Facile Reduction of Zeolite-Encapsulated Viologens with Solvated Electrons and Selective Dispersion of Inter- and Intramolecular Dimers of Propylene-Bridged Bisviologen Radical Cation

Yong Soo Park,† Kyungmi Lee,‡ Chongmok Lee,*‡ and Kyung Byung Yoon*†
Department of Chemistry, Sogang University, Seoul 121-742, Korea, and
Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea

Received November 1, 1999. In Final Form: February 11, 2000

Zeolite-Y (Y), zeolite-L (L), mordenite (M), and ZSM-5 exchanged with methyl viologen \( \text{C}_4\text{V}_2 \) and \( \text{N}, \text{N}’\text{- trimethylenebis[1-methyl-4,4’-bipyridinium] (henceforth bisviologen) C}_4\text{V}_2\text{C}_3\text{V}_2 \) were prepared. Treatment of the dried, viologen-doped zeolites with solvated electrons in diethyl ether readily yields the corresponding viologen radical cation, i.e., \( \text{C}_4\text{V}_2\text{C}_3\text{V}_2^+ \) and \( \text{C}_4\text{V}_2^+ \) within the zeolite pores. Although \( \text{C}_4\text{V}_2\text{C}_3\text{V}_2^+ \) readily forms its intramolecular dimer \( \text{C}_2\text{V}_2\text{C}_2\text{V}_2^+ \) in solution, it remains in the open form in the four zeolites. \( \text{C}_2\text{V}_2\text{C}_2\text{V}_2^+ \) readily forms its intramolecular dimer \( \text{C}_2\text{V}_2\text{C}_2\text{V}_2^+ \) at high concentrations in L but not in other zeolites. However, \( \text{C}_4\text{V}_2\text{C}_3\text{V}_2^+ \) does not dimerize by itself in any of the four zeolites at high concentrations. \( \text{C}_2\text{V}_2\text{C}_2\text{V}_2^+ \) readily forms its intramolecular dimer in Y, L, and M when the pores are filled with water. The hydration-induced dimerization also works well for \( \text{C}_4\text{V}_2\text{C}_3\text{V}_2^+ \) in L and M. This leads to selective formation of the unprecedented intermolecular dimer of bisviologen radical cation, i.e., \( \text{C}_4\text{V}_2\text{C}_3\text{V}_2^+ \) in L and M. The intramolecular analogue \( \text{C}_2\text{V}_2\text{C}_2\text{V}_2^+ \) can also be dispersed into Y, L, and M by direct occlusion of its bisperchlorate salt from the acetonitrile solution. The broad ~530 nm band of the viologen radical dimer splits into two when the viologen radical moieties are forced to juxtapose in the collinear conformation within the narrow and straight channels of L and M. The near-infrared band of the viologen radical dimer progressively blueshifts with decreasing the interannular distance. This paper thus demonstrates a novel use of zeolites to selectively disperse inter- and intramolecular dimers of diradical dication and to lock the viologen radical dimers into the collinear conformation which allows us to delineate the spectral variation of viologen radical dimers with changing the interannular conformation and distance.

Introduction

Zeolites are widely used as catalysts, ion exchangers, sorbents, etc., in industry. For academic purposes, they have also been extensively employed as organizing media to induce long-lived charge separation in photochemistry, hosts for various semiconductor quantum dots, and nanoreactors for various organic transformations. The presence of repeating units of nanosized crystalline voids is one of the key features that confer zeolites such a broad applicability.

Viologens \( \text{V}^{2+} \) have been widely applied as herbicides, redox indicators, electron mediators for electrochromic displays, and relays in the photochemical and biological systems. The viologen radical cations \( \text{V}^+ \) have been


