

Linkage Length Dependence of Intramolecular Photoinduced Electron Transfer Reactions in Aromatic Donor–Viologen Acceptor Molecules Linked by Polymethylene Bridges

Joon Woo Park,* Bi Ah Lee, and Soo Yeon Lee

Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea

Received: February 12, 1998; In Final Form: July 8, 1998

The intramolecular charge transfer (CT) complex formation and photoinduced electron-transfer reactions in aromatic donor–viologen acceptor dyad systems linked by polymethylene linkage $-(\text{CH}_2)_n-$ have been studied. The donors and the numbers of methylene unit in the linkages are 1-naphthoxyl with $n = 3, 6, 8$, and 10, 2-naphthoxyl with $n = 3-10$ and 12, and 2-dibenzofuranoyl with $n = 3, 6, 8$, and 10. The formation constants of the intramolecular CT complexes (K_{int}) were determined from the absorbance of CT absorption by using the absorptivities of the complexes determined from the intermolecular complexation between the model donor compounds, the 1-aryloxy-3-aminopropanes, and dimethyl viologen. The K_{int} values depend little on the length of the linkage and are about 0.2 for 1-naphthol and 2-naphthol derivatives, and 0.6 for dibenzofuranoyl derivatives. The addition of β -CD disrupts the formation of the intramolecular CT complexes. The 1:1 association constants of the dyad molecules with β -CD (K_{CD}) were estimated from the dependence of the CT absorption on the concentration of β -CD. Complexation of the dyad molecules with β -CD or methylated β -CD (Me- β -CD) also enhances the fluorescence intensity of the excited-state aromatic donors. The 1:1 complexes further associate with CD molecules resulting further enhancement of fluorescence intensity. This was attributed to the extension of the dyad molecules in the CD complexes. The electron-transfer quenching rate constants in the CD complexes formed in the presence of 150 mM Me- β -CD were calculated from fluorescence lifetime data and found to vary exponentially with the length of the linkage. The apparent β value is 0.86 \AA^{-1} ($1.09/\text{C}-\text{C}$ bond), regardless of the nature of donor moieties. The distance dependence of reorganization energies (λ) of the CD complexes was evaluated. Comparing the λ value with ΔG° of the reaction, it appears that the reactions stay near the top of the Marcus curve. Comparison of the effects of Me- β -CD on steady-state fluorescence intensity and excited-state lifetime indicated that through-space/through-solvent electron transfer is the predominant quenching pathway in the molecules having the linkage shorter than heptamethylene chain and the quenching rate is fast enough to show a static-like behavior.

Introduction

Photoinduced electron-transfer reaction plays a central role in photobiological processes, such as photosynthesis, and in various light-driven physical and chemical processes, and have drawn much interest in view of designing photochemical molecular devices and light energy conversion systems.^{1–7} The thermodynamic driving force for the electron-transfer reactions, the nature of intervening medium, and the distance and orientation between the donor and the acceptor affect the rate of the reactions.^{1,2} Among these, the distance is generally considered as the most important factor. To test the theoretical models of electron-transfer reactions and to design photochemical molecular devices, it is necessary to obtain electron donor (D)–acceptor (A) systems having restricted distance and orientation between D and A. This can be achieved by assembling of the donor–acceptor pair into supramolecular complexes,^{3,4} in monolayers at controlled distances,⁵ or in layered metal phosphonates.⁶ Another strategy is the synthesis of covalently bonded D–L–A molecules, where the linkage L is rodlike bridge consisting of steroid, norbornyl, aromatic, trypticene, or proline groups;^{2,7} the electron-transfer rate constant (k_{et}) varies exponentially with the distance (r_{DA}) between the

donor and the acceptor groups following $k_{\text{et}} = A \exp(-\beta r_{\text{DA}})$, where the β value depends on the nature of the linkage.

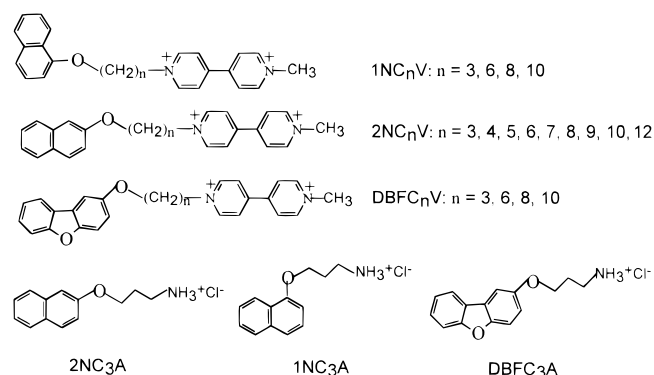
The D–L–A molecules with a flexible bridge-like polymethylene chain, $-(\text{CH}_2)_n-$, are easier to prepare than the molecules with rigid bridges. However, the study on the distance dependence of the electron-transfer reactions in the D–L–A molecules with flexible bridges is usually complicated due to a distribution of rate constants corresponding to different conformations of the molecules.⁸ A strategy to alleviate this difficulty is to extend the flexible chain with a complexing agent. It has been shown that cyclodextrins (CD), which are torus-shaped oligosaccharides capable of forming inclusion complexes with a variety of hydrophobic species in aqueous solutions,^{9,10} form rotaxane-type complexes with D–L–A molecules having polymethylene linkages and extend the molecules.^{11–15} This results in inhibition of intramolecular charge-transfer interaction^{11,12} and photoinduced electron-transfer reactions^{13,15} between the donor and acceptor.

Viologen (1,1'-dialkyl-4,4'-bipyridinium salt) is a prototypical electron acceptor moiety in photochemical donor–acceptor systems. Several groups^{13,16,17} have prepared D– $(\text{CH}_2)_n$ –A type molecules having viologen as an electron acceptor (A) and studied intramolecular electron transfer reactions in the molecules, where the electron donor (D) was mostly Ru(II) complexes, e.g., Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine). However,

* Corresponding Author. Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea. Tel: 82-2-360-2346. Fax: 82-2-360-2384. Internet: jwpark@mm.ewha.ac.kr.

there is little systematic study on the dependence of k_{et} on the length of the polymethylene bridge. Yonemoto et al. demonstrated that the polymethylene bridges of $\text{Ru}(\text{bpy})_3^{2+}-(\text{CH}_2)_n$ -viologen molecules, where $n = 7$ and 8, are extended by complexation with β -CD and that the k_{et} values of the extended molecules follow the same exponential dependence on r_{DA} as the molecules of shorter linkages ($n \leq 5$).¹³ They also reported that k_{et} of $\text{Ru}(\text{bpy})_3^{2+}-(\text{CH}_2)_n$ -viologen molecules ($n = 2-5, 7, 8$) decreases with increasing spacer length at zeolite-solution interface, where the aliphatic spacers and viologen are encapsulated by the zeolite framework.¹⁶

