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Synthesis of a Rhenium Complex Appending a Cyclodextrin Unit on a Ligand

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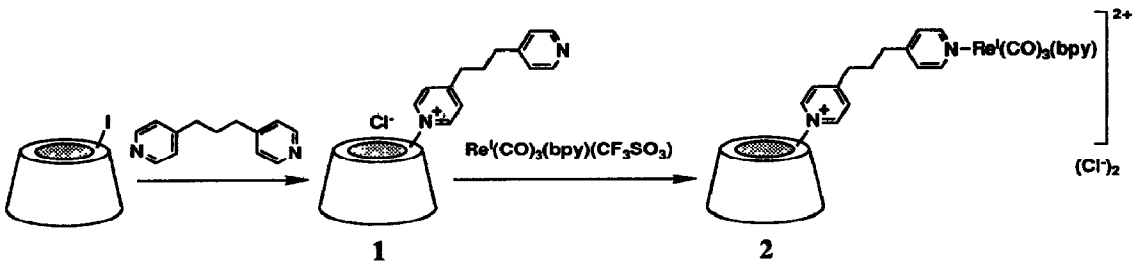
Key Words: Rhenium complex; Cyclodextrin; Inclusion; Supramolecule; Electron transfer.

Abstract: A supramolecular species has been designed for studying the mechanism of long-range electron transfer through non-covalent bonding. A rhenium complex with a cyclodextrin unit on the side arm of a ligand has been synthesized. The rhenium complex trapped *N,N*-diethylanilline into its cavity, and the luminescence from the host complex was quenched by the guest.

Development in the study of the three-dimensional structure of natural photosynthetic reaction centers has raised interest in the mechanism of intramolecular electron transfer (ET) in supramolecular species which are made of a photosensitizer unit (P) covalently linked to electron-acceptor (A) and/or electron-donor (D) units.[1] The mechanism of ET has been extensively discussed on the basis of the rate of photochemical forward and back ET which has been measured for these species. The rate of the intramolecular ET has been found to be enhanced by through-bond electronic coupling of P and A (or D).[2] Then a question arises: through what kind of pathway electron is transferred in the natural photosynthetic reaction centers in which P, D and A are attached non-covalently to protein matrices. To answer this question chemically modified metalloredox proteins have been used.[3] Theoretical studies have revealed that electron tunnels through a special pathway which has been chosen so as to maximize the electronic coupling of P and A (or D). The pathway includes covalent bonds, hydrogen bondings, and spaces between atoms interacting non-covalently with each other.[4]

Recently several supramolecular species assembled with non-covalent interactions have been synthesized. First, Harriman et al. have introduced a system composed of a porphyrin and a quinone making a pair by hydrogen bonding at their side chains.[5] Kuroda et al. have synthesized a porphyrin bearing two cyclodextrin units acting as binding sites for quinones.[6] The latter system is very interesting since the D–A pair is formed only by weak interactions such as van der Waals' or hydrophobic interactions.



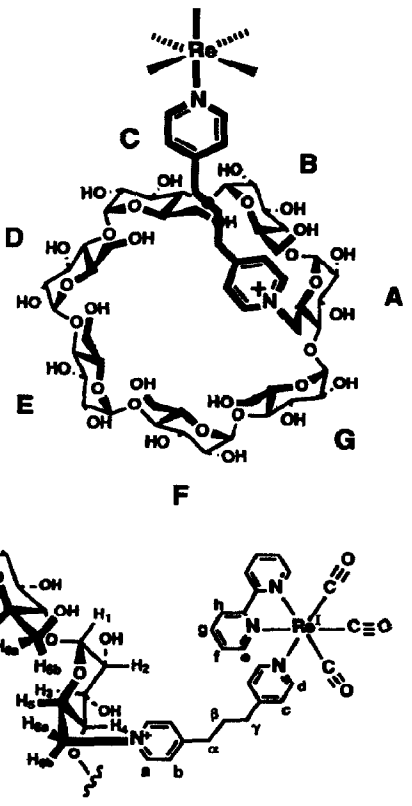
1 2

Scheme 1.

To determine the mechanism of ET we need a systematic study by varying free energy change for the ET reaction, and by changing the distance of the reacting partners. We have therefore designed another photosensitizer with a cyclodexrin (CD) unit. Scheme 1 shows the photosensitizer synthesized in the present study. A rhenium complex of the formula, *fac*-$[Re(CO)_3(bpy)(py)]^+$ (py = pyridine, bpy = 2,2'-bipyridine), was selected because redox potential is changeable by substituting the bpy ligand.[7] Moreover, this kind of complex has no chiral center unless bpy ligands are chemically substituted asymmetrically; if the metal complex had a chiral center like a $Ru(bpy)_2XY$, introducing a chiral cyclodextrin unit into a side chain of any ligands would result in the formation of diastereomer. A pyridinio group was selected as a hinge linking the CD unit to the spacer unit, since the conformational structure of the modified CD's with a pyridinio group had been characterized well by ^{1}H-NMR spectroscopy.[8,9]