10.1021/la991430+ CCC: $19.00 © 2000 American Chemical Society
Published on Web 04/21/2000
known to readily dimerize in solution with increasing the polarity of the solvent \(^{17}\) (or by decreasing the temperature) and with enhancing the hydrophobic interaction of the radical cations by increasing the length of alkyl chains.\(^{18}\) The characteristic purple color of the dimeric forms \([V^+\cdot]_2\) readily distinguish themselves from the blue monomeric forms. Unlike monomers, the dimeric forms are inefficient in mediating electrons during catalytic generation of hydrogen from water.\(^{19}\) Accordingly, elucidation of the behavior of dimerization and the nature of dimeric states of viologen radical cations has been a subject of extensive research since it can provide insight into the effective use of viologens as electron mediators for various electrochromic and solar energy conversion devices. For this matter, cyclodextrins and micelles have been tested as the media to selectively induce or suppress dimerization of \(V^+\) and to organize the resulting radical dimers.\(^{18,20-22}\) None of the above-mentioned media, however, showed the ability to selectively entrap the inter- and intramolecular dimers of bisviologen radical cation \(C_1V_2^+\cdot C_3V_1^+\) and to orient the viologen radical cations to a specific conformation in the dimeric states.

Various methods have been developed to reduce the substrates encapsulated within zeolites. However, the fundamental difficulties associated with the heterogeneity of the reaction conditions limit their diversification. Nevertheless, various reduction methods have been developed by now, and they can be classified into three types depending on the source of electrons: physical, chemical, and electrochemical. The physical methods involve exposure of substrates-bearing zeolites to high-energy radiations such as vacuum-UV,\(^{23}\) X- or \(\gamma\)-rays,\(^{24}\) electron beams,\(^{25,27,29,30}\) and hot alkali metal vapors.\(^{1,27,29,30}\) Since the required reaction temperatures are usually high, thermally stable metal ions or metal oxides have often been the subjects of chemical reduction. The electrochemical methods, on the other hand, have been demonstrated to be more suitable for reducing thermally sensitive species in zeolites.\(^{31-34}\) The electrochemical methods also have drawbacks arising from the basic requirement that zeolite powders should be immobilized onto the electrode surface and from the need of electrolytes which often leach the positively charged electroactive species out of the zeolite pores into solution. This method is also unsuitable for large-scale preparations.

In this paper, we introduce a highly efficient method to reduce zeolite-encapsulated viologens and a novel use of zeolites to selectively disperse the inter- or the intramolecular dimer of \(C_1V_2^+\cdot C_3V_1^+\) within zeolites and to lock the viologen radical dimers in the collinear conformation within channel-type zeolites.

### Experimental Section

**Materials.** Zeolite-Y (LZY-52, Lot No. 960807061020-S), zeolite-X (ELZ-L, Lot No. 981887041001-S), and mordenite (LZM-5, Lot No. 962487061023-S) were purchased from Union Carbide. ZSM-5 with the Si/Al ratio of 13.5 was a gift from ALSI-PENTA Zeolite GmbH. For convenience, the former three are designated as Y, L, and M, respectively. The zeolites were treated with aqueous 1 M NaCl solution and then subsequently washed with distilled deionized water until the silver ion test for chloride was negative. For L, treatment with 1 M NaCl solution was repeated for five times to exchange with Na\(^+\) before the final washing with distilled deionized water.

Methyl viologen dichloride (\(C_1V_2^+\cdot 2CI^-\)) from Hannon Chemical Co. was recrystallized repeatedly until colorless, \(N^\prime-N^\prime\) trimethylelenbis(1-methyl-4,4'-pyridinium) tetraiodide (\(C_1V_2^+\cdot 4CI^-\cdot 2I^-\)) was synthesized in a stepwise manner according to the following procedure.\(^{31}\) Into the acetonitrile solution of 4,4'-bipyridine, 0.5 equiv of 1,3-diiodopropane was added in a dropwise manner over a period of 24 h while the temperature of the reaction mixture was maintained at 70 °C. This yielded \(N^\prime-N^\prime\)-trimethylelenbis(4,4'-pyridinium) diiodide (\(C_1V_2^+\cdot 4CI^-\cdot 2I^-\)). The yellow precipitate was recrystallized over a hot water. \(\mathrm{H}^+\) NMR (D\(2\)O): \(\delta = 9.05 (4H, d), 8.77 (4H, d), 8.46 (4H, d), 7.90 (4H, d), 4.50 (4H, t), 2.94 (2H, quin). The propylene-bridged bisbipyridinium diiodide (\(C_1V_2^+\cdot 4CI^-\cdot 2I^-\)) was subsequently treated with methyl iodide in \(N,N\)-dimethylformamide (DMF) at 90 °C over a period of 6 h to yield \(C_2V_2^+\cdot 2CI^-\cdot 2I^-\). The red precipitate was collected and recrystallized in cold water. \(\mathrm{H}^+\) NMR (D\(2\)O): \(\delta = 9.22 (4H, d), 9.08 (4H, d), 8.61 (4H, d), 8.52 (4H, d), 5.00 (4H, t), 4.50 (6H, s), 2.92 (2H, quin). The red iodide salt of \(C_2V_2^+\cdot 2CI^-\cdot 2I^-\) was converted to colorless perchlorate salt by metathesis before the final washing.

