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First Observation of Monomer and Dimer Radical Cation upon Photoreduction of Cyanopyridinium Derivatives in Solution by Electron Spin Resonance and Absorption Spectroscopy

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The monomer radical and the dimer radical cation of cyanopyridinium derivatives have been studied by absorption and electron spin resonance (ESR) spectroscopies at room temperature in acetonitrile upon steady photolysis. The stable cyanopyridinyl radical of 1,3-bis(4-cyanopyridiniumyl)propane (acceptor) formed by one-electron transfer from tetraphenylborate anion (donor) interacted intramolecularly with a parent cation, forming a dimer radical cation. A charge resonance band was observed at 1360 nm and assigned to the formation of intramolecular dimer radical cations. The ESR spectra revealed that one unpaired electron in the intramolecular dimer radical cation was completely shared between two chromophores of photoreduced 1,3-bis(4-cyanopyridiniumyl)propane (**1**). On the other hand, the intermolecular dimer radical cation of 1-(4-cyanopyrdiniumyl)hexadecane (**2**) as a monochromophoric compound was not formed because no charge resonance band was observed in the near-infrared region. Clearly resolved ESR spectra of both the dimer radical cation and the monomer radical were observed, for the first time, upon photoreduction of these cyanopyridinium derivatives. The effect of the chromophore size on the charge resonance band in the near-infrared region was also demonstrated by homo- and hetero-type bichromophoric compounds containing 4-cyano- and 4-nitrostyryl-pyridinium.

1. Introduction

A large and very fast optical modulation of the refractive index in the near-infrared (NIR) region is an essential requirement for optical data processing applications that are compatible with present day light communication systems that operate in the wavelength range of 1300−1600 nm. Organic materials showing absorption changes in the visible (vis) to the NIR region, brought on by various types of photochemical or photophysical processes, can be used in molecular photonic devices having a guided wave geometry to control the reflected intensity or phase of the probe light in a parallel way.[1−5] Materials processing large changes, upon excitation, in refractive index and absorption in the 1300−1600 nm region and attractive chemical and physical properties are ideal candidates for consideration provided they also show charge resonance (CR) interactions.

Badger and Brocklehurst were the first to postulate the existence of a CR band for various aromatic cation radicals.[6] They attributed the appearance of new broad absorption bands in the NIR region to a CR band produced from dimeric cation radicals. In addition, absorption bands due to monomeric cation radicals were observed in the vis region. The CR band is identified with the transition between the split energy levels of singly occupied molecular orbitals (SOMO). These energy levels are formed from the electronic interaction between two chromophores of a dimer radical cation. The stabilization energy of a dimer radical cation is approximately equal to half the energy of its CR band. A number of examples for CR bands have been reported.[7−9] To date, all dimer radical cations, except those reported by Hermolin and Kosower[10] and Nagamura and coworkers,[11−23] are observed between cation radicals and their neutral counterparts. Hermolin and Kosower reported the appearance of a NIR absorption from 1,1-trimethylenebis(4-carbomethoxy)pyridinium diiodide that had been partially reduced either chemically or electrochemically.[10]

We reported, for the first time, the CR band of 1-alkyl-[4-(4-nitrostyryl)]pyridinium (NS^+) tetraphenylborate (TPB^-), which was formed by a photoreduction process in organic solutions at room temperature.[11] In this styrylpyridinium system, the relative stability of the radical, formed by the electron transfer from a counteranion upon photoexcitation, leads to a strong electronic interaction between the radical and its parent cation. The CR band produced by the dimer radical cation was centered at 950 nm in 1,2-dimethoxyethane (DME). It has been established that the behavior of CR bands in para-substituted styrylpyridinium compounds is significantly affected by the geometrical structure of the dimer, the length of the bridge between the two chromophores making up the dimer, the nature of electron-withdrawing group on the chromophores, the solvent, and the temperature.[12−23] Recently, we have also reported on the unusual electronic absorption changes around 1550 nm in *meso*-2,4-bis[4-(4-nitrostyryl)pyridiniumyl]pentane ditetraphenylborates following photoreduction.[22,23] The reason for this is probably because of the strong electronic interactions that exist between the styrylpyridinyl radical and the styrylpyridinium cation, which together form to a long and planar structure that allows for considerable delocalization. It has not yet been possible to observe both the monomer styrylpyridinyl radical

