Specific intramolecular electronic interactions of a photogenerated styrylpyridinyl radical and a parent cation in *meso*-2,4-bis-(4-(4-nitrostyryl)pyridiniumyl)pentane

Sang Hyun Park,[a] **Hideki Kawai**[b] **and Toshihiko Nagamura**[a,b]

[a] *Department of Electronic Materials Science, The Graduate School of Electronic Science and Technology, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432-8011, Japan*
[b] *Molecular Photonics Laboratory, Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432-8011, Japan*

Received (in Cambridge, UK) 24th October 2001, Accepted 5th December 2001

Steady state photolysis of tetraphenylborate salts of *meso*-2,4-bis(4-(4-nitrostyryl)pyridiniumyl)pentane and 1,3-bis(4-(4-nitrostyryl)pyridiniumyl)propane has been studied by absorption and electron paramagnetic resonance (EPR) spectroscopy in solution at room temperature. The absorption spectra of these compounds upon irradiation at 405 nm in an inert atmosphere showed a strong peak in the visible region and two broad peaks in the near infrared (NIR) region. The *meso*-2,4-pentane derivative caused stronger electronic interaction between a photogenerated styrylpyridinyl radical and a parent styrylpyridinium cation, and hence showed two slightly blue shifted NIR bands around 920 and 1734 nm compared with those in the 1,3-propane derivative. During storage in the dark, the NIR absorption peak at longer wavelength gradually changed its shape and showed a new band at 1559 nm, which increased until 20 h and was maintained over 100 h. The nature of electronic interactions responsible for such specific NIR bands was studied in detail spectroscopically. EPR spectra clearly indicated that the unpaired electron was not shared completely between two chromophores as in a normal dimer radical cation but was exchanged rather rapidly between them, probably due to the conformational confinement at one end of these molecules.

Introduction

The charge resonance (CR) band, which is formed by splitting of the energy levels of both the ground and the excited states resulting from the electronic interaction between two chromophores forming dimer radical cations, had been observed for intermolecular and intramolecular dimer radical cations formed by steady photolysis at very low temperature, and by nanosecond (ns) laser flash photolysis and ns pulse radiolysis at room temperature in solution.[1–12]

Yamamoto and co-workers studied the intramolecular CR bands by ns laser photolysis for carbazole, pyrene, naphthalene, anthracene and phenanthrene.[3–13] They observed the CR bands between 1050 and ~2000 nm in transient absorption spectra. The peak wavelength of the CR bands depended on the nature of the chromophores and the geometrical configuration between them. F. C. de Schryver *et al.* also reported that the dimer radical cations of *meso*- and *rac*-2,4-dicarbazol-9-ylpentane (*m*- and *r*-DCzPe) upon ns laser photolysis were in a fully and a partially overlapped conformation, respectively. The shorter wavelength band observed in *m*-DCzPe was associated with a greater overlap of chromophores and a larger stability than *r*-DczPe.[13,14]

The study of dimer radical cation formation in bichromophoric compounds bridged with propane has been an active research area because two aromatic chromophores can take a favorable conformation for intramolecular interaction between π-orbitals of both chromophores, as shown first by Hirayama for excimer formation.[15]

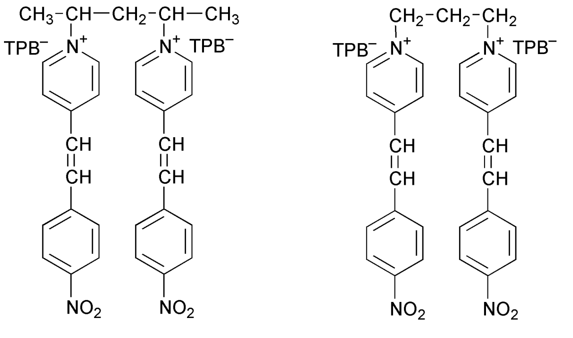
We reported, for the first time, the CR band of 1-alkyl-4-(4-nitrostyryl)pyridinium (NS^+) tetraphenylborate (TPB^-) formed upon steady photoexcitation in 1,2-dimethoxyethane (DME) solution at room temperature.[16] Their CR bands formed between a photogenerated nitrostyrylpyridinyl radical ($NS^\bullet$) and an unreacted nitrostyrylpyridinium cation (NS^+) showed a broad peak around 950 nm in the NIR region and were found to be markedly affected by the polarity of solvents, the structure of substituents at the *para*-position of the styryl group, the length of bridge, the geometrical configuration and so on.[16–27] We have also reported that transient absorption in both the visible and NIR regions showed a very rapid rise in less than 1 ps upon femtosecond laser excitation.[21]

More recently, we observed another stable dimer radical cation in 1,3-bis(4-(4-nitrostyryl)pyridiniumyl)propane bis(tetraphenylborate)s.[20] It showed two stable CR bands with peaks at 948 and 1742 nm upon steady photoexcitation in acetonitrile at room temperature. During storage in the dark, the former decayed monotonically, while the latter gradually changed its shape and showed a peak at 1505 nm after 3 h. Very recently we have briefly reported unusual electronic absorption changes in the 800–2200 nm region in *meso*-2,4-bis(4-(4-nitrostyryl)pyridiniumyl)pentane after photoirradiation.[27] The purpose of the present work is to elucidate the specific electronic interaction between radicals and parent cations formed by photoinduced electron transfer in *meso*-2,4-bis(4-(4-nitrostyryl)pyridiniumyl)pentane (*m*-SPPe) bis(tetraphenylborate)s (TPB^-). To clarify various factors affecting the intramolecular interaction, we made detailed studies on the absorption spectral changes and the EPR spectra by photoexcitation and during storage in the dark.