---


with NaClO₄ in water. Metallic potassium and 18-crown-6 were purchased from Aldrich. DMF was used as received (Aldrich).

**Ion Exchange.** C₃V₂Cl₂⁺ ion was introduced into zeolites by aqueous ion exchange of Na⁺. The exchanged amounts of C₃V₂Cl₂⁺ into zeolites were controlled to be 0.5 per unit cell (pcu) for lowly loaded zeolites. For highly loaded zeolites, the incorporated amounts were increased to 2 per supercage for zeolite-Y and 3 per supercage for channel-type zeolites. The unexchanged amounts of C₃V₂Cl₂⁺ ion in the wash were quantified by UV–vis spectrophotometry monitored at λ = 257 nm (ε = 2.0 × 10⁴ M⁻¹ cm⁻¹). The amounts of C₃V₂Cl₂⁺C₃V₂Cl₂⁺ exchanged into zeolites were controlled to be 0.025 pcu. The unexchanged amounts were quantified similarly with ε = 4.4 × 10⁴ M⁻¹ cm⁻¹ at 257 nm. All the viologen-doped zeolites were dried in the air at ambient temperatures. The air-dried zeolites were then briefly washed with methanol prior to subsequent evacuation (~10⁻³ Torr) for 2 h at room temperature. The dehydroxylation temperatures were then slowly increased to 200 °C. The samples were evacuated at the final temperatures for an additional period of 15 h and kept in the glovebox.

**Reduction of Zeolite-Encapsulated Viologens with Solvated Electrons.** 18-Crown-6 was purified by recrystallization in hot water. Diethyl ether was distilled over sodium and benzophenone. All the air- or moisture-sensitive compounds were handled in the glovebox charged with high-purity argon. Typically, 5 mL of diethyl ether was introduced into a vial containing 0.5 g of a dried, viologen-doped zeolite in the glovebox. To this slurry, metallic potassium and 18-crown-6 were added. The added amount of potassium was controlled to be slightly larger than 1 equiv with respect to the amount of C₃V₂⁺ moiety in the zeolite since excessive amounts result in reduction of the viologen moiety even to the neutral state. The added amount of crown ether was controlled to be 1 equiv to potassium. The slurry was then stirred until the supernatant solution stopped developing a blue color originating from solvated electrons. The obtained blue zeolites were filtered over glass frits and washed for three times with 5 mL of fresh diethyl ether. The blue zeolites were dried by evacuation for 10 min at room temperature.