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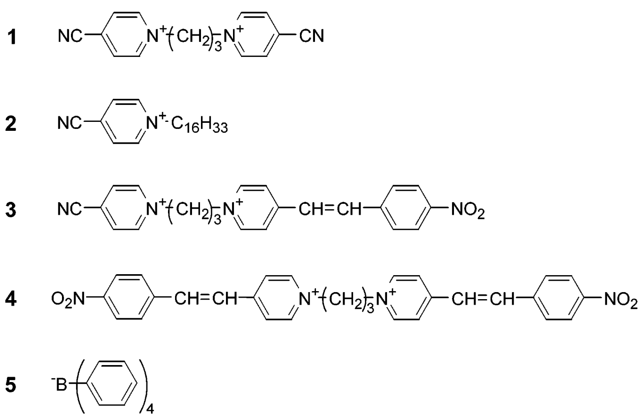


Figure 1. The structures and abbreviations of the compounds.

and the dimer radical cation under the same experimental conditions as were used for the styrylpyridinium derivatives.

In this study, we have used several cyanopyridinium compounds to examine the formation of monomer radicals and dimer radical cations in organic solution at room temperature. On the basis of ultraviolet (UV)−NIR absorption and electron spin resonance (ESR) spectra, it has now been clearly demonstrated, for the first time, that both dimer radical cations and monomer radicals are produced upon photoreduction of cyanopyridinium derivatives.

2. Experimental Section

The bromide salts of 1,3-bis(4-cyanopyridiniumyl)propane (**1**) and 1-(4-cyanopyridiniumyl)hexadecane (**2**) were synthesized by quarternization of 4-cyanopyridine with corresponding 1,3-dibromopropane and 1-hexadecylbromide, respectively. The bromide salt of asymmetric 1-(4-cyanopyridiniumyl)-3-[(4-nitrostyryl)pyridiniumyl]propane (**3**) was synthesized via a two-step quarternization from 4-cyanopyridine and 1,3-dibromopropane, followed by reaction with 4-(4-nitrostyryl)pyridine. 1,3-Bis[(4-nitrostyryl)pyridiniumyl]propane (**4**) was synthesized according to the method previously reported.[15] Counterions of all bromide salts were exchanged with sodium tetraphenylborate in methanol. The purity of the compounds was confirmed by ^{1}H NMR and HPLC. The structure and abbreviation of each compound are shown in Figure 1. Absorption spectra were recorded at room temperature by a Hitachi U-3500 UV−vis−NIR spectrophotometer before and after irradiation in vacuo with a 150 W Hg−Xe lamp through a band-pass filter ($\lambda_{ex} = 365$ nm). The ESR spectra were measured with a Bruker ESP 300E spectrometer (100 kHz field modulation) at room temperature.

3. Results and Discussion

The difference absorption spectra of compounds **1** and **2** after photoirradiation through a band-pass filter ($\lambda_{ex} = 365$ nm) for 4 min at the same chromophore concentration in acetonitrile (ACN) at room temperature are shown in Figure 2. The main absorption bands of **1** and **2** before irradiation were observed below 250 nm. The use of the band-pass filter limited the extent of excitation into the extended tail absorptions of the compounds, which was effective in prohibiting re-excitation of a photogenerated radical or dimer radical cation.

