

Specific Formation of Ion-pair Charge-transfer Complex and Photoinduced Electrochromism

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4, 4'-Bipyridinium salts with tetrakis [3, 5-bis(trifluoromethyl)-phenyl] borate anion (abbreviated to TFPB⁻) showed an ion-pair charge-transfer (CT) absorption above 350 nm and broad structureless CT fluorescence with a maximum at 525 nm. The CT absorbance and fluorescence intensity in 1, 2 dimethoxyethane (DME) increased very gradually to the equilibrium values. The excitation of a CT band in oxygen-free atmosphere resulted in the quenching of CT fluorescence accompanied by remarkable colour change from pale yellow to blue due to the accumulation of 4, 4'-bipyridinium radical cations by the photoinduced electron transfer reaction from TFPB⁻ to 4, 4'-bipyridinium ion.

The change of CT fluorescence intensity and colour were repeated reversibly in TFPB⁻ salts, whereas usual tetraphenylborate (TPB⁻) salts of 4, 4'-bipyridinium ion showed irreversible changes due to oxidative decomposition of TPB⁻. 4, 4'-Bipyridinium radical cations decayed thermally and almost exponentially with lifetime dependent on the temperature and microenvironment.

The decay in microcrystals or LB films was about 10-times faster than in polymer films and about 10-times slower than in solutions. The observed steady and reversible photoinduced electrochromism was attributed to the extraordinary bulkiness and chemical stability of TFPB⁻. These results demonstrated that 4, 4'-bipyridinium TFPB⁻ salts will be applied to photon-mode optical memory which can be read either with absorption or emission.