In this paper, we present the studies on the charge-transfer interaction and photoinduced electron transfer quenching reactions in a series of aromatic donor-viologen acceptor molecules covalently linked by polymethylene chains in the presence and absence of β -CD. The structures of the dyad molecules and model donor molecules which lack the viologen acceptor are shown below. We also evaluated the dependence of association constants of the aromatic- $(\text{CH}_2)_n$ -viologen molecules with β -CD on the length of linkage. The aromatic groups are selected as electron donor for the following reasons. First, the aromatic groups are good excited-state electron donors with oxidation potential of ca. 2.0 V¹⁸ and their intermolecular photoinduced electron-transfer reactions with viologen were reported in solution and in zeolite supercages.¹⁹ Second, they form ground-state charge-transfer complexes with viologens.^{4,11,12,20} Due to the flexibility of the linkage, the intramolecular charge-transfer interaction and thus photoinduced electron-transfer quenching reactions are expected to be facilitated. Third, the aromatic moiety as well as the aliphatic linkage is included into the cavity of β -CD.^{4,21,22} This allows the extension of the molecules consisting of the polymethylene linkages shorter than the depth of β -CD cavity by β -CD and enables us to investigate the dependence of k_{et} on the donor-acceptor distance in a wide range.



Experimental Section

Materials. The donor-acceptor dyad compounds were prepared according to a reported Scheme¹² by coupling aromatic hydroxyl compounds with 1, ω -dihaloalkane, followed by the reaction with 1-methyl-4,4'-bipyridinium iodide. Counteranions were exchanged to chloride by stirring the aqueous solution of the product in the presence of AgCl. All compounds gave appropriate ¹H NMR spectra (250 MHz) and elemental analysis data. The syntheses of the model donors, 3-(1-naphthoxyl)-1-aminopropane (1NC₃A), 3-(2-naphthoxyl)-1-aminopropane (2NC₃A), and 3-(2-dibenzofuranoxyl)-1-aminopropane (DBFC₃A), were reported previously.⁴ β -CD and methylated β -CD (Me- β -CD: degree of methyl substitution = 12-13; MW = 1318) were obtained from Aldrich and Cyclolab (Hungary), respectively, and used as received. The concentration of β -CD solutions was calculated from optical rotation data

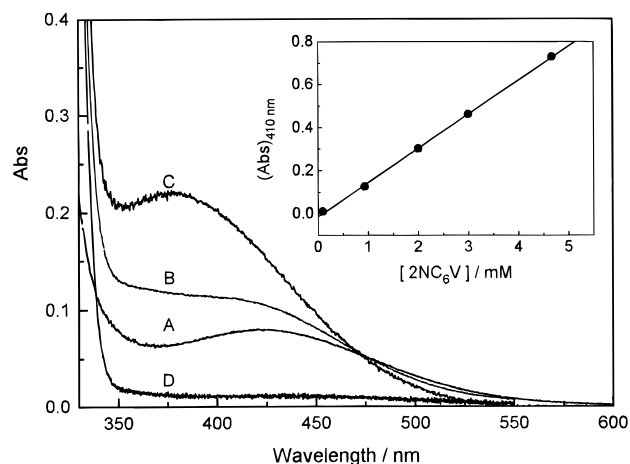


Figure 1. Absorption spectra of 1.0×10^{-3} M 1NC₆V (A), 2NC₆V (B), DBFC₆V (C), and equimolar (1.0×10^{-3} M) mixture of 2NC₃A and MV²⁺ (D). Inset shows the concentration dependence of the absorbance of 2NC₆V at 410 nm.

using $[\alpha]_{\text{D}}^{25} = 162.5^\circ$.⁹ Other chemicals were obtained from Aldrich and used without further purification. All solutions were prepared with distilled deionized water and adjusted to fixed ionic strength of 0.3 M with NaCl and pH 6.0 with 0.01 M cacodylate buffer.

Measurements. ¹H NMR spectra (250 MHz, D₂O solution) were measured with a Bruker DPX250 FT-NMR spectrometer. Absorption spectra were recorded with a GBC UV-vis 920 spectrophotometer. Difference spectra of charge-transfer complexation were taken with mixing tandem double cells of light path length of 0.882 cm, which are partitioned into two equal compartments, using the unmixed solutions as blank. For intermolecular complexation between the model donors and dimethyl viologen (MV²⁺), 1.0 mM donor solutions were titrated with MV²⁺ solution (30-150 mM) spectroscopically. The concentration of donor-acceptor dyad molecules was kept below 2.5 mM to avoid intermolecular association. Steady-state fluorescence spectra were obtained with a Hitachi F-3010 spectrofluorimeter from the solutions having absorbance below 0.1 at exciting wavelength. Excited-state lifetimes were measured with a picosecond time-resolved single photon counting system assembled at Korea Standard Research Institute. All measurements were carried out at 25 °C using appropriate temperature controller.

Results and Discussion

We first describe the intramolecular charge transfer complexation behavior of the covalently linked aromatic donor-viologen acceptor molecules and then association of the molecules with β -CD. We then present the results of steady-state fluorescence intensity and fluorescence lifetime experiments and explain how the intramolecular charge-transfer interaction and inclusion complexation with β -CD affect the distance dependence of the photoinduced electron-transfer reactions in the dyad molecules.

Intramolecular Charge-Transfer Complexation Behavior of Aromatic- $(\text{CH}_2)_n$ -Viologen Molecules. The covalently linked aromatic-viologen compounds show a diffused absorption band above 350 nm, which is not observed from the components of the dyad molecules (Figure 1). The absorbance value of the band was directly proportional to the concentration of the compounds. The new absorption bands are also observed in the mixtures of the model donors and MV²⁺, when the concentration of MV²⁺ is high. The absorption in the linked

TABLE 1: Parameters for Intermolecular Charge-Transfer Complexation between Ar–O–(CH₂)₃–NH₃⁺ and Dimethyl Viologen in Aqueous Solutions at 25 °C

| Ar | λ_{CT}/nm | $\epsilon_{CT}/M^{-1}cm^{-1}$ | K_{CT}/M^{-1} |
|-------------------------|-------------------|-------------------------------|-----------------|
| 1-naphthol | 422 ^a | 580 ± 70 | 3.7 ± 0.5 |
| 2-naphthol ^b | 410 ^b | 720 ± 50 | 3.6 ± 0.4 |
| 2-dibenzofuranol | 380 ^a | 580 ± 80 | 10.6 ± 0.7 |

^a Band maximum in difference spectra. ^b Not an isolated peak, but used to calculate the concentration of the intramolecular complex of 2NC_nV molecules.

compounds is due to intramolecular charge-transfer interaction and similar phenomena were observed with polymethylene chain linked carbazole–viologen¹¹ and anthracene–viologen¹² dyad molecules.