A 0.25 mM solution of **1** in ACN showed a broad NIR absorption with λ_{max} at 1360 nm in addition to two sharp peaks at 297 and 348 nm, as can be seen in Figure 2. A 0.5 mM solution of **2** in ACN yielded only weak absorptions around 300 and 350 nm and no new absorption in the NIR region. On the basis of these results, the new characteristic NIR band of **1** can clearly be attributed to a CR interaction between a photogenerated radical and a parent cation in the form of an intramolecular dimer radical cation ($Py^+-(CH_2)_3-Py^•$). An absorption at 1360 nm has been reported for 1,1-trimethylenebis-(4-(carbomethoxy)pyridinium) diiodide that had been partially (one-electron) reduced either chemically or electrochemically.[10] The absorption was attributed to an intervalence transition within a pyridinyl radical cation, but no direct evidence for it, such as ESR spectra, was given. The UV bands were assigned to the monomer radical or the local excitation (LE) band of a dimer radical cation. It should be noted that no CR band that could be assigned to an intermolecular dimer radical cation of **2**, in which only intermolecular interactions can be involved, was observed in the NIR region.

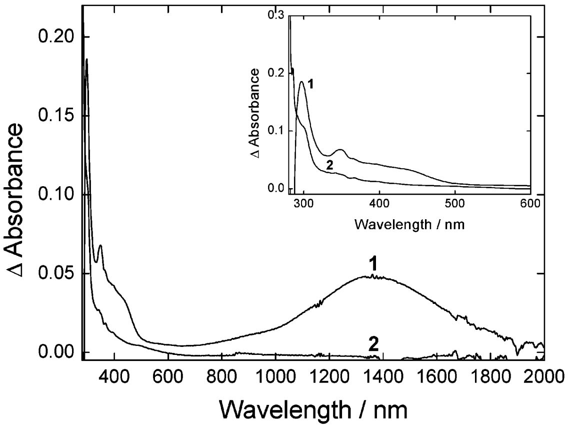


Figure 2. Difference absorption spectra in 280−2000 nm region after irradiation of **1** (0.25 mM) and **2** (0.5 mM) in ACN through a band-pass filter (365 nm) for 4 min. The inset shows the enlarged spectra in the 280−600 nm.

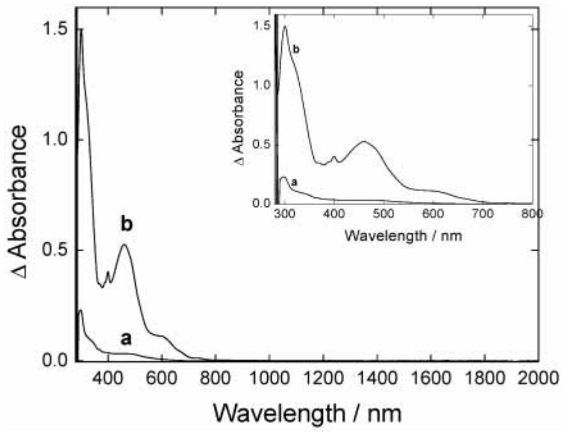


Figure 3. Difference absorption spectra in 280−2000 nm region after irradiation of **2** in (a) 1.0 mM ACN and (b) 0.5 mM DME through a band-pass filter (365 nm) for 4 min. The inset shows the enlarged spectra in the 280−800 nm.

The absorption spectra of **2** at 1.0 mM in ACN and 0.5 mM in 1,2-dimethoxyethane (DME), a less polar solvent, are shown in Figure 3. The cyanopyridinyl radical showed a very strong absorption in DME, almost 15 times greater than that in ACN (Figure 2). This enhanced absorption in DME is attributed to a higher probability of photoinduced electron transfer due to a decreased interionic distance between the donor−acceptor couple. However, no CR bands in the NIR were detected in Figure 3 for either solvent system. These results clearly indicate that when a cyanopyridinyl radical forms in a monochromophoric compound it has difficulty interacting intermolecularly

