

## First Charge Resonance Band observed by Steady Photolysis at Room Temperature in Solution

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The steady excitation of an ion-pair charge-transfer band of 1-octadecyl-4-(4-nitrostyryl)pyridinium tetraphenylborate formed a fairly stable 1-octadecyl-4-(4-nitrostyryl)pyridinyl radical accompanying, for the first time, a charge resonance band owing to its interaction with a parent cation at room temperature in organic solutions.

We have been studying photochemical and photophysical properties of ion-pair charge-transfer (IPCT) complexes.<sup>1-13</sup> By the use of tetrakis[3,5-bis(trifluoromethyl)phenyl] borate anion (TFPB<sup>-</sup>) as a counter ion of 4,4'-bipyridinium ions, we have achieved novel photochromism due only to the photo-induced electron transfer and thermal reverse reactions in organic solutions and in polymer or Langmuir-Blodgett films.<sup>1-12</sup> Very recently we have also reported novel second harmonic generation from IPCT complexes and its photochemical control using substituted styrylpyridinium salts.<sup>13</sup>

We now report, that the charge resonance (CR) band due to the electronic interaction between a photogenerated radical and a parent cation of substituted styrylpyridinium was observed at room temperature in organic solutions by steady photolysis. The CR band is characterized by the absorption spectrum in the near-IR region owing to the splitting of the energy levels of the ground and excited states by the electronic interaction between two groups of dimer radical cations.<sup>14</sup> Dimer radical cations have been studied by electron spin

resonance (ESR)<sup>15</sup> and optical absorption.<sup>14</sup> The CR band has been observed for dimer radical cations formed by  $\gamma$ -radiolysis<sup>14,16</sup> and pulse radiolysis<sup>17,18</sup> in rigid matrices at or near 77 K, and by nanosecond laser flash photolysis<sup>19-24</sup> at room temperature in solution. All these dimer radical cations were formed between neutral parent molecules (M) and radical cations (M<sup>+</sup>) generated from M.<sup>14-24</sup> Itoh reported the intramolecular association in pyridinyl radical and pyridinium cation in the cation radicals of bis(4-methoxycarbonylpyridinium iodides) with tri- and tetra-methylenes in solution at room temperature.<sup>25</sup> The broad new absorption at 430-450 nm was not assigned to the CR band.<sup>25</sup>

1-Octadecyl-4-(4-nitrostyryl)pyridinium (SP<sup>+</sup>) bromide was synthesized according to the similar method reported previously.<sup>13</sup> Counter ion was exchanged with tetraphenylborate (TPB<sup>-</sup>) using Na<sup>+</sup>TPB<sup>-</sup> to obtain pale-yellow crystals of an SP<sup>+</sup>TPB<sup>-</sup> salt. The SP<sup>+</sup>TPB<sup>-</sup> salt exhibited IPCT absorption spectra as an extended tail above *ca.* nm in 1,2-dimethoxyethane (DME). The photoreaction upon excitation of deaer-

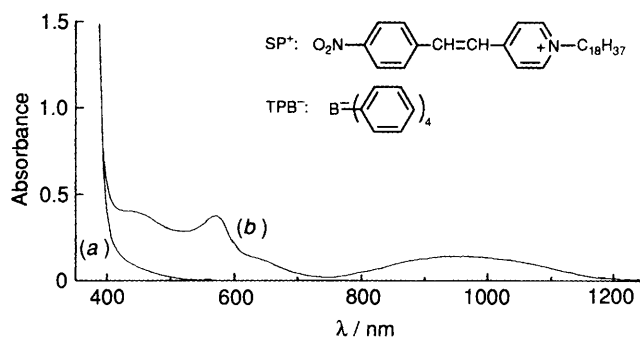


Fig. 1 Absorption spectra of a  $0.5 \text{ mmol dm}^{-3}$  DME solution of  $\text{SP}^+\text{TPB}^-$  (a) before and (b) after irradiation ( $\lambda_{\text{ex}} > 365 \text{ nm}$ ) for 1 min at room temp. The insert shows the structures of  $\text{SP}^+$  and  $\text{TPB}^-$ .