**Reduction of C₃V₂Cl₂⁺ into Zeolites.** Acetonitrile was treated with KMnO₄ and distilled over P₂O₅. The distilled solvents were stored in Schlenk flasks under argon and transferred into a glovebox. The perchlorate salt of C₃V₂⁺ was reduced with 2e⁻ to generate the corresponding salt of diradical C₃V₂⁺⁻C₃V₂⁺⁻ClO₄⁻ by treating the parent bisviologen salt with zinc amalgam in acetonitrile solution until the absorption at 260 nm due to C₃V₂⁺⁻ moiety disappeared completely. Since this bisviologen radical cation exists in the intramolecular dimeric form, it should better be designated as C₃(V⁺⁺)₂. The concentration of the filtered solution of C₃(V⁺⁺)₂ClO₄⁻ was determined by UV–vis spectrophotometric measurements at 540 nm using the reported molar extinction coefficient of 2.7 × 10⁴ M⁻¹ cm⁻¹. Zeolites with Na⁺ as the counterion were dehydrated at 300 °C for 15 h and kept in the glovebox prior to salt occlusion. To an aliquot (0.3 g) of each dried zeolite, 2 mL of fresh CH₃CN was added to soak the dried zeolite before addition of the viologen doped zeolites. It is entirely different from that of solvated electrons in diethyl ether shown in Figure 2. From the fact that the absorption spectrum of C₃V₂⁺⁻ gives characteristic bands at 396 and 602 nm while that of the dimer [C₃V₂⁺⁻] gives the corresponding maxima at 360, 530, and 850 nm, the absence of absorption bands at around 850 nm in the spectra allowed us to conclude that C₃V₂⁺⁻ exists only in the monomeric form in all the four dry zeolites. This procedure also worked equally well for a 10 g scale of C₃V₂Cl₂⁺-doped zeolites. It is important to note that none of the methods listed in Introduction are suitable for this large, preparative scale.

**Results and Discussion**

**Reduction of Intrazeolite C₃V₂Cl₂⁺ and C₃V₂⁺⁻C₃V₂⁺⁻ with Solvated Electrons.** The colorless C₃V₂Cl₂⁺-doped zeolites (0.5 pcu) immediately turned blue upon treating with solvated electrons in diethyl ether. Diffuse reflectance spectra of the blue zeolites (dried) revealed the presence of methyl viologen radical cation C₃V₂⁺⁻ within the zeolites as demonstrated by its characteristic absorption bands shown in Figure 1 (left) for the four prototypical zeolites, Y, L, M, and ZSM-5. It is worth noting that the spectrum of C₃V₂⁺⁻ is entirely different from that of solvated electrons in diethyl ether shown in Figure 2. From the fact that the absorption spectrum of C₃V₂⁺⁻ gives characteristic bands at 396 and 602 nm while that of the dimer [C₃V₂⁺⁻] gives the corresponding maxima at 360, 530, and 850 nm, the absence of absorption bands at around 850 nm in the spectra allowed us to conclude that C₃V₂⁺⁻ exists only in the monomeric form in all the four dry zeolites. This procedure also worked equally well for a 10 g scale of C₃V₂Cl₂⁺-doped zeolites. It is important to note that none of the methods listed in Introduction are suitable for this large, preparative scale.

Small amounts of unreduced C₃V₂Cl₂⁺ were usually noticed in the diffuse reflectance spectra of the blue samples judging from the residual absorption band at 260 nm due to parent dication (not shown). We attribute the incomplete
solution to generate an intramolecular dimer, i.e., C$_3$-

[C$_1$V$^{2+}$C$_1V_2$]$^{2+}$; almost quantitatively. By contrast, the diffuse reflectance spectra of the blue zeolites, in particular those of Y and ZSM-5 (Figure 4, A and D), did not show even a trace of the absorption band at ~850 nm for C$_3$-

[C$_1$V$^{+}$]. Similar results were obtained from L and M. However, scrutiny of the spectra of L and M at longer wavelengths region revealed the presence of weak absorption bands at ~900 and ~1000 nm, respectively, for L and M due to dimeric forms of the bisviologen radical cation. Since the spatial restrictions imposed by the zeolite pores (~13 Å) do not allow the large bisviologen radical cation (~29 Å) to fold into the intramolecular dimeric conformation, the spectra of the blue zeolites shown in Figure 4, A through D (left), are concluded to arise from the open (unfolded) form of the bisviologen radical cation, i.e., C$_1V^{+}$-C$_3$-VC$_1^{+}$. This is a unique situation to freeze the bisviologen radical cation only in the open form.