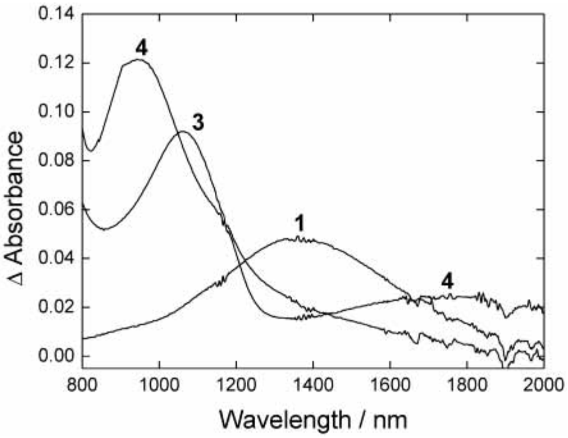


Figure 4. Difference absorption spectra in 800−2000 nm region after irradiation of **1**, **3**, and **4** in ACN (0.25 mM) for 4 min through band-pass filters, $\lambda_{ex} = 365$ nm for **1** and **3** and $\lambda_{ex} = 405$ nm for **4**.

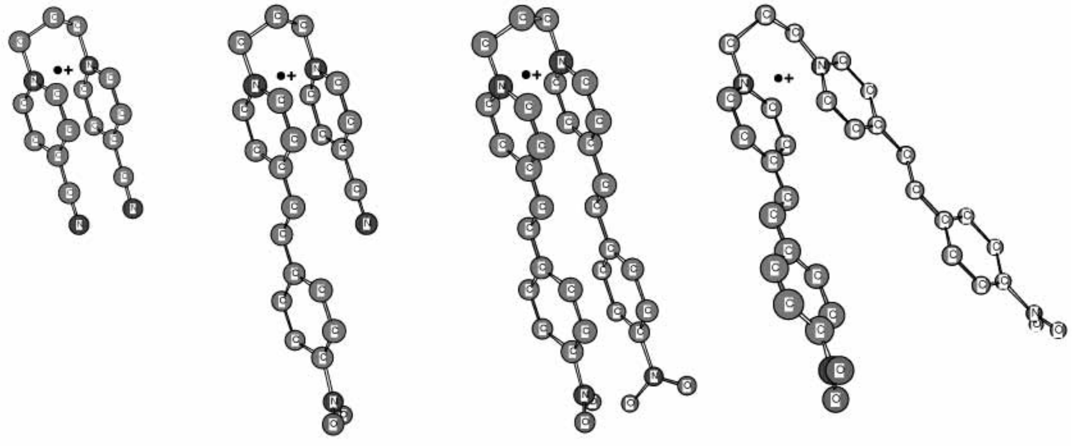
with a parent cation even at higher concentrations or in a low-polarity solvent. It is clear that a cyanopyridinyl radical that has little electron delocalization can only electronically interact with a cyanopyridinium cation under confined conditions to form a dimer radical cation such as in a bichromophoric compound that is linked by a propane bridge (**1**).

In the systems being examined, a higher stability of the pyridinyl radical has been achieved by the introduction of an electron-withdrawing group at the para-position and by inhibiting the reverse electron-transfer reaction following the oxidation of the anion **5** as a consequence of its decomposition following its one-electron oxidation.[11−23] The presence of a trimethylene bridge between two chromophores, as shown first by Hirayama,[24] is known to be effective in taking on a favorable conformation for intramolecular interaction of chromophores, such as excimer formation. From the above reasons, we can conclude that the relatively stable dimer radical cation is only created from compound **1** in ACN at room temperature. Its presence gives rise to the absorption band around 1360 nm that is assigned to a CR band. This band persisted for several hours in the dark after irradiation.