Results and discussion

Fig. 1(a) shows the difference absorption spectra of *m*-SPPe irradiated for 4 min in acetonitrile (ACN) (0.25 mM) through a band pass filter ($\lambda_{ex} = 405$ nm) at room temperature with respect to unirradiated *m*-SPPe. A main absorption peak was observed

DOI: 10.1039/b109705a



***m*-SPPe** **SPPr**

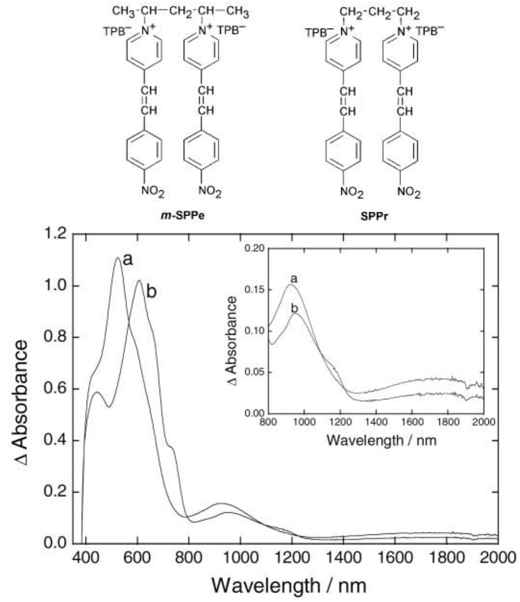


Fig. 1 Difference absorption spectra in the 350–2000 nm region after irradiating (a) *m*-SPPe and (b) SPPr in deaerated ACN solutions (0.25 mM) through a band pass filter (405 nm) for 4 min. The inset shows the enlarged spectra in the 800–2000 nm region. The structures of *m*-SPPe and SPPr are also shown.

at 342 nm for *m*-SPPe in ACN (0.02 mM) before irradiation. Upon irradiation, a new peak at 524 nm and two shoulders around 424 and 600 nm in the visible region were observed in addition to two broad peaks at 920 and at 1734 nm in the NIR region. These new absorption bands are most likely due to photogenerated radicals and their electronic interaction with parent cations, such as dimer radical cations according to eqn. (1)–(3) in comparison with similar results in SPPr.[20] But

$$SP^+\text{–}SP^+ + 2TPB^- \xrightarrow{h\nu} SP^+\text{–}SP^\bullet + TPB^\bullet + TPB^- \quad (1)$$

$$SP^+\text{–}SP^\bullet \longrightarrow \text{Intramolecular electronic interactions} \quad (2)$$

$$SP^+\text{–}SP^\bullet + SP^+\text{–}SP^+ \longrightarrow \text{Intermolecular electronic interactions} \quad (3)$$

the electronic state of photogenerated species observed in the present study is found to be slightly different from that in typical dimer radical cations, as discussed later in detail using EPR spectra. The intermolecular interaction such as dimer radical cation formation can be excluded by the fact that similar bichromophoric compounds bridged with butane or ethane did not show as strong an NIR absorption as *m*-SPPe and SPPr.

The band at 524 nm was assigned to the local excitation (LE) band of the dimer radical cation or radical monomer, as schematically shown in Fig. 2. It is considerably blue shifted compared with that at 607 nm in SPPr, as shown in Fig. 1(b). The blue shift strongly suggests that the angle between a transition dipole moment and a line connecting centers of two chromophores is larger than the magic angle (54.7°) as in H-aggregates. Such interaction can be more favorably formed in *m*-SPPe due to the presence of two methyl groups which are absent in SPPr.

From comparison of the NIR absorption bands with previous results[16–19] in similar *para*-substituted styrylpyridinium TPB^- upon photoexcitation, we attributed the NIR absorptions observed in bichromophoric compounds linked by a trimethylene bridge to the CR bands of intramolecular dimer radical cations.[20] The appearance of a CR band in the NIR region is due to interaction between the styrylpyridinium cation and its radical formed by photoinduced electron transfer from TPB^- to styrylpyridinium cation. The CR transition between the sub-levels is derived from splitting of HOMO (SOMO) and LUMO energy levels. The stabilization energy (ΔH) of the dimer radical cation is approximately equal to half the energy of the CR band as schematically shown in Fig. 2. The stabilization energy was evaluated as $\Delta H = 64.8$ kJ mol^{-1} at 920 nm and $\Delta H = 34.4$ kJ mol^{-1} at 1734 nm. On the other hand, both the radical monomer and the LE of the dimer radical cation contribute to the absorption in the visible region.

The shape, peak wavelength and/or intensity of the CR band are considerably influenced by the geometrical structure, stability of dimer radical cation, by the distance between two chromophores, temperature, solvent and so on. The absorption with a peak at 920 nm and the broader peak around 1734 nm in the NIR region were most probably attributed to the sandwich type conformation and partially overlapped peaks due to the intramolecular dimer radical cations, in a similar manner to that reported for SPPr.[20] The CR bands of *m*-SPPe showed stronger absorbance and slight blue shift compared with those of SPPr, indicating a more stable interaction of the dimer radical cation. The absorption spectra for SPPr irradiated for 4 min in ACN at room temperature showed similar intramolecular CR bands with peaks at 948 and 1742 nm and a new shoulder at about 1150 nm as shown in Fig. 1(b). The shoulder at about 1150 nm was assigned to the intermolecular dimer radical cation in comparison with the CR band observed in monochromophoric nitrostyrylpyridinium (NS^+) salts in ACN.[20,24] On the other hand, the intermolecular CR band at 1150 nm was not observed for *m*-SPPe. The two methyl groups in *m*-SPPe are presumed to be less favorable for intermolecular interaction. These results strongly suggested that the conformational confinement by the additional two methyl groups in *m*-SPPe greatly facilitated the the intramolecular CR band of the dimer radical cation.