For a given donor moiety, the shape of the difference spectra of the charge transfer absorption depends little on the length of linkage. Also, the spectra were virtually identical to those of intermolecular complexes which were obtained with the corresponding model donors in the presence of high concentration of MV²⁺. This implies that the UV–vis spectroscopic characteristics of the intramolecular complexes are the same as the corresponding intermolecular complexes. The molar absorptivity (ϵ_{CT}) and the formation constants of the intermolecular complexes (K_{CT}) were obtained from the analysis of the spectroscopic titration data of the model donor solution with MV²⁺ according to the Benesi–Hildebrand method (data not shown).²³ The results are summarized in Table 1.

It was shown that the π -ring systems of the charge transfer complexes are arranged cofacially to give the face-to-face interaction between the aromatic donor and viologen acceptor.²⁴ For such an interaction in the linked compounds, folding of the polymethylene linkage is required. The folded form is in equilibrium with the open extended conformer. The equilibrium constant for the intramolecular complexation (K_{int}) is defined as the ratio of the folded form to the open form.

Open (uncomplexed) \rightleftharpoons folded (CT-complex)

$$K_{int} = [\text{folded}]/[\text{open}] \quad (1)$$

The open form also gives charge-transfer absorption, though the magnitude of the absorption is much smaller than that of folded compact complex form.^{12,25} The absorbances of the long-range charge transfer (A_{∞}), which is the value expected when all of the molecules are present as open form, were estimated from the dependence of the charge-transfer absorption on the concentration of β -CD (vide infra). K_{int} values were calculated from eq 2 using the absorbance of charge-transfer band (A_{CT}) and A_{∞} value: C_o denotes the total concentration of the donor–acceptor molecule. The results, together with the absorptivities of the long-range charge-transfer absorption, $\epsilon_{\infty} = A_{\infty}/C_o$, were given in Table 2 (for method of calculation of these values, see the following section).

$$K_{int} = (A_{CT} - A_{\infty})/(C_o\epsilon_{CT} - A_{\infty}) \quad (2)$$

Table 2 shows that the intramolecular complex of dibenzofuranoyl–viologen system is more stable than the naphthoxyl–viologen complexes, and the position of substitution on naphthalene ring makes little difference in the stability of the intramolecular complexes. This trend accords well with the tendency of intermolecular complexation shown in Table 1.

Another interesting point in this work is the chain length dependence of the intramolecular interaction. Craenen et al. reported that the charge-transfer interaction in a series of

polymethylene chain-linked donor–acceptor molecules is greatest for trimethylene chain and decreases as the chain becomes longer.²⁶ On the other hand, Yonemura and co-workers reported that the intramolecular interaction between carbazole and viologen is favored for either a short ($n = 4$) or a long spacer ($n = 10$ and 12), but not for a medium sized linkage ($n = 6$ and 8).^{11a} It seems that the spacer length dependence of the intramolecular charge transfer interaction is highly dependent on the nature of the donor and acceptor pair, presumably due to the requirement of well-defined geometry for the optimum interaction.

Formation of β -CD Complexes of the Donor–Acceptor Molecules and Disruption of the Charge-Transfer Interaction. The addition of β -CD to a solution of the dyad molecules decreases the charge-transfer absorption (Figure 2). This is due to the complex formation between β -CD and the molecules: the face-to-face charge transfer interaction between donor and viologen moieties is inhibited sterically in the β -CD complexes. Considering the cavity size of β -CD, only the open form is considered to be in equilibrium with β -CD complex.

open + β -CD \rightleftharpoons β -CD complex

$$K_{CD} = \frac{[\beta\text{-CD complex}]}{[\text{open}][\beta\text{-CD}]} \quad (3)$$

Of course, the 1:1 β -CD complexes of the dyad molecules having longer spacer can bind with another β -CD molecule to form 1:2 complexes at high β -CD concentration. However, we can soundly assume that only 1:1 complexes are formed at low concentration of β -CD.²⁷ Under this condition, the fractional change of the charge-transfer absorption caused by β -CD is the fraction of the dyad molecules complexed with β -CD. Thus, the concentration of free β -CD, $[\beta\text{-CD}]$, is calculated from total concentrations of β -CD ($[\beta\text{-CD}]_{\text{total}}$) and the dyad molecule (C_o), and the A_{CT} values from eq 4.

$$[\beta\text{-CD}] = [\beta\text{-CD}]_{\text{total}} - \frac{[(A_{CT})_{[CD]=0} - (A_{CT})_{CD}]/[(A_{CT})_{[CD]=0} - A_{\infty}]C_o}{1} \quad (4)$$

where $(A_{CT})_{CD}$ and $(A_{CT})_{[CD]=0}$ are the absorbances of the charge-transfer band in the presence and in the absence of β -CD, respectively.

From the mass balance of the dyad molecules, the ratio of the fraction of the compact charge-transfer complex in the presence of β -CD (f_{CD}) to the fraction in the absence of β -CD ($f_{[CD]=0}$) is related to the equilibrium concentration of the free β -CD, K_{int} , and K_{CD} by eq 5.

$$\frac{f_{CD}}{f_{[CD]=0}} = \frac{(A_{CT})_{CD} - A_{\infty}}{(A_{CT})_{[CD]=0} - A_{\infty}} = \frac{1 + K_{int}}{1 + K_{int} + K_{CD}[\beta\text{-CD}]} \quad (5)$$

A brief description of the procedure for the estimation of K_{int} , K_{CD} , and A_{∞} values from the equations is as follows. We used the absorbance taken in the presence of 70 mM Me- β -CD as a trial value of A_{∞} . Using this value, the trial K_{int} was estimated from the charge-transfer absorbance measured in the absence of β -CD using eq 2. From the absorption data taken at various concentrations of β -CD, $[\beta\text{-CD}]$ and then K_{CD} values were estimated from eqs 4 and 5. A_{∞} and then the estimated K_{int} values were adjusted until the K_{CD} values calculated at various β -CD concentrations agree with each other in a reasonable range.²⁸ The fitted results are summarized in Table 2.

