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Effect of π-System on Long-Range Photoinduced Electron Transfer in Through-Ring α-Cyclodextrin Complexes of Carbazole-Viologen Linked Compounds

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Abstract: Carbazole-viologen linked compounds, with long spacers (ca. 2 nm), were incorporated into two α-cyclodextrins to afford rotaxane-type complexes. In the presence of a biphenyl unit in the spacer, the fluorescence lifetime of the carbazole moiety was reduced by 2 ns as compared with the case with a simple alkyl spacer (τ = 12 ns). Contribution of the superexchange mechanism to long-range electron transfer from the carbazole- to the viologen moiety was suggested. © 1998 Elsevier Science Ltd. All rights reserved.

During the last decade, long-range electron transfer has been recognized as one of the important processes in bioenergetics as represented by photosynthesis. A number of covalently bonded donor-acceptor systems as diad or triads have been reported to study long-range electron transfer mechanism.[1] Either flexible chain or rigid spacer has been used in these model systems. It was also reported that π-systems incorporated in donor-acceptor systems played important roles in photoinduced electron transfer processes and contributed to superexchange mechanism.[2] Recently, photoinduced electron-transfer reactions in supramolecular assemblies have been attractive research subjects in terms of artificial photosynthetic reaction centers.[3]

We discovered novel quasi-rigid supramolecular systems by complexation of donor-acceptor linked compounds with either α- or β-cyclodextrin (CD). Due to the formation of rotaxane-type "Through-Ring CD (TRCD) complexes", alkyl chains of the spacers were constrained to take extended forms.[4] In a previous paper, two α-CD molecules were also found to encase a hexadecyl spacer between the carbazole (Cz)- and the viologen (V^{2+}) moieties of a linked compound.[5]

In this paper, we report a new approach for the effect of π-system on long-range photoinduced electron transfer reactions in the TRCD complexes as supramolecular assemblies, in which the spacers are forced to take extended conformations. A biphenyl (Bp) moiety was incorporated at a central position of a long alkyl spacer in a carbazole- viologen linked compound and the effect of superexchange mechanism on photoinduced electron transfer between the two chromophores was examined.

Synthetic procedures of the compounds will be described elsewhere.[6] Spectroscopic studies were carried out by ^{1}H-NMR (JEOL model JNM-GSX 400), electronic absorption (Shimadzu UV-2200) and fluorescence (Hitachi F-3010) spectroscopies, and fluorescence lifetime (Hamamatsu Photonics picosecond photon-counting system C4780 with a N_2 laser) measurements.

Complexation of the linked compounds, **1**, **2** and **4**, were revealed by ^{1}H-NMR spectroscopy in D_2O solutions containing the linked compound (0.1 mM) and α-CD at various concentrations. As to **1**, **2** and **4**, distinct signals due to complexation between α-CD and the linked compound were observed apart from those of uncomplexed species, as typically shown in Figure 1 for an α-CD-**2** system. Detailed analysis indicated that

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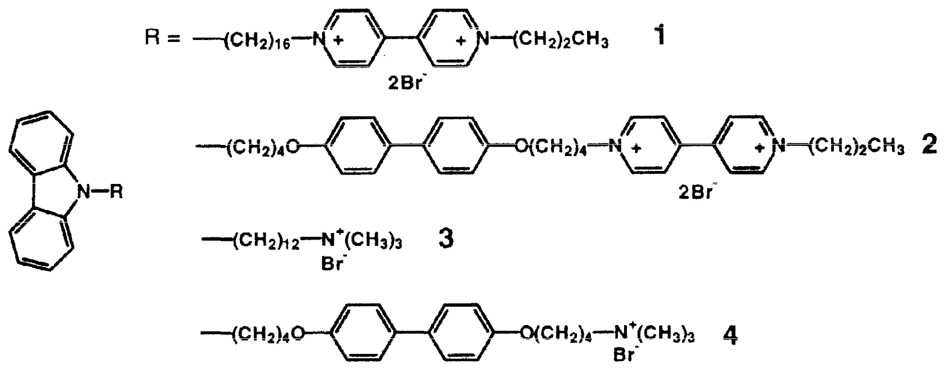

the spectra in Figure 1(C) were due to the 2:1 complex (α-CD vs. **2**) as previously reported with **1** (Figure 2).[5] On the basis of a space filling model with all-trans conformations for the methylene groups in the spacer, the edge-to-edge distance between Cz and V^{2+} moieties in the 2:1 TRCD complex should be as long as ca. 2 nm.

