Control of Molecular Orientation of 4,4′-Bipyridinium Cation Radicals in Novel Photochromic Monolayer Assemblies

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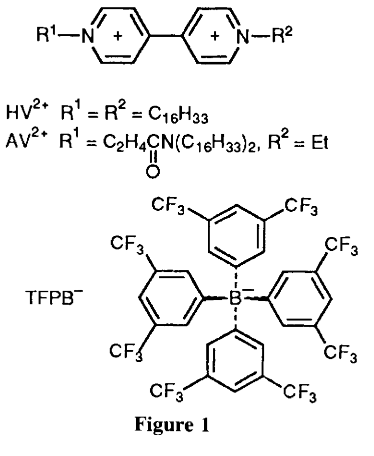
The orientation of 4,4′-bipyridinum cation radicals, reversibly formed in novel photochromic monolayer assemblies of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salts with *N,N′*-dihexadecyl-4,4′-bipyridinium and *N*-ethyl-*N′*-(2-ethylamide)-*N″, N″*-dihexadecyl-4,4′-bipyridinium ions *via* excitation of an ion-pair charge-transfer (CT) band ($\lambda_{ex.}$ >365 nm), was controlled by the substituents of the 4,4′-bipyridinium ion.

Recently we found the very specific formation of an ion-pair charge-transfer (CT) complex[1,2] of 4,4′-bipyridinium salts with the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion ($TFPB^-$)[3] in organic solutions. The persistent and reversible formation of 4,4′-bipyridinium cation radicals was achieved by these salts in the solid state[4—6] or in organic solutions[7] *in vacuo* or in Ar upon excitation of a CT band. Very recently we have reported a novel photochromic monolayer assembly system[8,9] in which we achieved photochromism due only to electron transfer *via* the excited ion-pair CT complex of the 4,4′-bipyridinium ion with $TFPB^-$. The photochemical colouring and thermal fading was highly reversible in all systems.[4—9]

We now report, for the first time, that the molecular orientation of 4,4′-bipyridinium cation radicals was controlled in monolayer assemblies by the substituents on these ions. 4,4′-Bipyridinium ions have attracted much attention as a basis for electrochromic display or photoelectrochromic memory systems and their molecular orientation is an important property to be controlled. However the only study, to our knowledge, on the orientation of 4,4′-bipyridinium cation radicals was made by Bewick *et al.*[10] during electrochemical deposition at an electrode.

Pale yellow salts of *N,N′*-dihexadecyl-4,4′-bipyridinium($TFPB^-$)$_2$ (HV) and *N*-ethyl-*N′*-(2-ethylamide)-*N″*, *N″*-dihexadecyl-4,4′-bipyridinium($TFPB^-$)$_2$ (AV) were prepared from the corresponding bromide salts and Na^+TFPB^-. The structure of these compounds is shown in Figure 1. A 1 : 4 mixture of HV or AV and arachidic acid (AA) was deposited at 18 °C and 20 mN m^{-1} on a quartz plate for UV-VIS or on a poly(ethyleneterephthalate) film (0.1 mm thick) for ESR measurements, from an aqueous subphase containing 0.25 mM $CdCl_2$ and 0.05 mM $NaHCO_3$ (pH 6.3). The deposition ratio was almost unity during 30 deposition cycles for both mixed monolayers. These samples were irradiated *in vacuo* by a Hamamatsu 150 W Xe-Hg lamp equipped with a Toshiba L-39 cut-off filter (λ >365 nm) and a 10 cm water filter to excite their CT absorption band alone. The incident angle dependences of both s- and p-polarized absorption for photogenerated 4,4′-bipyridinium cation radicals were measured *in vacuo* together with the polarization angle dependence at normal incidence. The ESR spectra were measured with varying the angle between the film plane and the static magnetic field.



HV^{2+} $R^1 = R^2 = C_{16}H_{33}$

AV^{2+} $R^1 = C_2H_4C(=O)N(C_{16}H_{33})_2$, $R^2 = Et$

Figure 1

Upon irradiation the colour of both monolayer assemblies (HV/AA and AV/AA) changed from pale yellow to blue. A UV-VIS absorption spectrum characteristic of the 4,4′-bipyridium cation radical monomer[11] was observed together with a broad single line ESR spectrum. The ESR spectra showed little anisotropy upon rotation of the dipping direction in the HV/AA system. The spectral width for the magnetic field parallel to the film plane of AV/AA monolayer assemblies was larger by about 6% than that with the magnetic field perpendicular. It was, however, difficult to get detailed information from ESR spectra on the orientation of 4,4′-bipyridinium cation radicals in monolayer assemblies due to the broad single line pattern. Homogeneous dispersion of HV and AV cation radicals in a matrix of AA was indicated from the UV-VIS and ESR spectra.

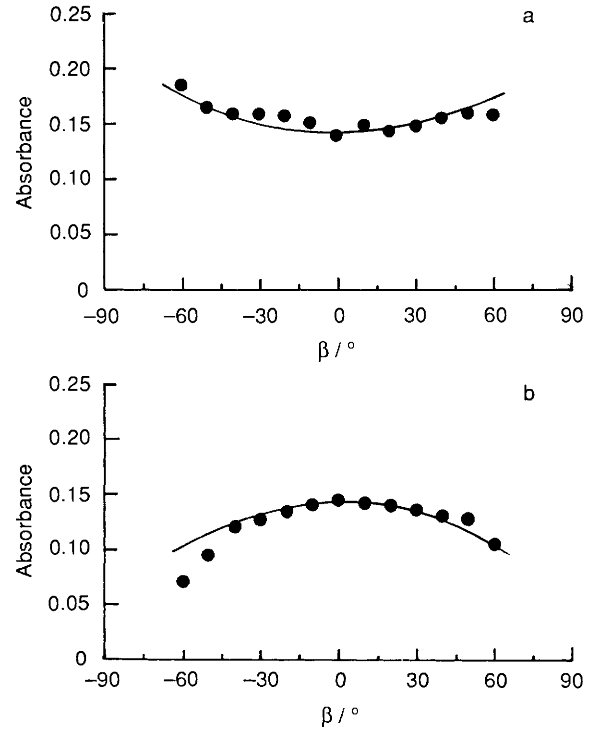


Figure 2. Incident angle (β) dependences of p-polarized absorption of 4,4′-bipyridinium cation radicals for (a) HV/AA and (b) AV/AA mixed monolayer assemblies. (●) Observed data corrected for the decay and optical path length. (—) Represents a calculated dependence. See text for details.