The above results also demonstrate that solvated electrons generated from metallic potassium and 18-crown-6 in diethyl ether are very convenient and efficient for reduction of zeolite-encapsulated viologens. We believe this method can be extended for reduction of various other substrates encapsulated within zeolites. In fact, the use of solvated electrons for reduction of intrazeolite species was first introduced by Subb and Stucky and their co-workers. They generated solvated electrons by dissolving europium metal in liquid ammonia. Edwards and co-workers later used sodium and primary alkylamines as the sources of solvated electrons. We introduced a more convenient way to generate solvated electrons by using alkali metals and crown ethers in ethereal solvents. The solvated electrons have also been shown to be highly effective for generation of alkali metal ionic clusters within zeolites. The use of liquid ammonia and primary alkylamines does not bear any problem for such purposes. However, the highly basic media are not suitable for


dimerization of the radical cation within the narrowest channels (<7.1 Å) of L and M, unlike in solution. Zeolites thus provide a valuable opportunity to investigate the characteristic features regarding the intermolecular dimer of bisviologen radical cation which otherwise undergoes rapid folding in solution.

The enabled formation of intermolecular dimer of \( C_1 V^+ \cdot \cdot \cdot C_3 - V^{-} \) in ZSM-5 is understandable from the fact that the ZSM-5 channels are too narrow to overlap two viologen units in one channel. The comparison of the kinetic diameter of each viologen unit (5.85 Å) with the size of the channels (5.6 × 5.3 or 5.6 × 5.1 Å) clearly supports the reasoning. However, the failure to form \( C_1 V^+ \cdot \cdot \cdot C_3 - V^{-} \) in Y is rather surprising. This may arise if the bisviologen radical cations exist in the bent conformation with the propylene bridge residing in the window while the two \( C_3 - V^{-} \) units are confined separately in the two adjacent supercages.

The hydration-induced dimerization of \( C_1 V^+ \cdot \cdot \cdot C_3 - V^{-} \) was found to be reversible within zeolite pores. Thus, the purple hydrated zeolites readily recovered the original blue color upon dehydration under vacuum. Accordingly, the diffuse reflectance spectra also restored the initial monomeric forms.

It has been known that \( C_3 - V^{-} \) readily dimerizes in aqueous solutions but not in any organic solvents, including methanol. This phenomenon was attributed to the hydrophobic interaction of the radical cations in such a high-dielectric medium since the monocationic form of the large organic cation is more hydrophobic than its dicationic analogue. We ascribe the hydration-induced intermolecular dimerization of \( C_1 V^+ \cdot \cdot \cdot C_3 - V^{-} \) to the similar reasons discussed above. For this reason to be viable there should be experimental proof regarding that the actual micropolarity of zeolite pores exerting on the radical cations is less than that of water. Our previous results have indeed suggested that the actual micropolarity of the supercage of Y is comparable to that of 50% aqueous acetonitrile or 50% aqueous DMF. Ramanurthy and co-workers also found that thionin and the related dyes readily dimerize in the supercage of Y upon hydration.

The high dielectric constant of water was proposed to be responsible, at least partially, for the above phenomenon. On the contrary, neutral aromatic compounds, such as anthracene and pyrene, intercalated within zeolite pores are known to exist in the dimeric states in the anhydrous condition at high loading but dissociate into separate molecules upon hydration. These results are not directly relevant to ours since neutral guest molecules may well undergo aggregation in the anhydrous zeolite pores.

Subtraction of the monomer component from the composite (monomer and dimer) spectra in hydrated M (Figures 5C and 3C, right) revealed that the resulting dimer spectra show an extra band at 625 nm as shown in Figure 5, A and D. The strong hyperbolic effect of the pore lining water may be responsible for the appearance of the unusual band.

Incorporation of \( C_3 [C_1 V^+] \) within Zeolite Pores by Salt Occlusion. The closed form, \( C_3 [C_1 V^+] \), was also effectively dispersed into the zeolites by salt occlusion of

---

**References**

(45) The ratio of the isomer ratio at 360 (dimer) and 390 nm (monomer).
Neither hydration nor subsequent dehydration of the salt-occluded Y altered the spectrum of the purple zeolite. Thus, the spectrum shown in Figure 6A essentially does not change even after hydration as shown in the inset. Knowing the fact that the unfolded $C_3V^{+\cdot}C_2VC^{+\cdot}$ generated in situ within Y cannot form intermolecular dimer even with the aid of hydration, it is concluded that the only possible species that can give rise to the absorption of dimeric viologen radical cations is the occluded $C_3^{-}[C_1V^+]_2$.

