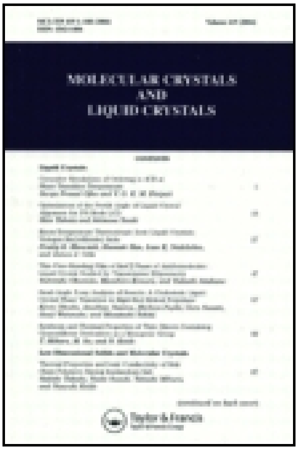

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Intramolecular Charge Resonance Interaction in *meso*-2,4-Bis(4-(4-nitrostyryl)pyridinium)pentane ditetraphenylborates upon Steady Photolysis in Solution

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A new ω,ω'- type bichromophoric model compound, *meso*-2,4-bis (4-(4-nitrostyryl)pyridinium)pentane (*meso*-B4SPC5^{2+}) ditetraphenylborates, has been prepared. A conformational analysis of *meso*-B4SPC5^{2+} was performed by using ^{1}H NMR spectroscopy. Its charge resonance bands were also studied by absorption spectroscopy upon steady photolysis at room temperature.

Keywords charge resonance (CR) band; dimer radical cation; *meso*-2,4-bis(4-(4-nitrostyryl)pyridinium)pentane ditetraphenylborates

INTRODUCTION

Intramolecular interaction between two chromophores is one of the interesting problems in science and technology and has been studied extensively. In the previous study, we reported 1,3-bis(4-(4-nitrostyryl)-pyridinium)propane (B4SPC3^{2+}) ditetraphenylborates salt showed two intramolecular charge resonance (CR) bands with remarkable color change [1]. Tri-methylene bridge gave more favorable configuration for intramolecular interaction of two chromophores than other type of compounds bridged with shorter or longer chains, e.g., ethane, butane and hexadecane [1,2].

In this study, we prepared *meso*-2,4-bis(4-(4-nitrostyryl)pyridinium)-pentane ditetraphenylborates (*meso*-B4SPC5^{2+}(TPB^{-})$_2$) expecting more stable geometrical conformation of intramolecular dimer radical cation than usual ω , ω '- type bichromophoric model compounds. We investigated the steady photoexcitation at room temperature in acetonitrile (ACN) solution.

SYNTHESIS

meso- and *d,l*-2,4-Pentanediol and their ditosylates (Ts^{-}) were synthesized according to Pritchard [3] and Eliel [4], respectively. *meso*-B4SPC5^{2+}(Ts^{-})$_2$ salt was obtained by reacting equimolar amounts of 4-(4-nitrostyryl)pyridine and *meso*-2,4-pentanediol ditosylates under stirring in dry ACN at 82 ℃ for 72 hr. The reaction flask was cooled to room temperature at the end of reaction. The precipitate was washed with the addition of ethyl acetate and dried in vacuum for 12 hr. Counter ions of *meso*-B4SPC5^{2+}(Ts^{-})$_2$ salts were exchanged with tetraphenylborate in methanol. The ^{1}H NMR spectrum showed all aromatic protons as well-defined doublets (δ = 7.770 - 9.187). The methyl group signal gave a doublet at δ = 1.961 (J = 6.593 Hz).

MEASUREMENTS

Purity was confirmed by using TLC, HPLC (JAI LC-918 R/U) and ^{1}H-NMR (300MHz). Absorption spectra were measured with Hitachi U-3500 at 0.25 mM in ACN. Solutions deaerated by the freeze-pump-thaw method were irradiated with a Hamamatsu 150 W Xe-Hg lamp through a band pass filter (λ_{ex} = 405 nm) at room temperature. The band pass filter was used to prohibit the excitation of radicals and dimer radical cations, which might change to another form at the excited states.

RESULTS AND DISCUSSION

De Schryver has proposed that TG/GT is the most stable conformation in *meso*-2,4-di(N-carbazolyl)pentane while TT and GG conformations are present at room temperature for *dd,ll*-2,4-di(N-carbazolyl)pentane [5]. T and G stand for trans and gauche configuration, respectively. Two adjacent styrylpyridinium groups in *meso*-B4SPC5^{2+}(TPB$^-$)$_2$ can also effectively interact upon photolysis at room temperature because electronic interactions between them may form fully overlapped alignment. In figure 1, the difference absorption spectrum of *meso*-B4SPC5^{2+}(TPB$^-$)$_2$ in 0.25 mM ACN solution, observed after irradiation through a band pass filter, shows four new bands with peaks at 424 nm and 524 nm in the visible (VIS) region and with peaks at 917 nm and 1679 nm in the near infrared region (NIR). Absorption peaks at about 424nm and 524 nm were assigned to the short and long axis transition of nitrostyrylpyridinium radicals. The NIR absorption peaks at about 917 nm and about 1679 nm were most probably caused by the

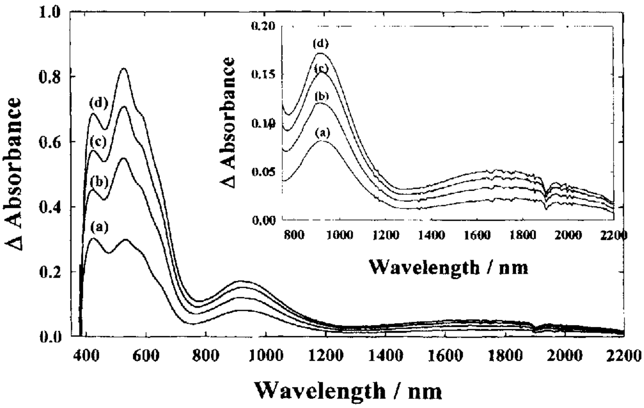

FIGURE 1 The difference absorption spectra in 350 - 2200 nm region of *meso*-B4SPC5^{2+}(TPB$^-$)$_2$ (0.25 mM) irradiated for (a) 1 min, (b) 2 min, (c) 3 min and (d) 4 min in ACN through a band pass filter (405 nm). The enlarged spectra in a 750 – 2200 nm region are shown in the insect.

charge resonance interaction of the sandwich form and partially overlapped form in intramolecular dimer radical cations with stabilization energy, ΔH = 65.2 kJ mol^{-1} and ΔH = 35.5 kJ mol^{-1}, respectively. These CR bands observed in *meso*-B4SPC5^{2+}(TPB$^-$)$_2$ were stronger and slightly blue shifted as compared with those in bichromophoric compounds, B4SPC3^{2+} [1]. These results clearly indicate that geometrical configuration in *meso*-B4SPC5^{2+}(TPB$^-$)$_2$ contributed to the formation of more stabilized intramolecular dimer radical cation. The present study will contribute a great deal to control the photoresponses in the NIR region.

CONCLUSION

To clarify various factors affecting the CR band in intramolecular dimer radical cation, we synthesized *meso*-2,4-bis(4-(4-nitrostyryl)-pyridinium)pentane ditetraphenylborates. It showed very stable and strong CR bands in the NIR region, which corresponded to the formation of more stabilized intramolecualr dimer radical cation.

Acknowledgments
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