ated DME solutions ( $1 \times 10^{-5} \sim 4 \times 10^{-3} \text{ mol dm}^{-3}$ ) of  $\text{SP}^+\text{TPB}^-$  salt with a Hamamatsu 150 W Xe-Hg lamp through an L-39 cut-off filter ( $\lambda_{\text{ex}} > 365 \text{ nm}$ ) and an IR-cut-off filter was monitored by a Shimadzu UV-3100 UV-VIS-NIR recording spectrophotometer and a JEOL JES-FE-1X ESR spectrometer at room and low temperatures.

Upon excitation the colour of DME solutions first changed from pale-yellow to pink or pale-red. Fig. 1 shows the absorption spectra of a  $0.5 \text{ mmol dm}^{-3}$  DME solution of  $\text{SP}^+\text{TPB}^-$  (a) before and (b) after irradiation for 1 min at room temperature. New absorptions were observed both in the visible and near-IR region. Prolonged irradiation and/or storage in the dark caused further colour changes, which will be reported elsewhere in detail. The difference spectra relative to the absorption before irradiation are shown in Fig. 2 for a  $0.5 \text{ mmol dm}^{-3}$  DME solution after three different irradiation times. The absorption in the visible region had two peaks at about 450 and 570 nm, while that in the near-IR region showed a peak at 950 nm. Contrary to the increase of absorbance in the visible region from (b) to (c) in Fig. 2, the absorbance of the near-IR band remained almost constant during irradiation for another 1 min. This suggests further reaction from the species that shows the near-IR band, as indicated by the increase of absorption near 650 nm. ESR spectra were also observed upon IPCT excitation as shown in Fig. 3 for a  $4 \text{ mmol dm}^{-3}$  DME solution irradiated at  $20^\circ\text{C}$ , which were composed of more than 15 lines. The yield of radicals was smaller at low temperatures ( $-30 \sim -55^\circ\text{C}$ ). A  $0.02 \text{ mmol dm}^{-3}$  solution in DME showed similar absorptions both in the visible and near-IR regions. Further dilute  $0.01 \text{ mmol dm}^{-3}$  solution showed a visible absorption alone.

Görner observed a transient absorption having peaks at 450–460 and 570–580 nm with a lifetime of 10  $\mu\text{s}$  upon excitation of 1-methyl-4-(4-nitrophenyl)pyridinium iodide at 353 nm and  $25^\circ\text{C}$  in solvents of moderate polarity.<sup>26</sup> He assigned it to the substituted (4-nitrophenyl)pyridinyl radical on the basis of flash photolysis and pulse radiolysis.<sup>26</sup> He also reported an absorption at  $>760 \text{ nm}$ , but did not mention its origin.<sup>26</sup> The absorption spectrum observed in the visible region in our system is thus unambiguously assigned to 1-octadecyl-4-(4-nitrophenyl)pyridinyl radical which was formed by the photoinduced electron transfer from  $\text{TPB}^-$  via the excited IPCT complex. This radical was fairly stable and was observed for about 1 h at room temperature. The reverse electron transfer reaction to oxidized  $\text{TPB}^-$  is prohibited, because  $\text{TPB}^-$  is known to decompose after one-electron oxidation.<sup>27</sup>

The absorption spectrum in the near-IR region with a peak at about 950 nm was most probably attributed to the CR band due to the electronic interaction between a photogenerated, fairly stable, 1-octadecyl-4-(4-nitrophenyl)pyridinyl radical and its parent cation from the following reasons. First, this band is broad and extends upto about 1250 nm. Most CR bands of dimer radical cations of aromatic molecules are known to have