F. C. de Schryver *et al.*[13] proposed that the TG/GT conformation (Fig. 3A) was most stable at room temperature among the nine conformations. (T and G stand for *trans* and *gauche* configuration, respectively.) M. Yamamoto *et al.*[8] also reported that the conformational change occurred from TG/GT to TT conformation upon laser flash photolysis of *m*-DCzPe at room temperature. The TT conformation formed the sandwich type dimer radical cation in *m*-DCzPe in which two chromophores interact most strongly as a donor (Cz) or an acceptor ($Cz^{+\bullet}$).[8] Similar conformational changes from the TG/GT form to the sandwich form (TT) and partially overlapped form are expected in *m*-SPPe upon photoinduced electron transfer for one of two pyridinium TPB^- salts at 2,4-positions of pentane to form the intramolecular dimer radical cation as shown in Fig. 3A. Structural models of the sandwich and partially overlapped forms of the intramolecular dimer radical cations formed upon photoexcitation of *m*-SPPe are shown in Fig. 3B. In the TT conformation, two chromophores can be arranged parallel to interact with each other fully in the sandwich eclipsed form (**I**), where the chromophore interaction becomes maximum. The structure of staggered sandwich form (**II**) can also show the full interaction with a small repulsive force between two chromophores. These conformations are expected to give the CR band

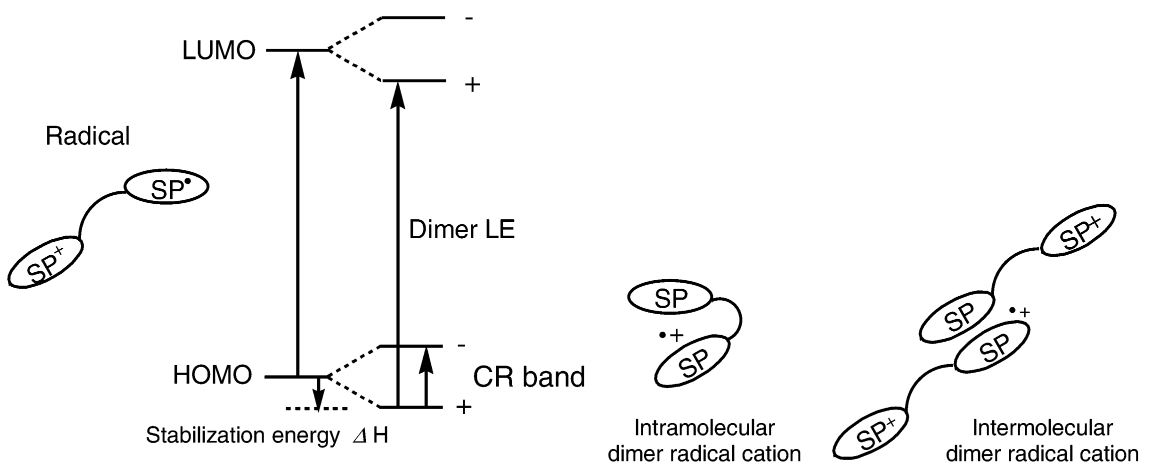


Fig. 2 Schematic representation of the energy levels in the styrylpyridinyl monomer radical and dimer radical cation upon electronic interaction with styrylpyridinium.

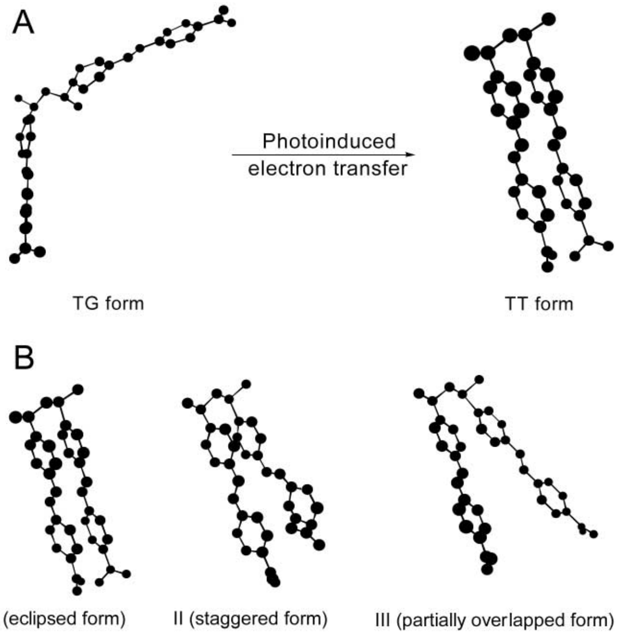


Fig. 3 A: Proposed internal rotation models of *m*-SPPe during photogeneration of radicals. Counter anions (TPB^-) and protons are omitted for simplicity. B: Proposed models of sandwich forms (**I**: eclipsed form and **II**: staggered form) and partially overlapped form (**III**) in the TT conformation of *m*-SPPe.