As to compounds **1** and **2**, intramolecular charge-transfer (CT) absorption bands were observed at 420- and 450 nm, respectively, in the aqueous solution (0.1 mM) without CD.[4c,7] On addition of excess α-CD (20 mM), the CT bands completely disappeared, in good agreement with the above suggested structure of 2:1 TRCD complex.

In the absence of α-CD, fluorescence emission from the Cz moiety of **1** and **2** (0.1 mM) was hardly observed. The reason may be ascribed to intramolecular electron transfer quenching of the S_1-state ($^1Cz^*$) of carbazole moiety by the terminal V^{2+}. In the presence of excess α-CD (20 mM), on the other hand, the fluorescence spectra of **1** or **2** became very close to that of the corresponding reference compound (**3** or **4**) with an ammonium head group. All of the above spectroscopic results strongly indicate that in the presence of excess α-CD the spacers of three linked compounds **1**, **2**, and **4** are encased in two α-CD molecules as shown in Figure 2. Formation of the 1:1 TRCD complex between α-CD and **3** has already been reported in a previous paper.[5]

Effects of the BP in the linked compound **2** on the fluorescence properties of the corresponding TRCD complex were examined. Fluorescence lifetimes of **1** – **4** were measured by the single-photon-counting method. The decomplexation process in the present TRCD complex can be negligible during the lifetime of carbazole due to the very slow exchange rate.[4c] A single exponential decay curve was obtained in each case. The results are summarized in Table 1. The data in Table 1 strongly indicate that the $^1Cz^*$ in the linked compound **1**, **3**, or **4** retains the same fluorescence intensity and fluorescence lifetime as far as the 2:1 TRCD complex is concerned in each case. In other words, the $^1Cz^*$ interacts neither with the terminal V^{2+} of **1** nor with the BP of **4**. Therefore, appreciable decrease in the relative fluorescence intensity and the fluorescence lifetime of **2** must be ascribed to the presence of the BP as a mediator between the Cz– and V^{2+}.

The fluorescence lifetime of the 1:1 TRCD complex, formed from α-CD and a Cz-V^{2+} linked compound with a shorter polymethylene spacer ($n \leqq 12$), is appreciably shorter than that of the reference compound **3**.[6] The electron-transfer quenching apparently becomes ineffective in the linked compound with a longer polymethylene spacer ($n>16$). The driving force (ΔG) for oxidation of the $^1Cz^*$ by the V^{2+} in water was estimated to be –1.97 eV by Weller approach[2, 8] using the energy of $^1Cz^*$ from the fluorescence spectra (3.52 eV), the oxidation potential of N-ethylcarbazole (–1.31 V vs. NHE)[9] and the reduction potential of dimethylviologen (–0.27 V vs. NHE) from CV measurements in CH_3CN, ion radii of Cz^+ (4Å) and V^+ (4Å)