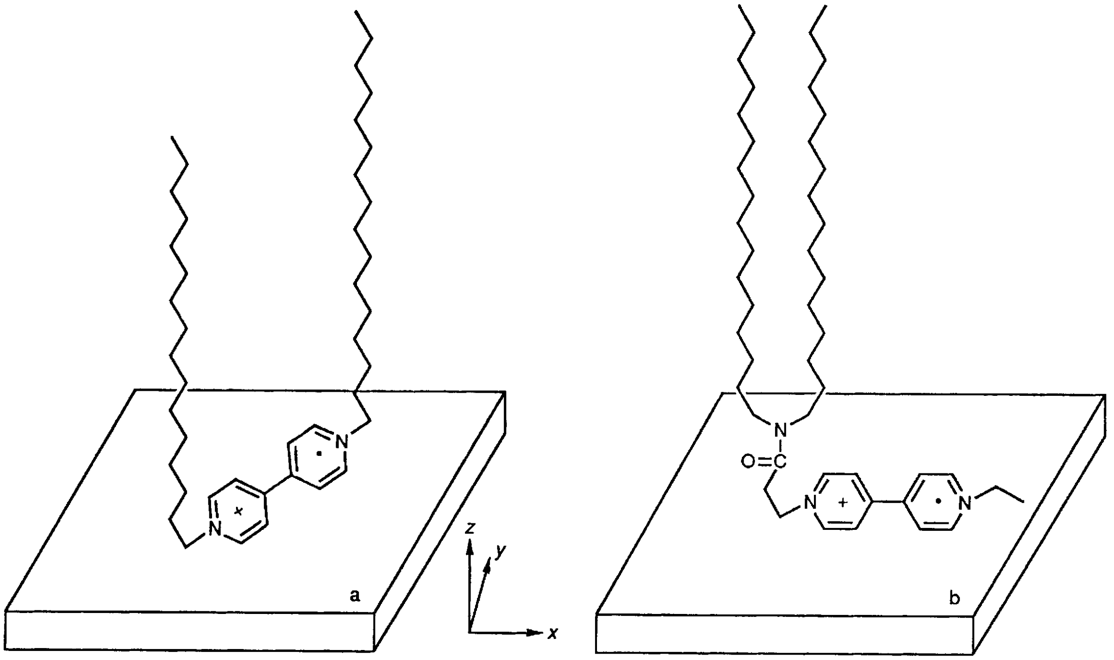


Figure 3. Schematic representation of the orientation of 4,4′-bipyridinium cation radicals in (a) HV/AA and (b) AV/AA mixed monolayer assemblies in the co-ordinate system, *xy*, the substrate surface, *z*, its normal. Counter anions (TFPB$^-$) and arachidic acid are not shown for simplicity.

Coloured species photogenerated in mixed monolayer assemblies of AV/AA, decayed reversibly and exponentially in the dark as already reported for a HV/AA system.[8,9] Corrections for such thermal decay of 4,4′-bipyridinium cation radicals and the optical path length at a given incident angle were made on observed angular dependences. The latter correction cannot be made by the incident angle β to a quartz plate due to reflection. It was made from the apparent dependence of s-polarized absorption on the incident angle, as reported previously,[12] after making corrections for thermal decay. The estimated correction factor cos β' was smaller than cos β. No polarization angle dependence was observed for both 4,4′-bipyridinium cation radicals in monolayer assemblies of AV/AA and HV/AA at normal incidence. This result indicated that the projection of transition moments of 4,4′-bipyridinium cation radicals was statistically distributed in the film plane.

The incident angle dependences of p-polarized absorbance at 400 nm are shown in Figure 2 for (a) HV/AA and (b) AV/AA monolayer assemblies. Closed circles show the observed data after correction for decay and optical path length. It is clearly indicated that two 4,4′-bipyridinium monolayer assemblies showed contrary dependences on the incident angle. The p-polarized absorption of 4,4′-bipyridinium cation radicals showed a minimum in a HV/AA system and a maximum in a AV/AA system at normal incidence. These results indicate that the angle between the surface normal and the molecular axis of 4,4′-bipyridinium cation radicals is smaller or larger than the magic angle (54.7°) in HV/AA and AV/AA systems, respectively. The solid line represents a calculated dependence evaluated from the corrected data. In these calculations transition moments are assumed to be distributed making angles between ϕ_1 and ϕ_2 from the surface normal.[12] From these results the following distribution is evaluated; $45 < \phi < 47°$ for HV/AA and $89 < \phi < 90°$ for AV/AA systems, respectively. In other words, 4,4′-bipyridinium cation radicals lie flat in AV/AA and oblique by about 46° in HV/AA monolayer assemblies as shown in Figure 3. It can be concluded that the molecular orientation of 4,4′-bipyridinium cation radicals was controlled in monolayer assemblies by the substituents on the 4,4′-bipyridinium ion.

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