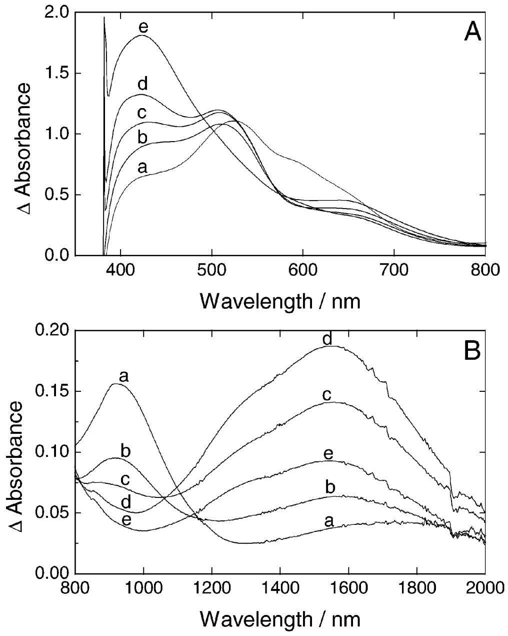


Fig. 4 Difference absorption spectral changes in the (A) 350–800 nm and (B) 800–2000 nm regions for *m*-SPPe in deaerated ACN solution (0.25 mM). (a) Just after irradiation for 4 min and after storage in the dark for (b) 2 h, (c) 6 h, (d) 20 h and (e) 100 h.

at 920 nm. The partially overlapped form (**III**) most probably contributes to the CR band around 1734 nm.

The absorption spectra of *m*-SPPe and SPPr irradiated for 4 min in ACN solution showed remarkable changes during storage in the dark at room temperature, as shown in Fig. 4 and 5. The absorption band with a peak at 524 nm in the visible region, observed after irradiation for 4 min, showed a small increase in absorbance and a blue shift to 507 nm during 20 h and a shoulder at 422 nm increased slowly as shown in Fig. 4A. The band at 422 nm remained after introduction of air and was attributed to the *cis*-isomer of a nitrostyrylpyridinium formed *via* a photogenerated radical. The broad band with a peak at 1734 nm observed just after irradiation for 4 min in the NIR region disappeared completely and the absorption with a peak at 920 nm decayed to about 60% at the initial state of storage in the dark. While these changes were occurring, a new band appeared at 1559 nm as shown in Fig. 4B. The blue shift of the longer wavelength NIR band from 1734 to 1559 nm, indicating higher stabilization of dimer radical cations, was attributed to a small conformational change of the partially overlapped dimer radical cation from the non-thermalized one with excess energy just after photoinduced electron transfer to the thermodynamically stabilized one. The absorbance at 1559 nm increased gradually after 2 h at the expense of the band at 920 nm with an isosbestic point at 1060 nm until 20 h as shown by curves (b)–(d) in Fig. 4B. After that, the total spectrum slowly decayed but radicals survived over 100 h as shown by curve (e) in Fig. 4B. These results strongly suggest that conformational changes of the *m*-SPPe dimer radical cation occurred slowly during storage in the dark from the sandwich form to the thermodynamically stabilized partially overlapped one, probably due to the repulsion of electronic clouds.

Very different spectral changes were observed for SPPr, similarly irradiated and stored in the dark, as shown in Fig. 5A and 5B. Fig. 5A showed an increase in absorbance of the band at 424 nm and a decrease at 612 nm. The increase of the band at 424 nm was similar to that of *m*-SPPe, while the band at 612 nm, which was assigned to the monomer radical or the LE band of the dimer radical cation, showed only a gradual decrease without changing the spectral pattern in the dark. The bands at 950 and 1742 nm assigned to the sandwich type and partially overlapped type of dimer radical cation in SPPr decreased rather quickly and a new peak at 1505 nm appeared

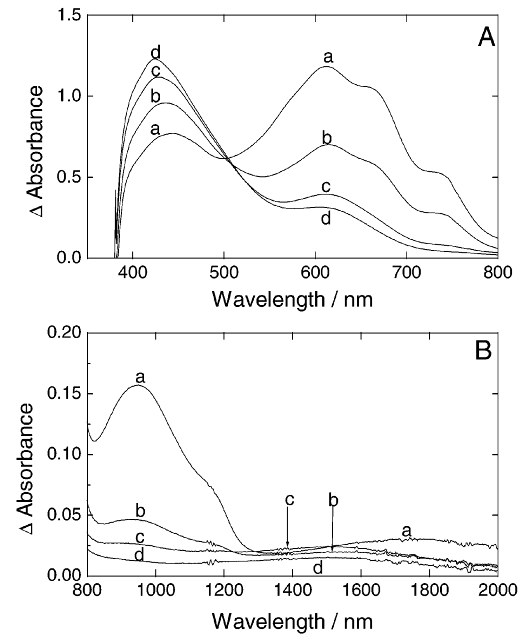


Fig. 5 Difference absorption spectral changes in the (A) 350–800 nm and (B) 800–2000 nm regions for SPPr in deaerated ACN solution (0.25 mM). (a) Just after irradiation for 4 min and after storage in the dark for (b) 1 h, (c) 3 h and (d) 6 h.

which showed the maximum absorbance after 3 h as shown in Fig. 5B. The blue shift of the longer wavelength NIR band from 1742 to 1505 nm was attributed to the small conformational change of partially overlapped dimer radical cation from the non-thermalized one, just after photoinduced electron transfer, to the thermodynamically stabilized one. The decay of the band at 950 nm did not result in the increase of the band at 1505 nm as observed for *m*-SPPe shown in Fig. 4. This result, together with the much smaller increase of the band at 1505 nm in SPPr during storage in the dark compared with that of *m*-SPPe, strongly suggests that the dissociation of intramolecular dimer radical cation occurred faster than in *m*-SPPe, probably due to less structural confinement in SPPr. Conformational restriction of two chromophores in the intramolecular dimer radical cation in *m*-SPPe with two additional methyl groups at 2- and 4-positions most probably contributed to the much larger absorbance at 1559 nm and to its much greater lifetime.