Interestingly, the spectrum of purple Y also includes weak absorption bands of monomeric $C_3V^{+\cdot}$ moiety at 390 and 600 nm in the diffuse reflectance spectrum (Figure 6A). This strongly contrasts with the spectrum of $C_3^{-}[C_1V^+]_2$ in acetonitrile which shows only that of the dimeric form. Since it will be difficult to generate two monomeric $C_3V^{+\cdot}$ moieties (if once enters) by unfolding from $C_3^{-}[C_1V^+]_2$ within the supercages of Y (due to steric reasons), the absorption bands of the monomeric $V^{+\cdot}$ moiety should rather be concluded to arise from the open form of the bisviologen radical cation, i.e., $C_3V^{+\cdot}C_2VC^{+\cdot}$ which entered supercages as such. This strongly indicates that equilibrium must exist between the open and the closed forms in acetonitrile (eq 1) although this is not so apparent in solution due to the absence of the monomeric form in the spectrum.

$$C_3^{-}[C_1V^+]_2 \rightleftharpoons C_3V^{+\cdot}C_2VC^{+\cdot}$$

The estimated ratio for closed to open forms within Y was 1.4. Similar results were observed from L and M (Figure 6B,C), and the corresponding ratios were estimated to be ~1.5 for both channel-type zeolites. From the very high propensity of bisviologen radical cation to exist in the closed (folded) form in acetonitrile, the presence of the open form as much as 40% in the zeolite pores reflects much more facile incorporation of the open form from the solution into the zeolites. In the case of L, it is also interesting to note that the intensity of the NIR band dramatically increases and concomitantly blue shifts to 813 nm from the value of 850 nm in solution.

In the case of ZSM-5 with the channels being too small to accommodate dimeric forms of viologen radical cations, the developed color was blue than purple. The diffuse reflectance spectrum of the blue zeolite showed that the absorption bands arise mainly from the open form. This result further demonstrated the preference of $C_3^{-}[C_1V^+]_2$ to enter the zeolite pores in the open form as the pore size decreases. In the case of Y with large spherical cages, the equilibrium between the tightly closed and the slightly open forms may also exist, and this may contribute to the absorption of the monomeric $V^{+\cdot}$ moieties in the observed spectrum (Figure 6A) if the corresponding equilibrium constant is high in the supercages of Y.

### Relationship between the Conformation of the Dimeric Viologen Radical Cations and Observed Spectra.

The ~530 nm band of $[C_1VC_4^+]_2$ usually shows up as a broad, single absorption band in solution as shown in Figure 7A. So was the absorption band of the dimer in the large spherical cages of Y (Figure 7B). In contrast, however, the ~530 nm band accompanies a shoulder band at ~500 nm when the dimer was incorporated within the straight channels of L and M as shown in Figure 7C,D. The spectra of $C_3^{-}[C_1V^+]_2$ and $[C_1V^{+\cdot}C_2VC^{+\cdot}]_2$ assembled in the straight channels of L and M also showed the

---


(52) Scrutiny of the obtained spectra also revealed the presence of $V^{2\cdot}$ moiety. This indicates that oxidation of some of bisviologen radical cations also occurs during salt occlusion. Reduction of the resulted $C_3V^{2\cdot}$ moiety with solvated electrons did not alter the spectra shown in Figure 6.

(53) The ~530 nm band of $[C_1VC_4^+]_2$ in water was obtained by subtracting the corresponding spectrum of the monomer which exists in equilibrium with the dimer in water.
characteristic two-humped shape as demonstrated in Figure 7E–H. In fact, it should be noted that even the broad ~530 nm band of t3[C1V–C1+]2 in solution is not single Gaussian and can be decomposed into two absorption bands. In this regard the splitting of the ~530 nm bands of [C1V–C1+]2, C2[[C1V+]2], and [C1V–C1–C1V–C1+]2 into ~500 and ~530 nm bands within the straight channels of L and M is proposed to occur due to more pronounced displacement between the two closely overlapped bands in the straight channels than in solution or in the large spherical cage. The forced juxtaposition of the two viologen rings in the parallel or collinear conformation from the energetically more favorable one is proposed to give rise to the larger displacement between the two bands.