The association of a dyad molecule with β -CD is schematically presented in Scheme 1. For the compounds having short linkage, the complexation is mainly inclusion of the aromatic

TABLE 2: Equilibrium Constants of Intramolecular Charge Transfer Complexes (K_{int}), Long-range Charge Transfer Absorptivity (ϵ_{∞}) of Open Form, the 1:1 Association Constants with β -CD (K_{CD}), and Fluorescence Lifetimes (τ_{F}) and Photoinduced Electron Transfer Rate Constants (k_{et}) of Ar-O-(CH₂)_n-Viologen in Aqueous Solutions at 25 °C

| n | K_{int}^a | $\epsilon_{\infty}/\text{M}^{-1}\text{cm}^{-1}$ | $(K_{\text{CD}}/\text{M}^{-1})^b$ | in water ^c | | in 0.15 M Me- β -CD ^d | |
|----------------------------|--------------------|-------------------------------------------------|-----------------------------------|-----------------------------|-------------------------------------|----------------------------------------|-------------------------------------|
| | | | | $\tau_{\text{F}}/\text{ns}$ | $k_{\text{el}}/10^9 \text{ s}^{-1}$ | $\tau_{\text{F}}/\text{ns}$ | $k_{\text{el}}/10^9 \text{ s}^{-1}$ |
| 1NC _{<i>n</i>} V | | | | | | | |
| 3 | 0.20 | 65 | 150 ± 50 | | | | |
| 6 | 0.20 | 16 | 270 ± 90 | 0.053 | 19 | 0.073 | 14 |
| 8 | 0.21 | 11 | 690 ± 210 | 0.19 | 5.2 | 0.50 | 1.9 |
| 10 | 0.21 | 8 | 4300 ± 700 | 0.41 | 2.4 | 2.9 | 0.25 |
| 2NC _{<i>n</i>} V | | | | | | | |
| 3 | 0.16 | 33 | 450 ± 160 | | | | |
| 4 | 0.23 | 15 | 660 ± 90 | 0.021 | 48 | 0.028 | 35 |
| 5 | 0.23 | 15 | 1100 ± 200 | 0.046 | 22 | 0.056 | 18 |
| 6 | 0.23 | 15 | 1500 ± 400 | 0.10 | 9.9 | 0.10 | 18 |
| 7 | 0.13 | 14 | 2200 ± 540 | 0.18 | 5.6 | 0.24 | 4.1 |
| 8 | 0.15 | 12 | 2800 ± 620 | 0.35 | 2.8 | 0.75 | 1.3 |
| 9 | 0.10 | 11 | 3100 ± 730 | 0.51 | 1.9 | 2.4 | 0.34 |
| 10 | 0.18 | 9 | 3700 ± 910 | 0.71 | 1.3 | 5.1 | 0.12 |
| 12 | 0.14 | 9 | 5700 ± 700 | 1.02 | 0.90 | 10.0 | 0.017 |
| DBFC _{<i>n</i>} V | | | | | | | |
| 3 | 0.62 | 47 | 1900 ± 300 | | | | |
| 6 | 0.60 | 13 | 2300 ± 200 | 0.066 | 15 | 0.086 | 11 |
| 8 | 0.58 | 10 | 4200 ± 700 | 0.26 | 3.7 | 0.72 | 1.2 |
| 10 | 0.62 | | | 0.51 | 1.7 | 2.5 | 0.21 |

^a The estimated uncertainty is ca. 20% mainly due to the error in ϵ_{CT} . However, relative uncertainty among the values for the same homologous series is estimated to be less than 10%. ^b Average \pm standard deviation of the values obtained at more than seven different concentrations of β -CD.

^c The fluorescence lifetimes of Ar-O-(CH₂)₃-NH₃⁺ were 8.51, 11.7, and 4.40 ns for Ar = 1-naphthol, 2-naphthol, and DBF, respectively. ^d The fluorescence lifetimes of Ar-O-(CH₂)₃-NH₃⁺ were 9.47, 12.2, and 5.37 ns for Ar = 1-naphthol, 2-naphthol, and DBF, respectively.

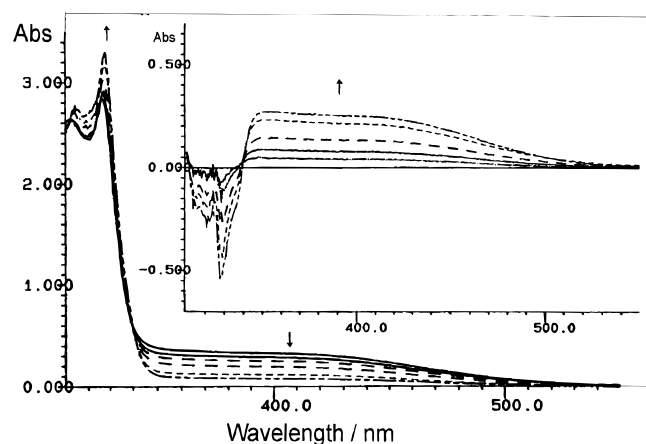
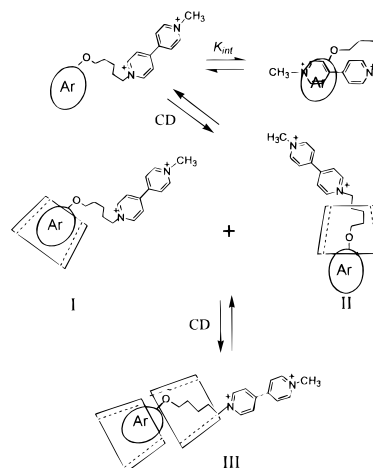


Figure 2. Effect of β -CD on the absorption spectra of 2.2×10^{-3} M 2NC₆V. The concentrations of β -CD are 0.00, 0.47, 0.97, 1.94, 3.88, and 7.75 mM. Inset shows the difference spectra, which correspond to the spectra of complexes dissociated by the addition of β -CD, calculated by subtracting the spectrum taken in the presence of β -CD from the spectrum in the absence of β -CD. The arrows indicate the increasing direction of the concentration of β -CD.