Further information about the conformational changes in *m*-SPPe was obtained by the absorption spectrum of a highly viscous solution. Fig. 6 shows the difference absorption spectral changes of *m*-SPPe in ACN solution containing poly(methyl methacrylate) (PMMA, 2.9% w/v). The *m*-SPPe irradiated for 4 min in the presence of PMMA in ACN solution at room temperature showed smaller absorption at 920 nm and around 1700 nm compared with those in Fig. 4 without PMMA at the same chromophore concentration, indicating a smaller probability of photoinduced electron transfer from TPB$^-$ to the styrylpyridinium ion due to the increased viscosity of solutions. This solution was again stored in the dark for 6 h. The absorption changes in the dark as shown by curves (b)–(d) in Fig. 6 showed only a small increase of the band at 1514 nm accompanied by the decay of absorption at 920 nm and around 1700 nm. The band at 1514 nm started to decay after 3 h due most probably to the dissociation of the dimer radical cation. These results strongly suggested that the increased viscosity unfavorably contributed to the formation of partially overlapped dimer radical cation.

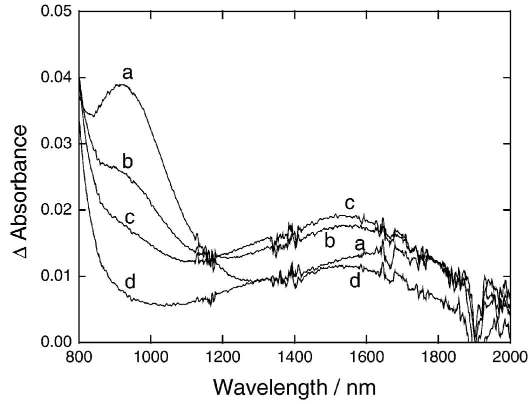


Fig. 6 Difference absorption spectra in the 800–2000 nm region of (a) irradiated *m*-SPPe (0.25 mM) for 4 min at room temperature in deaerated ACN solution containing PMMA (2.9% w/v) and after subsequent storage in the dark for (b) 1 h, (c) 3 h and (d) 6 h.

The temperature dependence of conformational changes of dimer radical cation was investigated by changing the temperature during storage in the dark from 4 to 40 °C. The absorption spectra of samples irradiated for 4 min at room temperature in ACN solution (0.25 mM) and stored in the dark below 15 °C showed only the decay of absorption at 920 nm without increase of the band around 1550 nm in the NIR region as shown in Fig. 7A and 7B. Faster changes were observed at 40 °C as shown in Fig. 7C as compared with those at room temperature (26 °C). These results indicate that the spectral change in the NIR (1500–1750 nm) region was due to the conformational change in the intramolecular dimer radical cations, which had a high activation barrier.

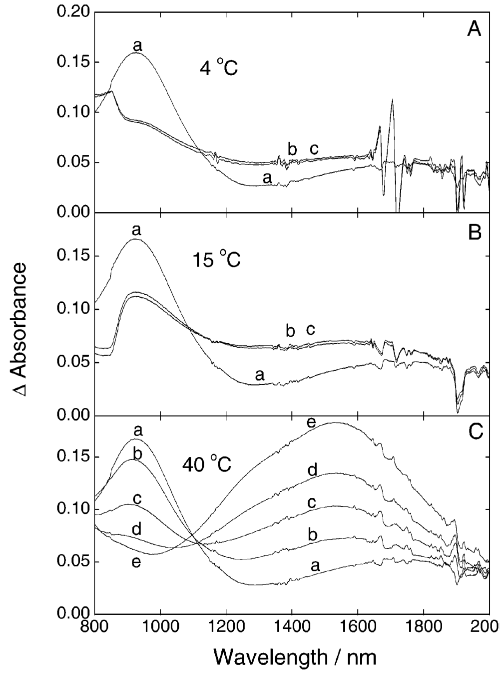


Fig. 7 Difference absorption spectra in the 800–2000 nm region of *m*-SPPe in deaerated ACN (0.25 mM) irradiated for 4 min at room temperature and subsequently stored in the dark at (A) 4 °C (B) 15 °C and (C) 40 °C. A: (a) Just after irradiation and after storage in the dark for (b) 1 h and (c) 3 h. B: (a) Just after irradiation and after storage in the dark for (b) 1 h and (c) 3 h. C: (a) Just after irradiation and after storage in the dark for (b) 1 h, (c) 3 h, (d) 6 h and (e) 10 h.

The EPR spectrum of *m*-SPPe in ACN (1.0 mM), just after irradiation for 5 min with stirring in a branch of an EPR cell through a band pass filter (405 nm), decreased gradually changing the line width during storage in the dark as shown in Fig. 8. The line width (ΔH_{msl}) of broad singlet spectra observed just after irradiation for 5 min increased gradually from 0.79 to 1.06 mT during storage in the dark until 20 h. As reported in the previous paper,[19] the EPR spectrum of the 1-hexadecyl-4-(4-(dicyanovinyl)styryl)pyridiniumyl (DSC$^+$C$_{16}$) radical formed