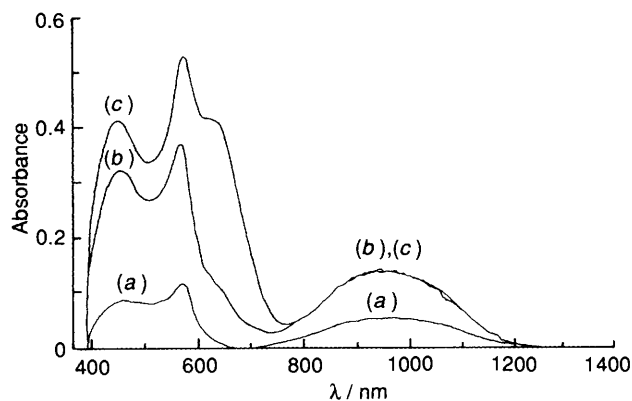


Fig. 2 The difference spectra for a  $0.5 \text{ mmol dm}^{-3}$  DME solution after irradiation for (a) 10 s, (b) 1 min and (c) 2 min at room temperature. The spectrum before irradiation was used as a reference.

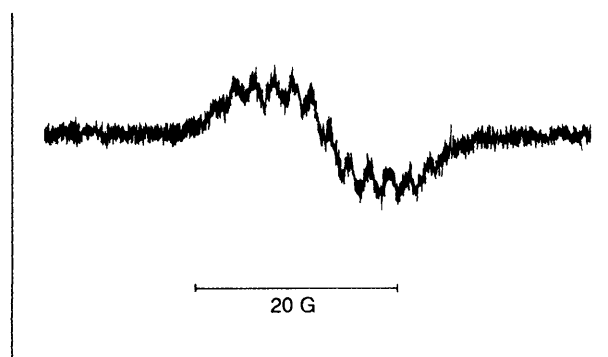


Fig. 3 The ESR spectrum of a  $4 \text{ mmol dm}^{-3}$  DME solution irradiated at  $20^\circ\text{C}$  for 20 min

a peak at  $900 \sim 2000 \text{ nm}$  depending on their stabilization energy.<sup>16–24</sup> The wavelength of the near-IR band observed in the present experiment corresponds with that (930–935 nm) of a CR band of a benzene dimer radical cation.<sup>17</sup> Secondly, in very dilute solutions ( $< 1 \times 10^{-5} \text{ mol dm}^{-3}$ ) the band in the near-IR region was not observed, while the absorption in the visible region due to the radical itself was observed as mentioned above. This result strongly suggested that the near-IR band was caused by the intermolecular interactions. Thirdly, the near-IR band was observed as long as 1-octadecyl-4-(4-nitrophenyl)pyridinyl radicals survive, but showed different time dependence.

The stabilization energy  $\Delta H$  is known to be roughly equal to half the energy of the observed CR transition. The value of  $\Delta H$  estimated from the peak wavelength (950 nm) is  $15.0 \text{ kcal mol}^{-1}$  ( $1 \text{ cal} = 4.184 \text{ J}$ ). This value is larger than those ( $8\text{--}10 \text{ kcal mol}^{-1}$ ) of fused aromatics such as pyrene,<sup>22–24</sup> and is comparable to that of benzene dimer radical cation.<sup>17</sup> The stabilization energy is determined by the attractive charge-transfer interaction together with the electronic and steric overlap repulsive forces. The molecular structures of both cation and radical forms of 1-octadecyl-4-(4-nitrophenyl)pyridinium are shown to be planar from MOPAC calculations. Higher stabilization of our system can be expected from such long and planar structures with extensive charge delocalization which favour the electronic interaction between an electron-withdrawing parent styrylpyridinium cation and an electron-donating neutral radical. Stronger tendency of the association of styrylpyridinium molecules was also shown from the spectral changes in the dark as mentioned above.

These results indicate that the near-IR band observed at room temperature in DME solutions upon steady photolysis is the CR band due to the electroic interaction between photogenerated styrylpyridinyl radical and its parent cation.

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