moieties of the compound into the cavity of β -CD (complex I in Scheme 1). The similarity of the magnitude of the K_{CD} values for the dyad molecules having trimethylene linkage with the association constants of the corresponding model donors with β -CD⁴ supports this. As the linkage becomes longer, the K_{CD} value increases reflecting the contribution of the linkage to β -CD binding. The increase of the K_{CD} values with the linkage length is observed even when the length of linkage is shorter than the depth of β -CD-cavity, ca. 7 Å, which corresponds to the length of hexamethylene chain. This suggests that the complexes of type II, where β -CD extends over the aromatic moiety and polymethylene linkage, are also formed. The CPK model and ¹H NMR spectra²⁹ showed little steric and energy barrier for penetration of β -CD through the aromatic moieties. This is quite

SCHEME 1. Schematic Presentation of Complexation of the Dyad Molecules with β -CD. The Position of β -CD in Complexes II and III Depends on Length of Linkage. Also, the Orientation of β -CD in the Complexes Can Be Reversed



different from the behavior of R-(CH₂)_n-viologen, where R is anthracene,¹² carbazole,¹¹ phenothiazine,¹⁵ or Ru(bpy)₃²⁺.¹³ In those compounds, inclusion of the R groups and viologen moiety into the cavity of CD is highly unfavorable because of their bulkiness and/or hydrophilicity, and therefore the complexation of the dyad molecules with CD is expected only for the molecules having polymethylene linkage longer than the depth of CD cavity. This limits the studies of the molecules on the chain length dependence of CD complexation and properties of the CD-extended molecules to those having the linkages longer than hexamethylene chain. Molecules in the present work do not suffer the limitation.

Photoinduced Electron-Transfer Reactions. The photoinduced electron-transfer reactions in the aromatic donor–

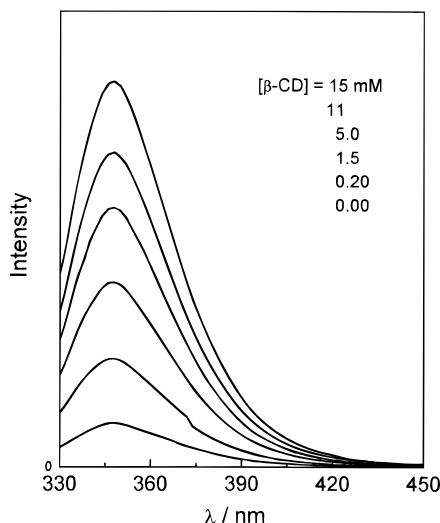


Figure 3. Fluorescence spectra of 5.0×10^{-5} M 2NC₁₀V solution in the presence of various concentrations of β -CD.

viologen acceptor molecules were studied by steady-state fluorescence intensity and lifetime measurements.

The fluorescence intensity of the aromatic moiety of the linked compounds is much less than that of the corresponding model donors which lack viologen acceptor. This reflects extensive intramolecular quenching in the dyad molecules. Since there is little overlap between the fluorescence spectra of donor moieties and absorption spectra of the viologen, the possibility of the energy transfer quenching is ruled out and the quenching is attributed to the electron transfer from excited donor moieties to viologen. When β -CD or its derivative is added, a large enhancement of emission intensity without noticeable change in spectral shape is observed (Figure 3). The enhancement could be partly due to the increase in the fluorescence quantum yield of the aromatic donors upon binding to β -CD.²² A previous study⁴ with the model donors indicated that the enhancement is 20–50%, which is far less than the observed enhancement with the dyad molecules. Thus, a major contribution to the enhancement is attributed to the decrease of intramolecular electron-transfer quenching by the formation of rotaxane-type CD complexes.¹⁵

The solubility of β -CD in water is 1.85 g/100 mL (16.3 mmol/L). As is judged from K_{CD} values (Table 2), the solubility is not high enough to convert the linked compounds, especially those of naphthalene derivatives having short linkage, into the β -CD complexes quantitatively. Also, the fluorescence intensity vs $[\beta\text{-CD}]$ profile does not show saturation behavior in the solubility limit of β -CD even for the molecules whose K_{CD} value is large enough to expect almost quantitative formation of β -CD complexes. The latter behavior implies that the donor–acceptor pair is further apart by association of another β -CD molecules with the 1:1 β -CD/dyad complexes to form CD-complexes of higher stoichiometric ratio (type III complex in Scheme 1). For this reason, we used Me- β -CD (solubility > 40 g/100 mL) to examine the fluorescent properties of β -CD complexes of the linked compounds: at the same concentration, β -CD and Me- β -CD showed similar effects on the absorbance and fluorescence intensity indicating that the methyl substitution of β -CD does not change the binding property of the host with the dyad molecules significantly. The dependence of fluorescence intensity of 1NC_{*n*}V series molecules on the concentration of Me- β -CD is shown in Figure 4. The compounds of other series exhibited similar trend. The fluorescence intensity is virtually leveled off when the concentration of Me- β -CD is above 100

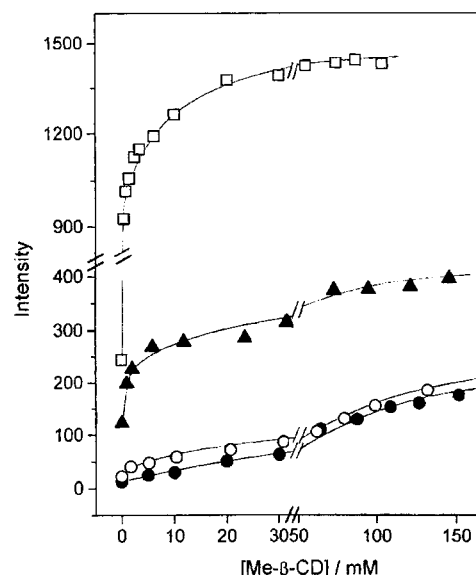


Figure 4. Dependence of fluorescence intensity of 1NC_{*n*}V on the concentration of Me- β -CD. The measured emission intensity was corrected for inner filter effects and light absorbed by $I_{\text{corr}} = I_{\text{obs}} \text{antilog}\{-(A_{\text{ex}} + A_{\text{em}})/2\}/(1 - 10^{-A_{\text{ex}}})$. Excitation and emission wavelengths are 310 and 370 nm, respectively. The numbers of methylene units in the linkage are 3 (●), 6 (○), 8 (▲), and 10 (□).

mM. Thus we measured the fluorescence lifetimes of the dyad molecules in the presence of 150 mM Me- β -CD to investigate the linkage length dependence of the electron-transfer quenching rate of the dyad molecules encased by CD.