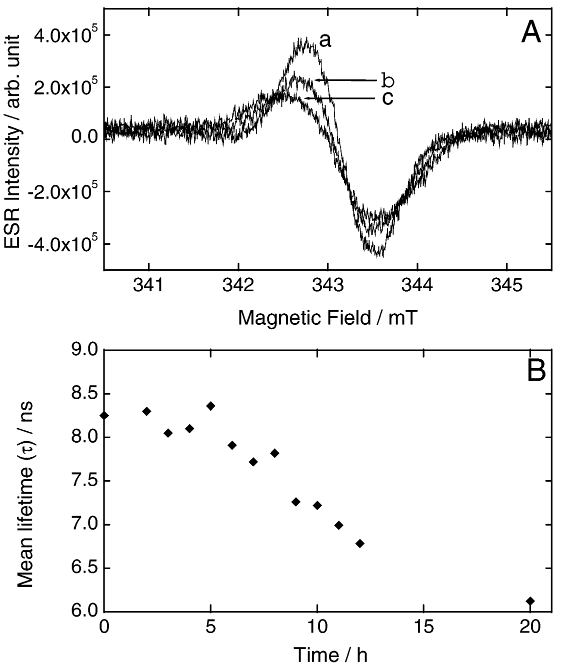
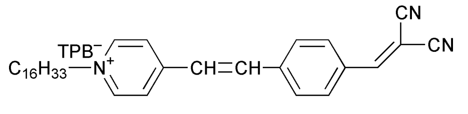


Fig. 8 A: EPR spectrum of *m*-SPPe (a) just after irradiation for 5 min with stirring and after storage in the dark for (b) 6 h and (c) 20 h in deaerated ACN solution (1.0 mM) at room temperature. B: The mean lifetime (τ) of electron exchanges of *m*-SPPe during storage in the dark until 20 h in deaerated ACN solution (1.0 mM) at room temperature.

by photoinduced electron transfer, which can make only intermolecular interactions, showed a broad singlet spectra in DME solution just after irradiation for 5 min and the spectral width slightly decreased from 0.87 to 0.62 mT during storage in the dark for 1.5 h.



DSC^+C_{16}

After mixing DSC^+C_{16} with an unirradiated sample in the branch, the broad singlet spectrum showed a marked change in its shape, resulting in a sharp spectrum with at least nine hyperfine peaks overlapped with the broad singlet. The broad singlet was due to the exchange broadening by high local concentration of radicals of DSC^+C_{16} formed by irradiation of the solution in a tube directly without stirring. The observed hyperfine structure was unambiguously assigned to the dimer radical cation sharing one unpaired electron between two chromophores by comparison with the simulated EPR spectrum.[19]

In the case of *m*-SPPe, no spectral changes were observed in the broad singlet pattern by mixing with the unirradiated one in a similar manner as for DSC^+C_{16}. These results together with the absorption spectra indicate that the broadening of the EPR spectrum observed in *m*-SPPe is most probably due to an intramolecular electron exchange reaction between a photogenerated styrylpyridinyl radical and a styrylpyridinium cation, which is slightly different from the electronic state in usual dimer radical cations. In other words, the new absorption spectra in the NIR region, as shown in Fig. 4B, may not be contributed by a species sharing one electron between two chromophores, just like a single molecule, but by a species exchanging one electron in a very short time from one chromophore to another. Such difference can be attributed to the fact that one end of two chromophores is linked by a trimethylene chain. In other words, they cannot form a conformation that shares an electron completely. It can be concluded that the intramolecular interaction, which gave the absorption spectral changes in the NIR region in *m*-SPPe, is similar to that of dimer radical cation except the lifetime of electronic exchange has a finite value. The exchange broadening observed in the EPR spectrum in *m*-SPPe as shown in Fig. 8A can be explained by Anderson's theory[28] which was applied to the electron exchange between the naphthalene anion radical and naphthalene.[29] The mean lifetime (τ) between exchanges for a *m*-SPPe radical can be calculated from the use of line width values by eqn. (4),[29] in which ΔH_{msl} (mT) is the line width as measured between points of maximum slope.

$$\frac{1}{\tau} = (2\pi)(2.83 \times 10^7)\frac{\sqrt{3}}{2}\Delta H_{\mathrm{msl}} \qquad (4)$$

The mean lifetime calculated from the EPR spectrum of *m*-SPPe just after irradiation is 8.2 ns and gradually decreased to 6.1 ns after storage in the dark for 20 h as shown in Fig 8B. These results most probably reflected conformational change of intramolecular electronic interactions in *m*-SPPe corresponding to the increase of a new absorption around 1559 nm during storage in the dark.

