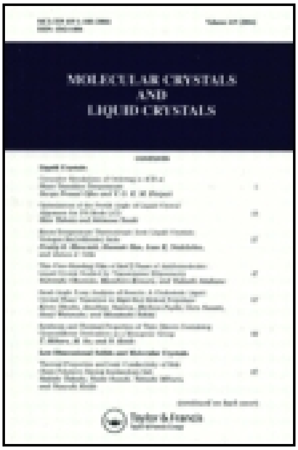

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Ultrafast Absorption Changes Both in the Visible and Near- Infrared Regions Due to Photoinduced Electron Transfer Reactions of Dicyanovinylstyrylpyridinium Tetraphenylborate

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Ultrafast Absorption Changes Both in the Visible and Near- Infrared Regions Due to Photoinduced Electron Transfer Reactions of Dicyanovinylstyrylpyridinium Tetraphenylborate

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Ultrafast dynamics of photoinduced electron transfer reaction and dimer radical cation formation of ion pair charge transfer complexes between dicyanovinylstyrylpyridinium cation and tetraphenylborate anion were studied at room temperature in less polar solvents by femtosecond laser flash photolysis. Transient absorptions were observed both in the visible and near-infrared regions. They showed very rapid rise in less than one picosecond, which was limited by the time resolution of our flash photolysis system.

Keywords: photoinduced electron transfer; dimer radical cation; charge resonance band; femtosecond laser flash photolysis

INTRODUCTION

The charge resonance (CR) band is characterized by the absorption spectrum in the near-infrared region owing to the splitting of the energy levels of both the ground and the excited states by the electronic interaction between two chromophores of dimer radical cations. The CR bands had been observed for the electronic interactions between neutral molecules and radical cations formed by γ-radiolysis and pulse radiolysis in rigid matrices at or near 77 K, and by nanosecond laser flash photolysis and nanosecond pulse radiolysis at room temperature in solutions.

We reported, for the first time, the CR band at room temperature upon steady photoexcitation of styrylpyridinium tetraphenylborate (TPB^-) in 1,2-dimethoxyethane (DME) solution as a result of electronic interaction between a photogenerated styrylpyridinyl radical and an styrylpyridinium cation.[1-6] We now report the results from femtosecond (fs) laser photolysis on the radical formation and charge resonance interaction by photoinduced electron transfer reactions in dicyanovinylstyrylpyridinium salts.

EXPERIMENTAL

1-Hexadecyl-4-(4'-dicyanovinyl)styrylpyridinium bromides (DCS^+) were synthesized according to the similar method reported previously.[4] Counter ions of dicyanovinylstyrylpyridinium bromide salts were exchanged with tetraphenylborate (TPB^-) in methanol to obtain yellow crystals of DCS^+TPB^- salts. Details of the femtosecond laser photolysis system were reported previously.[6]

RESULTS AND DISCUSSION

DCS^+TPB^- salts exhibited ion-pair charge-transfer (IPCT) absorption as an extended tail above about 450 nm in less polar solvents such DME due to the electronic interaction at the ground state between TPB^- anion as a donor and DCS^+ cation as an acceptor.[4] The time profiles of transient absorption at both 650 nm and 960 nm, corresponding to the radical monomer and the CR band of the dimer radical cations, are shown in Figure 1(a) and (b) for DCS^+TPB^- in DME solution (0.5 mM) upon excitation with a femtosecond laser at 400 nm. Transient absorption at 650 nm showed a very rapid rise in less than 1 ps after excitation, which was limited by the time resolution of our measurement system. A dicyanovinylstyrylpyridinyl radical ($DCS^{\bullet}$) was thus formed in a sub-picosecond time scale by the photo-induced electron transfer from the donor (TPB^-) to the acceptor (DCS^+).

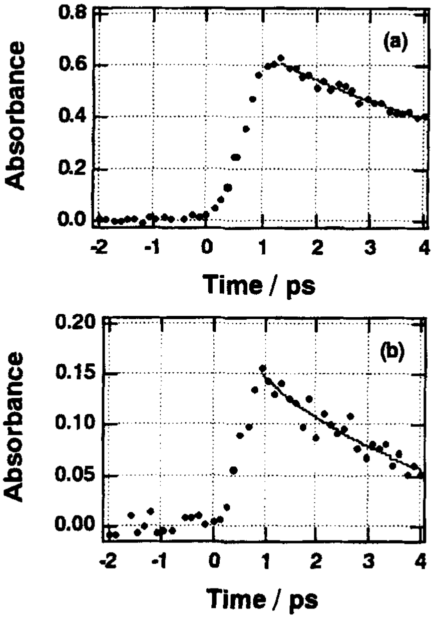

FIGURE 1. Time profile of transient absorption of DCS^+TPB^- in DME solution (0.5 mM), excited with a 400 nm fs laser pulse; (a) at 650 nm; (b) at 960 nm.