The fluorescence of the linked compounds decayed single exponentially with lifetimes smaller than those of the model donors. The fluorescence lifetime data obtained from the decay profiles taken in water and in the presence of 150 mM Me- β -CD are compiled in Table 2. The entry and exit rate constants of naphthalene or alkyl groups into and from the β -CD cavity are usually on the order of $10^7 \text{ M}^{-1} \text{ s}^{-1}$ and 10^4 s^{-1} , respectively,³⁰ while the rate constants for the decay of the excited state of the dyad molecules are greater than 10^8 s^{-1} . Thus we can soundly assume that the CD complexes remain frozen in the time scale of the excited-state's lifetime. Therefore, we can regard the lifetimes obtained in the presence of 150 mM Me- β -CD as those of the type III CD-complexes which adapt extended form held by β -CD. Without β -CD, various spacer chain conformations are possible. However, the time scale of the conformational changes is shorter than or comparable to the excited-state lifetime giving single-exponential fluorescence decay profile.¹³ The intramolecular electron-transfer rate constants were calculated from eq 6 and included in Table 2: we took the fluorescence lifetimes of the corresponding model donors as τ_0 .

$$k_{\text{et}} = 1/\tau - 1/\tau_0 \quad (6)$$

Figure 5 summarizes the dependence of electron-transfer rate constants on the length of the linkages. The rate constant k_{et} determined in the presence of Me- β -CD decreases exponentially with the length of linkage. The apparent β value is 1.09 per methylene unit, which corresponds to 0.86 \AA^{-1} as the through-bond length increases by 1.27 \AA per CH_2 group.¹³ This value is smaller than that for forward electron transfer (1.38 \AA^{-1}) in $\text{Ru}(\text{bpy})_3^{2+}-(\text{CH}_2)_n$ -viologen, but greater than the value for backward thermal electron transfer (0.66 \AA^{-1}) in the charge-separated state of the Ru(II)-viologen system.¹³ How-

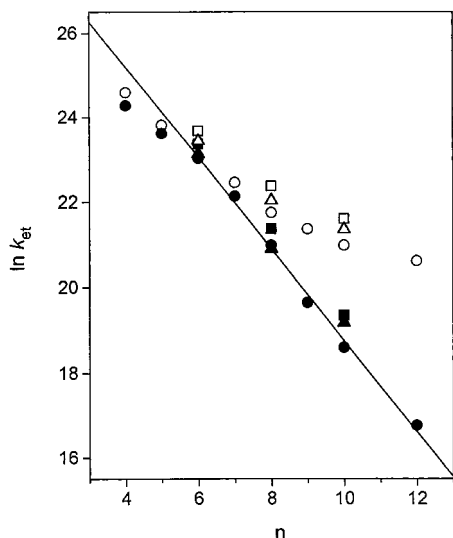


Figure 5. Dependence of electron-transfer quenching rate constants on the number of carbon atoms (n) of linkages of $1\text{NC}_n\text{V}$ (■, □), $2\text{NC}_n\text{V}$ (●, ○), and DBFC_nV (▲, △). Filled symbols are data taken in 150 mM Me- β -CD, and open symbols are in water. Solid line is drawn for $\beta = 1.09$ per methylene unit.

ever, the value is close to $0.85\text{--}0.88 \text{ \AA}^{-1}$ obtained for the preexponential factor of k_{et} (proportional to $|V|^2$, see below) of norbornyl bridge-linked dimethoxynaphthalene-dicyanovinyl systems.³¹ In the absence of Me- β -CD, the linearity between $\ln k_{\text{et}}$ and the number of carbon atoms (n) of the linkage is observed up to $n = 6$ and the dependence of k_{et} on n becomes much weaker for longer linkage. This parallels the observation with $\text{Ru}(\text{bpy})_3^{2+}\text{--}(\text{CH}_2)_n\text{--viologen}$ molecules.¹³

In the classical limit, the k_{et} of a covalently bonded donor-acceptor system is related to the electron coupling matrix element between donor and acceptor ($|V|$), standard Gibbs free energy change of the electron-transfer step (ΔG°), and the sum of molecular (λ_i) and solvent (λ_s) reorganization energies (λ), where $\lambda = \lambda_s + \lambda_i$, by eq 7.^{7,13,32}

$$k_{\text{et}} = (2|V|^2/h) (\pi^3/\lambda RT)^{1/2} \exp[-(\Delta G^\circ + \lambda)^2/4\lambda RT] \quad (7)$$

The $|V|^2$ term depends strongly on donor-acceptor distance decreasing exponentially with the r_{DA} . Also, the solvent reorganization energy λ_s depends on the distance. To extract the distance dependence of $|V|^2$, it is necessary to know the dependence of λ_s on r_{DA} . We applied the simple Marcus two-sphere model³³ to estimate the dependence of λ_s on distance.

$$\lambda_s = (e^2/4\pi\epsilon_0)(1/2r_D + 1/2r_A - 1/r_{\text{DA}})(1/\epsilon_{\text{op}} - 1/\epsilon_s) \quad (8)$$

In eq 8, r_A and r_D are radii of the acceptor and donor group, and ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent. As a matter of fact, the model cannot be applied to the present systems as the donor and acceptor are not spherical, and they are in different solvent microenvironment. However, an estimation of λ_s is possible with the model using the approach of Yonemoto et al.¹³ The r_{DA} values were estimated from CPK model by assuming fully extended conformation for the CD complexes. The average radii of viologen¹³ and 2-naphthyl³⁴ groups were taken as 4.8 and 5.1 Å, respectively, from literature. The estimated solvent reorganization energies of $2\text{NC}_n\text{V}$ molecules are in the range of 1.04 (for $n = 5$)–1.24 eV (for $n = 12$).

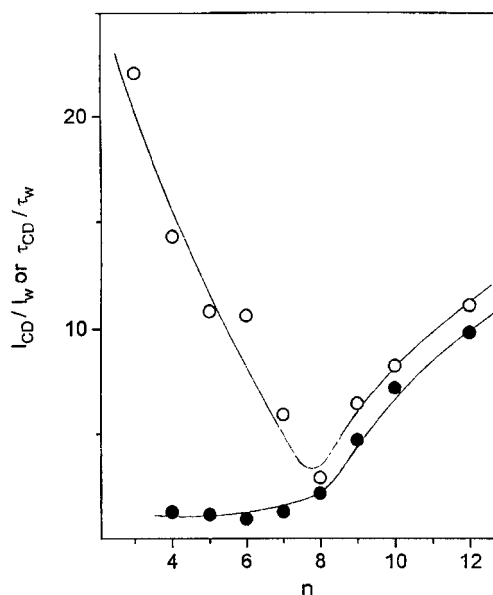


Figure 6. Linkage length dependence of the enhancement in fluorescence intensity (○) and lifetime (●) of $2\text{NC}_n\text{V}$ by the addition of Me- β -CD (150 mM).