Conclusion

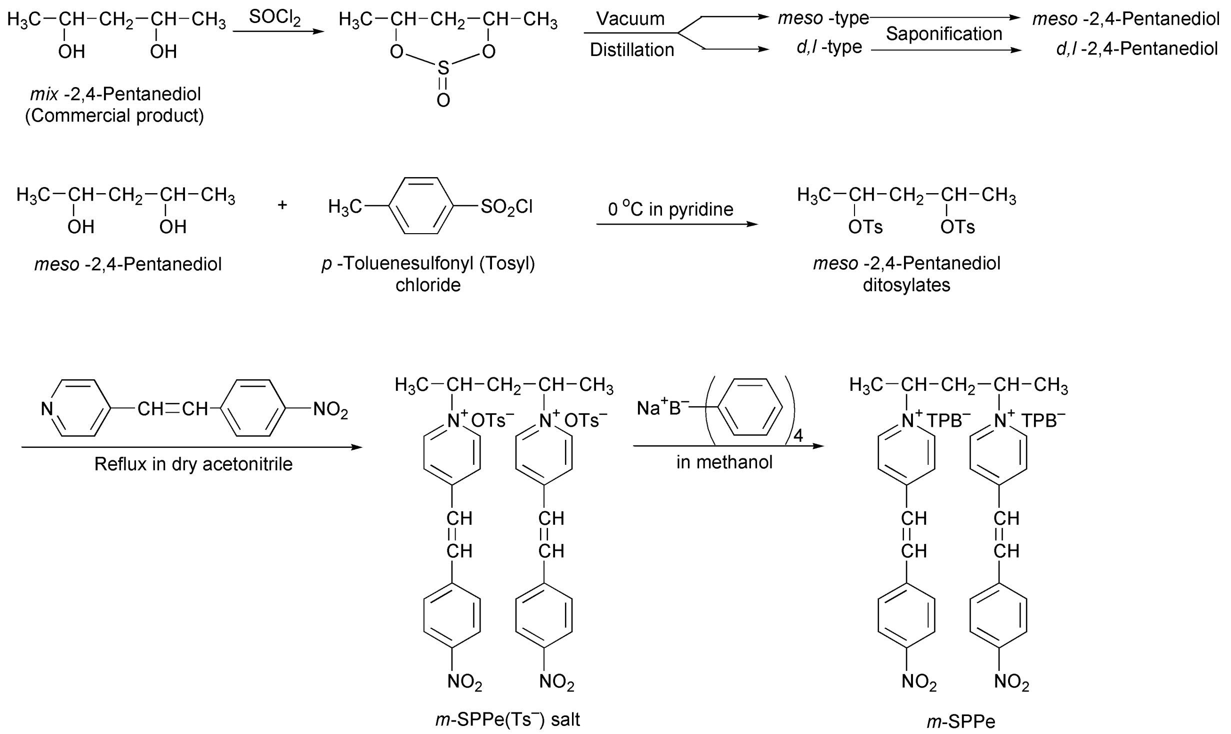
Effects of two additional methyl groups at 2- and 4-positions of newly synthesized *m*-SPPe on intramolecular electronic interactions of the nitrostyrylpyridinyl radical with the nitrostyrylpyridinium cation were clearly demonstrated in comparison with the corresponding 1,3-propane derivative (SPPr). Upon irradiation, the sandwich type and the partially overlapped dimer radical cation gave two stronger and slightly blue shifted CR bands at 924 and 1734 nm, respectively, compared with those of SPPr. Their conformations changed during subsequent storage in the dark showing a new peak at 1559 nm. Absorbance of the new band gradually and considerably increased up to 20 h and survived over 100 h. The absorbance and the lifetime of the new band were much higher than those in SPPr. From the EPR measurement, it was found that a photogenerated styrylpyridinyl radical in *m*-SPPe was formed to exchange an electron with a styrylpyridinium cation in the same *m*-SPPe molecule rather rapidly. Such intramolecular interaction most probably gave the new band around 1559 nm. It can be concluded that intramolecular electronic interaction between two chromophores gives absorption bands similar to the CR band in usual dimer radical cations. These results will contribute a great deal to the control of photoresponses and to the development of materials showing fast and large absorption changes in the NIR region for ultrafast molecular photonic devices compatible with the present light communication system.

Experimental

The preparation of *meso*- and *dl*-pentane-2,4-diol from mixtures *via* a cyclic sulfoester and *meso*-pentane-2,4-diyl ditosylates† was mostly according to Pritchard and Vollmer,[30] and Eliel and Hutchins.[31] The toluene-*p*-sulfonate (Ts^-) salt of *m*-SPPe was prepared directly by reacting equimolar amounts of 4-(4-nitrostyryl)pyridine and *meso*-pentane-2,4-diyl ditosylates as shown in Scheme 1. Counter ions of *m*-SPPe were exchanged with sodium tetraphenylborate in methanol. The purity of each product was confirmed by HPLC and 300 MHz ^{1}H NMR spectra. The preparation of pure *dl*-SPPe did not succeed due to conformational changes to the racemic-form during quaternization of *dl*-pentane-2,4-diol ditosylates with 4-(4-nitrostyryl)pyridine.

---

† The IUPAC name for tosylate is toluene-*p*-sulfonate.



Scheme 1 Synthetic route to *meso*-2,4-bis(4-(4-nitrostyryl)pyridiniumyl)pentane bis(tetraphenylborate) (*m*-SPPe).

All sample solutions were 0.25 mM and deaerated by the freeze–pump–thaw method in absorption spectral measurements. These solutions were irradiated with a Hamamatsu 150 Xe–Hg lamp through a band pass filter (λ_{ex} = 405 nm) at room temperature. The electronic absorption spectra were recorded with a Hitachi U-3500 UV-VIS-NIR spectrophotometer. The use of a band pass filter in all measurements was effective to prohibit the excitation of radicals and dimer radical cations, which might transform at the excited states. The EPR spectra were measured with a Bruker ESP300E spectrometer. The same conditions of measurement were used as those for absorption spectra except for the concentration (1.0 mM).

meso-2,4-Bis(4-(4-nitrostyryl)pyridiniumyl)pentane ditosylate salt (*m*-SPPe (Ts^-) salt)

m-SPPe (Ts^-) salt was prepared by reacting *meso*-pentanediyl ditosylates (2.46 g, 5.96 mmol) and 4-(4-nitrostyryl)pyridine (2.70 g, 11.9 mmol) in dry acetonitrile (35 ml) for 72 h at 82 °C. After cooling to room temperature, the precipitate was filtered off and washed with ethyl acetate and dried under vacuum for 12 h. Recrystallization from methanol gave yellow crystals (0.576g, 11%), mp 214–216 °C; δ_H(300 MHz; CD_3OD) 1.808 (6H, d, Me), 2.388 (6H, s, Me in Ts), 2.799–3.057 (2H, t, $-CH_2-$), 5.017 (2H, sextet, –CH–), 7.277 (4H, d, Ph in Ts), 7.564 (2H, d, Ph*CH*), 7.760 (4H, d, Ph in Ts), 7.826 (4H, d, Ph), 7.941 (2H, d, Py*CH*), 8.173 (4H, d, Ph), 8.205 (4H, d, Py), 8.922 (4H, d, Py).