In a situation in which two V+ moieties are linked by two o-xylyl groups, the only possible conformation for the interannular interaction is the collinear one.40 The spectrum of this well-defined collinear structure also showed the splitting of the ~530 nm band with narrow channels (type III). On the basis of this reasoning, the intramolecular dimer C3[C1V+]2 is proposed to retain the collinear conformation both in solution and in the large spherical cages of Y.

As a corollary, the crossing conformation is proposed to be preferred in aqueous solutions and in the large spherical cages of Y. Consistent with this, the reported crystal structure of C2[V–C1+]2PF6 shows that the radical cation forms infinite stacks at an angle of 37° relative to the adjacent ones. The diffuse reflectance spectrum of the crystals also shows a broad ~530 nm band without a shoulder.44 Accordingly, we propose that the degree of splitting of the ~530 nm band can serve as a criterion for the degree of collinear conformation of the dimeric viologen radical cations [V+]+.

The zeolites employed in this study can be categorized into three types: Y with large spherical cages (type I), L and M with intermediate channels (type II), and ZSM-5 with narrow channels (type III). On the basis of the results described so far, the conformation of C1V–C1+]2 can be depicted according to Chart 1 (A and B), depending on the pore structure. Thus, in type I zeolites, the dimer is allowed to maintain the crossing conformation (A) as in the solid state or in solution. This crossing conformation can be rationalized to be more stable than the collinear one considering the steric repulsion between the two methyl groups and electrostatic repulsion between the nitrogen centers that carry high positive charge densities.

(B or C) was suggested to be unfavorable in solution, all the three conformations are possible within type II channels with some fractions of monomers. Thus, type II zeolites can provide a unique opportunity to disperse various intermolecular (A, B, and C) and intramolecular (D) dimers of bisviologen radical cation. In type II zeolites, only the monomeric bisviologen radical cation should be dispersed within the zeolites, as depicted in Chart 3E.

The sharp decrease of the bandwidth of the NIR band from 0.69 (fwhm) in \( Y \) to 0.34 eV in \( L \) and \( M \) might directly reflect the conformational difference of \([C_1VC_1^{+}]_2\) within the two different types of zeolite pores (I and II). In general, it is believed that the NIR band arises from the face-to-face charge-transfer (CT) interaction between the two \( V^{+} \) moieties. Although there are numerous factors that govern the spectral broadness for a given structure of a CT complex, the geometrical variation such as the variation of the interacting angle and the interannular distance between the two planar systems should in principle be taken into account for the observed spectral width. Since the intermolecular distance cannot vary significantly within the restricted confines of the zeolite pores, the angle variation between the two long plane axes is proposed to be partially responsible for the observed unusually large bandwidth of the NIR band in \( Y \).

The progressive blue shift of the NIR band of \([C_1VC_1^{+}]_2\) upon decreasing the pore size of the zeolite host (i.e., 920, 830, and 760 nm for \( Y, L \), and \( M \), respectively) is primarily ascribed to the decrease of the interannular distance between the two \( C_1VC_1^{+} \). The same trend was observed in a series of bisviologen radical cations linked by two bridges. However, the change in the geometry of the dimeric forms that could occur while the pore size decreases should also be considered to account for the observed blue shift. Nevertheless, from the same hypsochromic shift of the NIR band it can be inferred that the preferred site for \([C_1VC_1^{+}]_2\) is the large spherical cage of \( Y \) but not the connecting windows.

**Acknowledgment.** We thank the Korea Science and Engineering Foundation (KOSEF) for supporting this work (951-0303-024-2 and 97-05-01-04-01-3). K.B.Y. also thanks the Creative Research Initiatives Program of the Ministry of Science and Technology (MOST) of the Korean Government for financial support.

---

(55) Mulliken, R. S.; Person, W. B. Molecular Complexes; Wiley: New York, 1969; Chapter 8.