The oxidation potentials of $1\text{NC}_3\text{A}$ and $2\text{NC}_3\text{A}$ in water are measured to be $1.30 \pm 0.03 \text{ V}$. The emission maxima of the compounds are ca. 350 nm, and the reduction potential of the viologens is about 0.47 V in water. These data give ΔG° of the electron-transfer reaction as -1.7 eV . To estimate the total reorganization energies, we used 0.45 eV as λ_i .^{7,34} From these and λ_s values, the $(\Delta G^\circ + \lambda)$ values are estimated to be in the range of -0.01 (for $n = 12$) to -0.21 eV (for $n = 5$): though the full extension of the molecules is not ensured, the weak dependence of λ_s on the donor-acceptor distance suggests that the $(\Delta G^\circ + \lambda)$ values may not differ significantly from 0. This implies that the reaction in the present systems might stay near the top of the Marcus curve. The β value calculated for the dependence of $|V|^2$ on r_{DA} using eq 7 was 0.87 \AA^{-1} . The similarity of the dependence of k_{et} and $|V|^2$ on r_{DA} is well expected from the equation when $\Delta G^\circ + \lambda \approx 0$.

Comparison of the fluorescence intensity (Figure 4) and lifetime data (Table 2) gives several noteworthy features. The enhancement of fluorescence intensity (I_{CD}/I_w) by the addition of Me- β -CD is much greater than that of fluorescence lifetime (τ_{CD}/τ_w) for the compounds of $n \leq 7$ (Figure 6), while I_{CD}/I_w is only slightly greater than τ_{CD}/τ_w for the compounds of $n \geq 8$. This indicates that extensive static-like quenching is involved in compounds of shorter linkages. The formation of the compact charge-transfer complexes, which is revealed as the charge-transfer absorption, can be one of the sources of the quenching. Since the fraction of this complex is estimated to be in the range of 0.09–0.19 from the K_{int} values, the disruption of the charge transfer complexation may result in less than 25% increase in fluorescence intensity. The observed enhancement is much greater than this expectation. Therefore, there should be other pathway for the static-like quenching in the linked compounds. The flexibility of the linkage allows relatively close proximity of the donor and acceptor. This seems to result in through-space/through-solvent electron-transfer quenching, of which the rate is too fast to be resolved in experimental time scale. Such a static-like quenching without involving complex formation was demonstrated in host-guest complexes.^{3h,4} The quenching rate appears to decrease greatly by the addition of Me- β -CD because the donor and acceptor are further apart in the Me-

β -CD complexes. The through-space/through-solvent transfer rate also varies exponentially with the donor-acceptor distance.¹³ For the compounds of $n \geq 8$, the fraction of conformers having the distance short enough to show the static-like quenching would be small and the quenching rate seems to be comparable with the through-bond transfer rate. This might be the reason we observe a nearly parallel increase in fluorescence intensity and lifetime by the addition of Me- β -CD.

Another factor affecting the fluorescent properties of the dyad molecules upon complexation with Me- β -CD is change of the polymethylene linkage to trans configuration. This increases the through-bond electron-transfer rate, as all trans arrangement of σ bonds is optimal for through-bond electron transfer.³⁵ Contribution of this to the overall effect of Me- β -CD seems to be small as we always observe the enhancement in fluorescence intensity and lifetime by the addition of Me- β -CD.

In conclusion, we have shown that the aromatic donor (1-naphthoxyl, 2-naphthoxyl, or 2-dibenzofuranoyl)-viologen acceptor dyad molecules linked by polymethylene bridges form intramolecular charge-transfer complexes. The stability of the complexes parallels that of the intermolecular complexes and depends little on the length of the linkage. Complexation of the dyad molecules with β -CD disrupts the charge transfer interaction and extends the molecules, resulting in a large enhancement of fluorescence intensity and lifetime. The electron transfer quenching rate in the CD-complexes at high CD concentration varies exponentially with the length of linkage. The apparent β value is 0.86 \AA^{-1} , regardless of the nature of donor moieties. The distance dependence of solvent reorganization energies was estimated. Using the dependence and standard Gibbs free energy of the electron-transfer reactions, it was suggested that the reaction stays near the top of the Marcus curve. Comparison of the effects of Me- β -CD on steady-state fluorescence intensity and excited-state lifetime indicates that through-space/through-solvent electron transfer is the predominant quenching pathway for the molecules having the linkage shorter than heptamethylene group.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation (Grant 94-0501-05-01-3) and the Ministry of Education of the Republic of Korea through the Basic Science Research Institute Program (Grant BSRI 96 and 97-3427). We acknowledge Drs. D. Kim and N. Song of the Korea Standard Research Institute for lifetime measurements.