Figure 4 shows the absorption spectra in the 800−2000 nm region observed for compounds **1**, **3**, and **4** irradiated for 4 min through a band-pass filter ($\lambda_{ex} = 365$ nm for **1** and **3** and $\lambda_{ex} = 405$ nm for SPPr) in 0.25 mM ACN solutions at room temperature. Compound **4** showed two characteristic absorption peaks at 950 and 1742 nm, which has been previously reported.[15] The absorption bands were assigned to sandwich and partially overlapped intramolecular dimer radical cations, respectively.[15] The NIR absorption of **3** showed a peak at 1063 nm, which is different from that of the intermolecular CR band observed at 1150 nm in monochromophoric *N*-alkyl-4-(4-nitrostyryl)pyridinium tetraphenylborate in ACN solutions.[12,15,17] The intramolecular CR band at 1360 nm in **1** is considerably red-shifted by about 297 and 410 nm as compared with those of **3** and **4**, respectively. The stabilization energies of the intramolecular dimer radical cation were evaluated as $\Delta H = 43.\ 9$ kJ mol^{-1} for **1**, 56.1 kJ mol^{-1} for **3**, and 62.8 kJ mol^{-1} for **4**. The absorbance of the NIR band increased in the order of **1**, **3**, and **4** (at 950 nm). The order of stabilization energies reflects the degree of overlap between two chromophores in a sandwich configuration. The CR bands observed in the NIR region shifted to longer wavelength on decreasing the size of the functional group attached to the pyridinium rings, from 4-nitrostyrylpyridinium to 4-cyanopyridinium. These results clearly indicate that the extent of electron delocalization with the chromophores also affects the stabilization of the dimer radical cation and hence the CR band in the NIR region.

Figure 5 shows the proposed structural models of the sandwich intramolecular dimer radical cation formed upon photoexcitation of **1**, **3**, and **4** and partially overlapped one for **4**. Two chromophores can be arranged parallel to each other in the sandwich form, permitting interaction. The absorption spectra observed in the NIR region as shown in Figure 4 most probably stem from the sandwich form of various dimer radical cations. The exception is the absorption at 1742 nm of **4**, which has been attributed to the dimer radical cation in its partially overlapped form.[15,23] Absorption bands of **1** and **3** at longer wavelengths should not be assumed to arise from sandwich structures because the extent of electron delocalization in the cyanopyridinium derivatives is too small to form partially overlapped structures such as those that occur with 4-nitrostyrylpyridinium.

Figures 6 and 7 show the ESR spectra observed in ACN solutions of bichromophoric **1** (1.0 mM) and monochromophoric **2** (1.0 mM) immediately following 5 min of irradiation through a band-pass filter ($\lambda_{ex} = 365$ nm) at room temperature. These



1 **3** **4**-sandwich form **4**-partially overlapped form

Figure 5. Proposed models of their sandwich intramolecular dimer radical cations **1**, **3**, and **4** and partially overlapped one of **4** formed by electron transfer from anion **5**. Counteranions (**5**) and protons are omitted for simplicity.

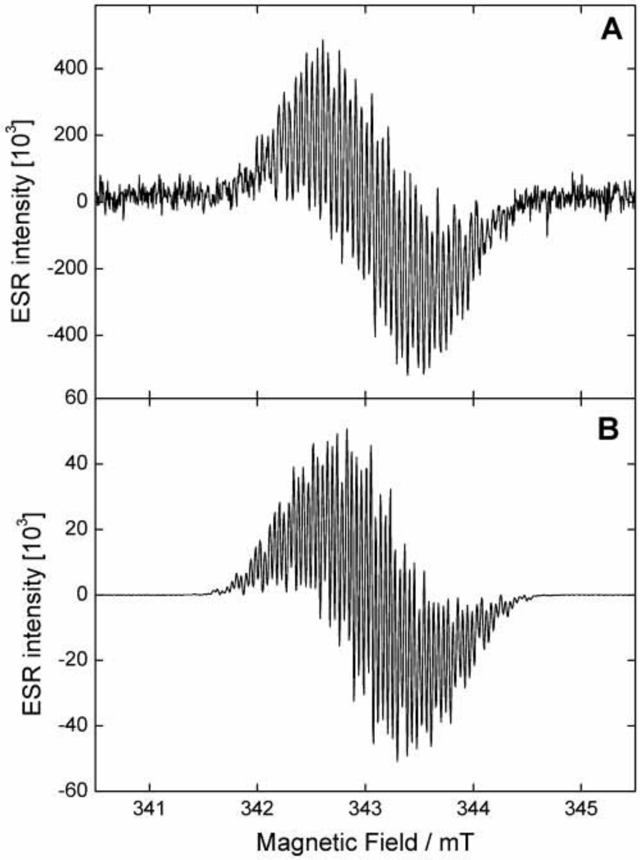


Figure 6. The ESR spectrum of **1** (A) observed after irradiation in ACN (1.0 mM) through a band-pass filter (365 nm) for 5 min and (B) the simulated one.