meso-2,4-Bis(4-(4-nitrostyryl)pyridiniumyl)pentane bis(tetraphenylborate) (*m*-SPPe)

A solution of sodium tetraphenylborate (0.158 g, 0.231 mmol) in methanol (2 ml) was slowly added to a solution of *m*-SPPe (Ts^-) salt (0.200 g, 0. 231 mmol) in methanol (50 ml). After stirring for 10 min at room temperature, the precipitate was filtered off and washed with methanol. Drying under reduced pressure gave yellow crystals (0.137g, 51%), mp 147–149 °C; δ_H(300 MHz; CD_3COCD_3) 1.961 (6H, d, Me), 2.382–3.340 (2H, t, $-CH_2-$) 5.357 (2H, sextet, –CH–), 6.811 (8H, t, Ph in TPB), 6.960 (16H, t, Ph in TPB), 7.377 (16H, br s, Ph in TPB), 7.777 (2H, d, Ph*CH*), 7.925 (4H, d, Ph), 8.132 (2H, d, Py*CH*), 8.256 (4H, d, Ph), 8.362 (4H, d, Py), 9.175 (4H, d, Py).

Acknowledgements

This work was partly supported by the Grant-in-Aid for Scientific Research on Priority Areas "Molecular Synchronization for Design of New Materials System" (No. 13022230) and the Grant-in-Aid for Scientific Research for Encouragement of Young Scientists (A) (No. 13750757). The authors would thank Dr T. Arimura of AIST Tsukuba Central 5 for NMR measurements. S. H. Park greatly acknowledges the Amano Foundation for a scholarship.

References

1 I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, 1965, **43**, 2712.
2 M. Itoh, *J. Am. Chem. Soc.*, 1971, **93**, 4750.
3 M. Yamamoto, Y. Tsujii and A. Tsuchida, *Chem. Phys. Lett.*, 1989, **154**, 559.
4 A. Tsuchida, Y. Tsujii, S. Ito, M. Yamamoto and Y. Wada, *J. Phys. Chem.*, 1989, **93**, 1244.
5 Y. Tsujii, A. Tsuchida, Y. Onogi and M. Yamamoto, *Macromolecules*, 1990, **23**, 4019.
6 Y. Tsujii, K. Takami, A. Tsuchida, S. Ito, Y. Onogi and M. Yamamoto, *Polym. J.*, 1990, **22**, 319.
7 A. Tsuchida, Y. Tsujii, M. Ohoka and M. Yamamoto, *J. Phys. Chem.*, 1991, **95**, 5797.
8 Y. Tsujii, A. Tsuchida, M. Yamamoto, T. Momose and T. Shida, *J. Phys. Chem.*, 1991, **95**, 8635.
9 Y. Tsujii, A. Tsuchida, S. Ito and M. Yamamoto, *Macromolecules*, 1991, **24**, 4061.
10 A. Tsuchida, H. Takamura, M. Yamamoto, B. Lee, T. Ikeda and S. Tazuke, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 909.
11 A. Tsuchida, H. Takamura and M. Yamamoto, *Chem. Phys. Lett.*, 1992, **198**, 193.
12 A. Tsuchida and M. Yamamoto, *J. Photochem. Photobiol., A: Chem.*, 1992, **65**, 53.
13 J. Vandendriessche, P. Palmans, S. Toppet, N. Boens, F. C. de Schryver and H. Masuhara, *J. Am. Chem. Soc.*, 1984, **106**, 8057.
14 H. Masuhara, N. Tamai, N. Mataga, F. C. de Schryver and J. Vandendriessche, *J. Am. Chem. Soc.*, 1983, **105**, 7256.
15 F. Hirayama, *J. Chem. Phys.*, 1965, **42**, 3163.
16 T. Nagamura, A. Tanaka, H. Kawai and H. Sakaguchi, *J. Chem. Soc., Chem. Commun.*, 1993, 599.

17 T. Nagamura, H. Kawai, T. Ichihara and H. Sakaguchi, *Synth. Met.*, 1995, **71**, 2069.

18 H. Kawai and T. Nagamura, *Mol. Cryst. Liq. Cryst.*, 1995, **267**, 235.

19 T. Nagamura, T. Ichihara and H. Kawai, *J. Phys. Chem.*, 1996, **100**, 9370.

20 T. Nagamura, S. Kashihara and H. Kawai, *Chem. Phys. Lett.*, 1998, **294**, 167.

21 H. Kawai and T. Nagamura, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 3581.

22 S. H. Park, H. Kawai and T. Nagamura, *J. Photopolym. Sci. Technol.*, 2000, **13**(2), 197.

23 W. S. Xia, H. Kawai and T. Nagamura, *J. Photochem. Photobiol., A: Chem.*, 2000, **136**, 35.

24 H. Kawai and T. Nagamura, *Mol. Cryst. Liq. Cryst.*, 2000, **344**, 209.

25 S. H. Park and T. Nagamura, *J. Photopolym. Sci. Technol.*, 2001, **14**(2), 227.

26 S. H. Park and T. Nagamura, *Mol. Cryst. Liq. Cryst.*, 2001, **370**, 249.

27 S. H. Park and T. Nagamura, *Chem. Commun.*, 2001, 2344.

28 P. W. Anderson, *J. Phys. Soc. Jpn.*, 1954, **9**, 316.

29 R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, 1957, **79**, 2086.

30 J. G. Pritchard and R. L. Vollmer, *J. Org. Chem.*, 1963, **28**, 1545.

31 E. L. Eliel and R. O. Hutchins, *J. Am. Chem. Soc.*, 1969, **91**, 2703.