References and Notes

- (1) For recent reviews, see: (a) Wasielewski, M. R. *Chem. Rev.* **1992**, 92, 435. (b) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, 26, 198. (c) Speciser, S. *Chem. Rev.* **1996**, 96, 1953.
- (2) Arnaut, L. G.; Formosinho, S. J. *J. Photochem. Photobiol. A* **1996**, 100, 15.
- (3) Harriman, A.; Kubo, Y.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, 114, 388. (b) Turro, C.; Chang, C. K.; Leroy, G. E.; Cukier, R. I.; Nocera, D. G. *J. Am. Chem. Soc.* **1992**, 114, 4013. (c) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1993**, 115, 10418. (d) Sun, L.; von Gersdorff, J.; Niethammer, D.; Tian, P.; Kurreck, H. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 3, 2318. (e) Durr, H.; Bossmann, S.; Kropf, M.; Hayo, R.; Turro, N. J. *J. Photochem. Photobiol. A* **1994**, 80, 341. (f) Sun, L.; von Gersdorff, J.; Sobek, J.; Kurreck, H. *Tetrahedron* **1995**, 21, 471. (g) Kropf, M.; Joselevich, E.; Durr, H.; Willner, I. *J. Am. Chem. Soc.* **1996**, 118, 655. (h) David, E.; Born, R.; Kaganer, E.; Joselevich, E.; Durr, H.; Willner, I. *J. Am. Chem. Soc.* **1997**, 119, 7778.
- (4) Park, J. W.; Park, S. H.; Lee, B. A.; Lee, S.-Y. *Chem. Lett.* **1997**, 1043.
- (5) Mobius, D. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, 82, 848. (b) Kuhn, H. *Pure Appl. Chem.* **1979**, 51, 341. (c) Kuhn, H. *Pure Appl. Chem.* **1982**, 53, 2105.
- (6) Vermuelen, L. A.; Thompson, M. E. *Nature* **1992**, 358, 656. (b) Ungashe, S. B.; Wilson, W. L.; Katz, H. E.; Scheller, G. R.; Putvinski, T. M. *J. Am. Chem. Soc.* **1992**, 114, 8717. (c) Vermuelen, L. A.; Snover, J. L.; Sapochak, L. S.; Thompson, M. E. *J. Am. Chem. Soc.* **1993**, 115, 11767. (d) Vermuelen, L. A.; Thompson, M. E. *Chem. Mater.* **1994**, 6, 77.
- (7) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: New York, 1991; pp 89-160 and references therein.
- (8) Siemiarz, A.; McIntosh, A. R.; Ho, T. F.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1983**, 105, 7224. (b) Magata, N.; Karen, A.; Okada, T.; Nishitani, S.; Kurata, N.; Sakada, Y.; Misumi, S. *J. Phys. Chem.* **1984**, 88, 5138.
- (9) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1978.
- (10) Park, J. W.; Song, H. J. *J. Phys. Chem.* **1989**, 93, 6454.
- (11) Yonemura, H.; Kasahara, M.; Saito, H.; Nakamura, H.; Matsuo, T. *J. Phys. Chem.* **1992**, 96, 5765. (b) Yonemura, H.; Nojiri, T.; Matsuo, T. *Chem. Lett.* **1994**, 2097.
- (12) Toki, A.; Yonemura, H.; Matsuo, T. *Bull. Chem. Soc. Jpn.* **1993**, 66, 3382.
- (13) Yonemoto, E. H.; Saupe, G. B.; Schmehl, R. H.; Hubig, S. M.; Riley, R. L.; Iverson, B. L.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, 116, 4786.
- (14) Wylie, R. S.; Macartney, D. H. *J. Am. Chem. Soc.* **1992**, 114, 3136. (b) Macartney, D. H.; Waddling, C. A. *Inorg. Chem.* **1994**, 33, 5912.
- (15) Yonemura, H.; Nakamura, H.; Matsuo, T. *Chem. Phys. Lett.* **1989**, 155, 157. (b) Yonemura, H.; Nakamura, H.; Matsuo, T. *Chem. Phys.* **1992**, 162, 69.
- (16) Yonemoto, E. H.; Kim, Y. I.; Schmehl, R. H.; Wallin, J. O.; Shoulders, B. A.; Richardson, B. R.; Haw, J. F.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, 116, 10557.
- (17) Sakura, K.; Sakamoto, T.; Matsuo, T. *Chem. Lett.* **1982**, 1651. (b) Yamada, S.; Koide, Y.; Matsuo, T. *J. Electroanal. Chem.* **1997**, 426, 23. (c) Clark, C. D.; Debad, J. D.; Yonemoto, E. H.; Mallouk, T. E.; Bard, A. J. *J. Am. Chem. Soc.* **1997**, 119, 10525.
- (18) Julliard, M.; Chanon, M. *Chem. Ber.* **1982**, 115, 588.
- (19) Sankararaman, S.; Yoon, K. B.; Yabe, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, 113, 1419.
- (20) Tamaru, K.; Ichikawa, M. *Catalysis by Electron Donor-Acceptor Complexes*; Halsted Press: New York, 1975. (b) Summers, L. A. *The Bipyridinium Herbicides*; Academic Press: New York, 1980. (c) Yoon, K. B.; Kochi, J. K. *J. Phys. Chem.* **1991**, 95, 3780. (d) Tsukahara, K.; Kaneko, J.; Miyaji, T.; Abe, K. *Tetrahedron Lett.* **1996**, 37, 3149.
- (21) Yorozu, T.; Hoshino, M.; Imamura, M.; Shizuka, H. *J. Phys. Chem.* **1982**, 86, 4422.
- (22) Park, H. R.; Mayer, B.; Welschann, P.; Kohler, G. *J. Phys. Chem.* **1994**, 98, 6158.
- (23) Benesi, H. A.; Hildebrand, H. *J. Am. Chem. Soc.* **1949**, 71, 2703.
- (24) Yoon, K. B.; Kochi, J. K. *J. Phys. Chem.* **1991**, 95, 3780.
- (25) Penfield, K. W.; Miller, J. R.; Paddon-Row, M. N.; Cotsaris, E.; Oliver, A. M.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, 109, 5061.
- (26) Craenen, H. A. H.; Verhoeven, J. W.; de Boer, J. *Rec. Trav. Chim. Pays-Bas*, **1972**, 91, 405.
- (27) Typically, the concentration of the linked compound was ca. 1.6 mM and the concentration of β -CD was varied up to about 3 mM in more than 7 steps. Higher concentration was avoided to prevent the formation of 1: 2 complexes.
- (28) The criteria for the agreement was the least-squares deviation of the calculated K_{CD} values taken at different β -CD concentration from the average value.
- (29) The addition of β -CD shift the signals from protons in viologen and aromatic rings, and α and β -protons (with respect to ether linkage) of the polymethylene linkages to lower field with respect to those of free species. However, unlike in carbazole-viologen linked compounds,^{11a} the complexes do not show separated signals indicating rapid exchange of β -CD molecule across the aromatic groups: the complexes of α -CD show separated signals reflecting large energy barrier for penetration.
- (30) Turro, N. J.; Okubo, T.; Chung, C.-J. *J. Am. Chem. Soc.* **1982**, 104, 1789.
- (31) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Warman, J. M. *Tetrahedron*, **1989**, 45, 4751. (b) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, 109, 3258.
- (32) Sutin, N. *Prog. Inorg. Chem.* **1983**, 30, 441.
- (33) Marcus, R. A. *J. Chem. Phys.* **1965**, 43, 679.
- (34) Johnson, M. D.; Miller, J. R.; Green, N. S.; Closs, G. L. *J. Phys. Chem.* **1989**, 93, 1173.
- (35) Szejtli, J. *Cyclodextrin Technology*; Kluwer: Dordrecht, 1988.
- (36) Hoffmann, R.; Imamura, A.; Here, W. J. *J. Am. Chem. Soc.* **1968**, 90, 1499.