Figure 1(b) also showed a very rapid rise at 960 nm within less than 1 ps, which was as fast as the photoinduced electron transfer shown Figure 1(a). From ultrafast rise of transient absorption at 960 nm, it is further indicated that dimer radical cation formation occurred very rapidly in almost the same time scale as radical formation itself. The very fast rise of the CR band strongly suggests that the electronic interaction between the photogenerated dicyanovinylstyrylpyridinyl radical and the dicyanovinylstyrylpyridinium cation occurred without a diffusion process. A similar very fast rise was observed for the nitro-substituted styrylpyridinium salts.[6]

Neither spectral shift nor broadening was observed for the absorption spectra of DCS^+TPB^- in DME solutions (0.05-5.0 mM) before excitation, which clearly indicated that DCS^+ chromophores did not make any intermolecular electronic interactions before photoinduced electron transfer. The MM2 calculation for two pairs of DCS^+TPB^-, in which each ion was optimized by MOPAC calculations, gave the optimized geometry that two DCS^+ are located in a face-to-face manner separated by 0.57 nm. The electronic interactions between positively charged DCS^+ cations are hardly expected at such a distance, which is the case as mentioned above. The positive charge of one DCS^+ molecule is neutralized when photoinduced electron transfer from TPB^- to DCS^+ occurs upon excitation. Then the Coulombic repulsion disappears and the CT interaction will work between the $DCS^\bullet$ radical as the donor and the DCS^+ ion as the acceptor as a driving force to decrease the mutual distance between them. These situations will contribute to a very fast rise of the CR band observed in the present study. Diffusionless intermolecular electron transfer was also reported to occur from the butyl(tris-*p*-*tert*-butylphenyl)borate anion to an excited *N*,*N'*-diethyl-2,2'-cyanine cation, which self-associated as ion pairs, in a non-polar solution.[7]

The transient absorption in the visible region for DCS^+TPB^- was reported previously.[6] The time profile at 650 nm was composed of a fast decay component ($\tau_{1/e}$ = 3.8 ps) and a slow decay one ($\tau_{1/e}$ = 17.4 ps). The fast and slow components were attributed to the back electron transfer reactions from the dimer radical cation and the monomer radical, respectively.[6] The very fast decay ($\tau_{1/e}$ = 1.3 ps) was also observed at 580 nm, which was attributed to the excited singlet DCS^+.[6]

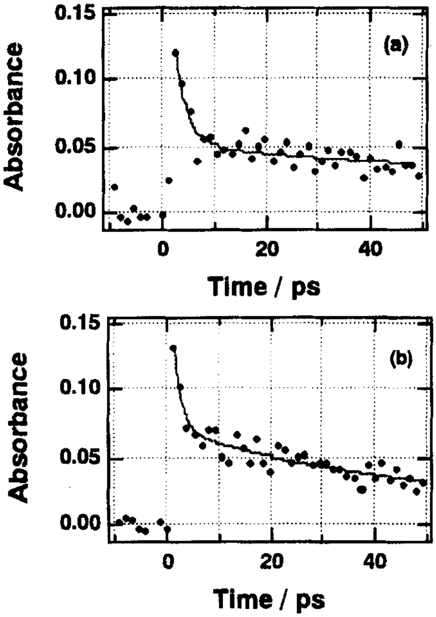

FIGURE 2. Time profile of transient absorption of $DCS^{+}TPB^{-}$ in DME solution (0.5 mM), excited with a 400 nm fs laser pulse; (a) at 960 nm; (b) at 1050 nm.

From steady state ESR and near-infrared absorption measurements, two broad absorptions with peaks at 1050 nm and 1120 nm were attributed to the CR band of dimer radical cations and the charge transfer (CT) band of dicyanovinylstyrylradical dimers, respectively.[4] The time profiles of transient absorption at 960 nm and 1050 nm of $DCS^{+}TPB^{-}$ in DME solution (0.5 mM) are shown in Figure 2(a) and (b). The transient absorption at 960 nm was composed of a fast decay component ($\tau_{1/e}$ = 3.2 ps) and a very long lived one. The transient absorption at 1050 nm was composed of a fast decay component ($\tau_{1/e}$ = 2.8 ps) and a slow decay one ($\tau_{1/e}$ = 57.4 ps). The fast components were attributed to the back electron transfer reaction from the dimer radical cation to the oxidized $TPB^{\bullet}$.[6] The very long lived component corresponded to the dimer radical cation observed by steady photolysis due to oxidative decomposition of TPB^{-}.[6] From these results, the slow decay component ($\tau_{1/e}$ = 57.4 ps) corresponded to the CT band of dicyanovinylstyrylradical dimers, since their steady state absorption was extended below 1050 nm. The slow decay was most probably due to the back electron transfer reaction from the radical dimer to the oxidized $TPB^{\cdot}$.

CONCLUSION

Transient absorption of both radicals and dimer radical cations (CR band) showed a very rapid rise in less than 1 ps in $DCS^{+}TPB^{-}$ salts. The present study will contribute to develop ultrafast response materials using the visible and the near-infrared light.

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