u.v. light was reported to show photochromism.<sup>7</sup> U.v. irradiation of 4,4'-bipyridinium ion is not necessarily appropriate, since it would lead to undesirable side reactions.<sup>8</sup>

We now report a novel system in which we have accomplished photochromism due only to electron transfer *via* the excited ion-pair C.T. complex of 4,4'-bipyridinium ion with TFPB<sup>-</sup> in monolayer assemblies without exciting both component ions.

The pale yellow *N,N'*-dihexadecyl-4,4'-bipyridinium (TFPB<sup>-</sup>)<sub>2</sub> salt (HV) was prepared from the corresponding bromide and Na<sup>+</sup>TFPB<sup>-</sup>. A 1:4 mixture of HV and arachidic acid (AA) was deposited using the Langmuir-Blodgett technique at  $13^\circ\text{C}$  and  $20\text{ mN m}^{-1}$  on a quartz plate for u.v.-visible measurements or on a poly(ethylene-terephthalate) film (0.1 mm thick) for e.s.r. and X-ray analyses from an aqueous subphase containing 0.25 mM CdCl<sub>2</sub> and 0.05 mM NaHCO<sub>3</sub> (pH 6.3). The deposition ratio was almost unity during 30 deposition cycles. The small-angle X-ray scattering of mixed monolayer assemblies gave sharp diffraction patterns up to 7th order. The observed spacing of  $54.6 \pm 0.6 \text{ \AA}$  coincided with that of cadmium arachidate monolayers within experimental error. These results indicated that mixed monolayers of HV and AA were deposited as a well-defined Y-type film. Microcrystals of *N,N'*-dimethyl-4,4'-bipyridinium (TFPB<sup>-</sup>)<sub>2</sub> salt were prepared on a quartz plate from 1,2-dimethoxyethane solution by evaporation. These samples were irradiated *in vacuo* or in Ar using 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 C.T. absorption band alone.<sup>3</sup>

Upon irradiation the colour of the monolayer assemblies changed from pale yellow to blue and the u.v.-visible spectrum characteristic of 4,4'-bipyridinium cation radical monomer<sup>9</sup> was observed (Figure 1). No indication of dimer formation between 4,4'-bipyridinium cation radicals in monolayer assemblies was found (Figure 1). A broad singlet e.s.r.



**Figure 2.** Time-dependence of  $\ln(\text{absorbance})$  at 605 nm at  $20^\circ\text{C}$  for (A) mixed monolayers and (B) microcrystals irradiated under the same conditions as in Figure 1.

spectrum ( $g$  2.003,  $\Delta H_{\text{msl}}$  14.5 G) was observed upon irradiation of monolayer assemblies, which coincided with the calculated spectra of 4,4'-bipyridinium cation radicals using a component width of 2.5 G ( $G = 10^{-4}\text{ T}$ ). These results indicated the photoinduced electron transfer from TFPB<sup>-</sup> to 4,4'-bipyridinium ion<sup>1,5</sup> and also the homogeneous dispersion of HV in a matrix of AA.

Coloured species photogenerated in mixed monolayer assemblies reversibly decayed as already reported for similar salts in solution or microcrystals.<sup>1,5</sup> Formation of a blue colour by irradiation and thermal fading in monolayer assemblies were repeated many times without formation of by-products.

The time-dependencies of the absorbance at 605 nm monitored by a microcomputer every 10 min for (A) mixed monolayer assemblies and (B) microcrystals at  $20^\circ\text{C}$  are shown in Figure 2. These results show that the decay of coloured species was almost exponential in both systems with a similar lifetime [ $\tau_{1/e}$  (A) 4.3 h and (B) 4.0 h]. The e.s.r. spectrum of photogenerated 4,4'-bipyridinium cation radicals also showed similar thermal decay. The steady and reversible charge separation between 4,4'-bipyridinium ion and TFPB<sup>-</sup> found in solution or microcrystals<sup>1,5</sup> was mainly due to the extraordinary bulk and chemical stability<sup>4</sup> of TFPB<sup>-</sup>. Such specific properties of TFPB<sup>-</sup> are most likely responsible for the photochromism in the present system. The microenvironment around charge-separated species in mixed monolayer assemblies of HV and AA was deduced to be similar to that in microcrystals from Figure 2.

Efforts are being made to control the molecular orientation of the photochromic 4,4'-bipyridinium ion in monolayer assemblies.

We thank Prof. M. Hayashi, Kyushu University for the use of an e.s.r. spectrometer, and the Center of Advanced Instrumental Analysis, Kyushu University, for the X-ray analysis. This work was partly supported by a Grant-in-Aid on

Special Project Research from the Ministry of Education, Science and Culture, Japan (61300011, 62213025). Partial support by the Mazda Foundation is also acknowledged.

Received, 14th March 1988; Com. 8/00998H

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