two well-resolved ESR spectra show totally different hyperfine structures and total spectral width. The observed ESR spectra of **1** and **2** shown in Figures 6A and 7A consist of sharp hyperfine structures with at least 44 lines overlapping a broad spectrum and those with at least 17 lines, respectively. A computer simulation of these spectra was made for the dimer radical cation and for the monomer radical using the WinSIM software (Brukers). The simulation results are shown in Figures 6B and 7B. Its can be seen that these simulated spectra almost coincided with the observed spectra. The hyperfine splitting (hfs) constants for the best fits are summarized in Table 1. Itoh and Nagakura studied the ESR spectra of 1-methyl-4-substituted pyridinyl radicals with carbomethoxy, carbamide, acetyl, and cyano groups upon chemical reduction.[25] The hfs constants of the 4-cyano derivative reported by them corresponded closely to those for **2** given in Table 1. The hfs constants of radical **1** obtained from the spectrum in Figure 6 were approximately one-half of those of the monomer radicals of **2** in Figure 7. The reason for this reduction in the unpaired electron density of radicals of **1** is most likely because of a decrease in the electron delocalization between the two interacting chromophores. These results clearly indicate that radicals in **1** formed by the photoinduced electron transfer from counteranions were almost quantitatively converted into intramolecular dimer radical cations. In contrast, the photogenerated radicals of **2** persisted as monomers without forming significant intermolecular interactions. These results are consistent with the features of the absorption spectra as shown in Figures 2 and 3.

To date, no clear ESR identification of the monomer radical or the dimer radical cation has been made for pyridinium derivatives upon chemical, electrochemical, or photoreduction of compounds containing the same chromophores, although their existence had been predicted. Itoh reported that ESR spectra of bis(4-carbomethoxy)pyridinium with tri-, tetra-, and pentanmethylene briges partially (one-electron) reduced chemically were unexpectedly very similar to those of the corresponding diradicals.[26] They interpreted their results to indicate the formation of an open-structured dimer in which there was insignificant intramolecular interactions between a pyridinium cation and a pyridinyl radical. They did not observe a CR band, which would be present at a wavelength greater than 1400 nm.[26] Tripathi et al. reported ESR spectra of the neutral and cationic forms of reduced isonicotinamide, 4-carbamylpyridinyl radicals generated by photolysis in aqueous solution containing acetone and isopropyl alcohol.[27] Howarth and Fraenkel[28] reported that the ESR spectrum of the naphthalene dimer radical cation, generated by two sets of eight equivalent protons, was observed upon chemical oxidation at low temperature. The hfs constants obtained were approximately one-half the hyperfine splitting constants of the naphthalene negative ion radical. Recently, Kochi et al.[9] also reported that the molecular association of the octamethylbiphenylene cation radical (OMB$^{+\bullet}$) with its neutral counterpart produced a dimeric cation radical ((OMB)$_2^{+\bullet}$). The ESR spectra showed at least 15 lines having approximately one-half the hfs constants of the protons from the monomeric OMB$^{+\bullet}$ in dichloromethane at −80 °C.[9]