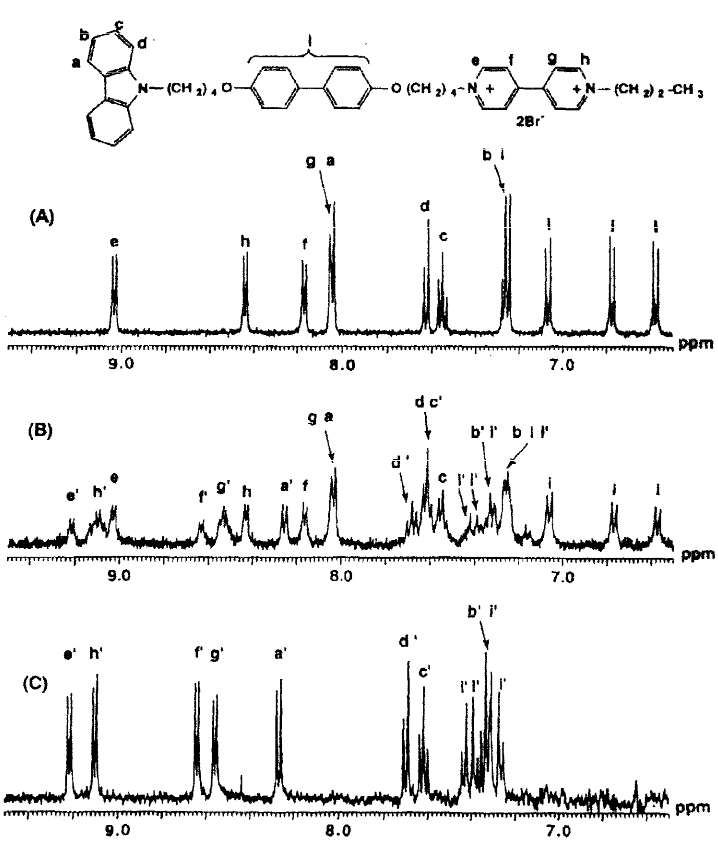

Figure 1. Effects of α-CD on ^{1}H-NMR spectra of aromatic moieties for **2** (0.1 mM) in D_2O solution at 30°C : (A) without α-CD, (B) with α-CD (2 mM), and (C) with α-CD (20 mM). The peaks due to complexed species are indicated by prime letters.

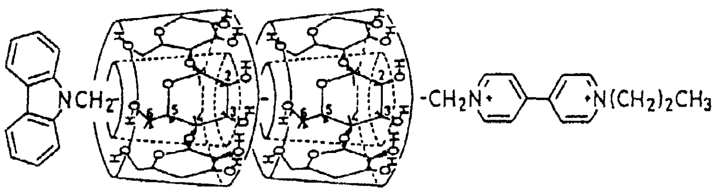

Figure 2. Proposed 2:1 TRCD complex between α-CD and a linked compound **1**,**2**, or **4**.

Table 1. Fluorescence lifetimes and relative fluorescence intensities of **1** - **4** (0.1 mM) in an aqueous solution containing α-CD (20 mM) at 25°C.

Compound	1	2	3	4
I/I_0 [a]	1.01	0.85	1.00	1.02
τ (ns) [b]	12.1	10.2	12.1	12.1

a: Relative fluorescence intensity versus the reference compound **3** (excitation wavelength: 340 nm)
b: Fluorescence lifetime at 370 nm (excitation wavelength: 337.1 nm)

by assuming, a center-to-center distance (24.8 Å) in **2**, and solvent dielectric constants (ε=35.9 in CH_3CN and ε=78.5 in water). The energy difference (δE) between Cz^+-BP^--V^{2+} (3.58 eV) and $^1Cz^*$-BP-V^{2+} (3.52 eV) in water is small in the superexchange mechanism[2], it can also be evaluated from the reduction potential of BP (–2.36 V vs. NHE)[10] and ε=36.71 for DMF by the same approach. Thus, the Cz^+-BP^--V^{2+} state should contribute to the superexchange mechanism. The total reorganization energy (λ) is the sum of an internal contribution (λ_i (0.3 eV))[8] and a solvent contribution (λs). The λs value of **2** in water was calculated to be 1.67 eV using two sphere model.[8] Since the λ value (1.96 eV) is very close to the -ΔG value (1.97 eV), it is suggested that the long-range electron transfer reaction in **2** may occur at the top region in Marcus theory. Accordingly, the most possible explanation for the distinct decrease in the fluorescence lifetime of **2** is the contribution of superexchange interaction with the small δE via the BP at the top region, which must facilitate the electron-transfer interaction between the $^1Cz^*$ and the terminal V^{2+}.

Donor-acceptor linked compounds in "Through-Ring CD complexes" afforded a useful model system to study the contribution of superexchange interaction to the long-range photoinduced electron-transfer process. Further investigations on carbazole-viologen linked compounds with various spacers are now in progress.

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