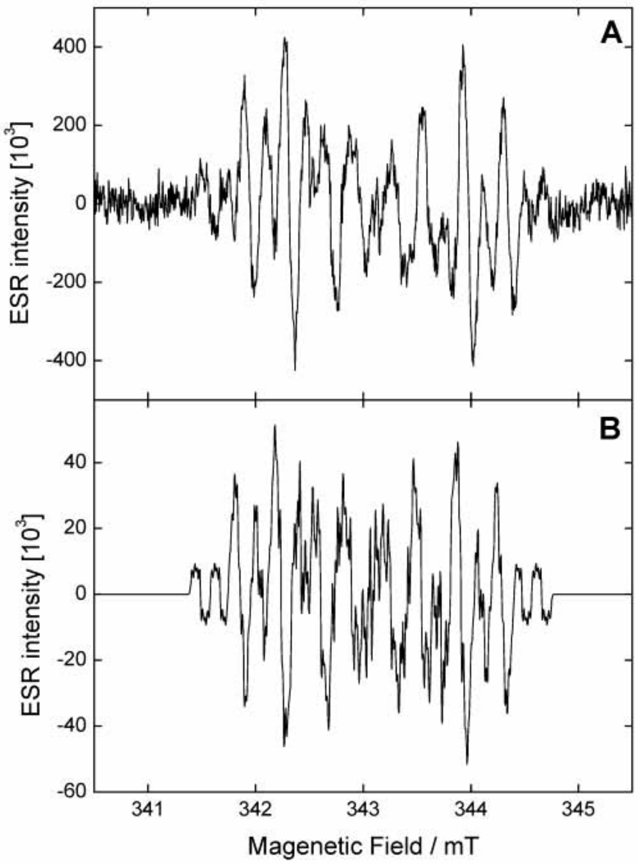


Figure 7. The ESR spectrum of **2** (A) observed after irradiation in ACN (1.0 mM) through a band-pass filter (365 nm) for 5 min and (B) the simulated one.

TABLE 1: Hyperfine Splitting Constants of 1 and 2 in ACN at Room Temperature

compd	N_1	$H_{2,6}$	H_β	H_γ	$H_{3,5}$	N(CN)
1	3.17	2.19	1.735	0.13	0.31	0.915
2	6.52	4.02	3.47	0.24	0.45	1.83

The ESR spectrum of the styrylpyridinyl radical at room temperature was reported in our previous papers.[14,19,23] The ESR spectrum of the 1-hexadecyl-4-[4-(dicyanovinyl)styryl]pyridinyl (DSC^+C_{16}) radical, as a monochromophoric compound in DME, which was formed by photoinduced electron transfer after irradiation for 5 min, showed a broad singlet due probably to the high local concentration of radicals or their strong interaction. The ESR spectrum showed a dramatic change after mixing the irradiated solution with an unirradiated sample. A sharp spectrum was observed with at least nine hyperfine peaks overlapping with a broad singlet.[14,19] The final spectrum was assigned to intermolecular dimer radical cations that had formed from the interaction of photogenerated radicals and unirradiated cations. In this structure, one unpaired electron is shared between two chromophores on the basis of a comparison with a simulated ESR spectrum. The *meso*-2,4-bis[4-(4-nitrostyryl)pyridiniumyl]-pentane (*m*-SPPe) radical, as a bichromophoric compound in ACN solution, also produced a broad singlet ESR spectra.[23] However, the shape of the ESR spectrum was not changed when mixed with an unirradiated sample. The broadening of the ESR spectrum observed in *m*-SPPe was attributed to a strong intramolecular electron exchange reaction between a photogenerated styrylpyridinyl radical and a styrylpyridinium cation.[23]

4. Conclusions

Dimer radical cations and monomer radicals formed by the photoreduction of cyanopyridinium derivatives were clearly identified, for the first time, by absorption and ESR spectroscopies. The stable intramolecular dimer radical cation of **1** formed by a photoinduced electron transfer from an anion **5** to a pyridinium cation in ACN at room-temperature results in the formation of a broad charge resonance band with a peak at 1360 nm. On the other hand, photogenerated radicals of monochromophoric **2** did not lead to an intermolecular interaction with a parent cation. The hyperfine splitting constants of dimer radical cation of **1** and monomer radical of **2** were evaluated from ESR simulation spectra. The dimer radical cation of **1**, with at least 44 sharp lines overlapping a broad signal, has one-half the hyperfine splitting constant of the monomer spectrum that has at least 17 lines. These results clearly indicated, for the first time, the formation of monomer radicals and dimer radical cations from the same cyanopyridinium cations by photoinduced electron transfer in ACN at room temperature. The effect of electronic delocalization in chromophores on the CR band was also clearly demonstrated for three bichromophoric compounds.

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