Synthesis of the pyridine ligand which has a β-cyclodextrin (β-CD) moiety (**1**) was achieved by a slight modification of the method by Du et al.[10] Mono-6-deoxy-6-iodo-β-cyclodextrin and 1,3-di(4-pyridyl)propane were heated in DMF at 80°C for 40 h. After reprecipitation with acetone, the product was purified by ion-exchange chromatography on a SP-Sephadex C-25 column and adsorption chromatography on a Diaion HP-20 column (a high-porous polystyrene gel, Nippon Rensui Co.). The product **1** was reacted with *fac*-$Re(CO)_3(bpy)(CF_3SO_3)$[11] at reflux in 2:1 methanol/water for 12 h. The product was purified by chromatography on a SP-Sephadex C-25 column. The purified product gave satisfactory data on 500-MHz ^{1}H-NMR spectroscopy.[12]

Combined use of various two-dimensional NMR techniques in 500-MHz ^{1}H-NMR spectroscopy[13,14] have enabled us to assign most of the peaks in a one-dimensional (1D) spectrum, and to elucidate the three-dimensional (3D) structure of the relevant compound. Large shifts were observed in the 1D ^{1}H-NMR spectrum of the compound **2** at the resonance peaks for H-6's and H-5's of the glucose units of both A and B (Table 1). Similar



Scheme 2. A scheme showing proposed 3D structure and the notations for the protons of **2**.

Table 1. ^{1}H-NMR Chemical Shifts of the Specified Protons of **2**, **3**, and Native β-CD.

Compound	Chemical shifts / ppm				
	A6a	A6b	A5	B6a	B6b
β-CD[a]	3.79–3.86 (m)	3.79–3.86 (m)	3.79–3.86 (m)	3.79–3.86 (m)	3.79–3.86 (m)
2	5.09 (dd)	4.61 (dd)	4.15–4.19 (m)	2.76 (dd)	2.54 (dd)
3[b]	5.25 (dd)	4.78 (dd)	4.28–4.32 (m)	2.95 (dd)	2.68 (dd)

[a] Chemical shifts for H-6's and H-5's of the β-CD cannot be resolved because the resonance peaks for the protons overlap in a narrow region. [b] For the method of the assignment of the peaks, see ref. 8.

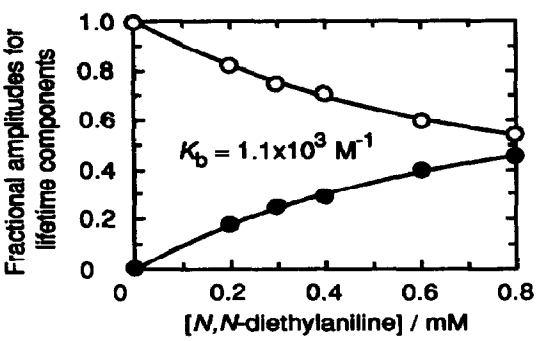


Figure 1. Change in the fractional amplitudes for the lifetime components as a function of DEA concentration.

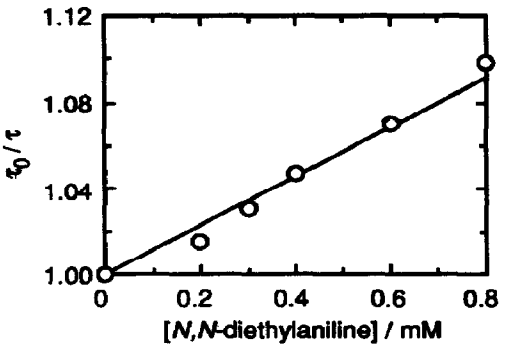


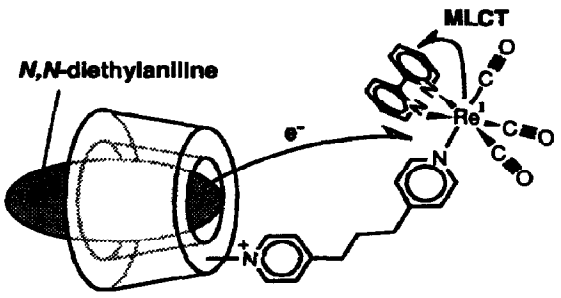
Figure 2. A Stern-Volmer plot for the longer-lived component against DEA concentration.

kinds of shifts have been reported for mono-6-deoxy-6-pyridinio-β-CD (3) and the related compounds.[8,9] The upfield and downfield shifts have been attributed to anisotropic ring current effect and/or electrostatic effect of the pyridinio cation. The strong resemblance in the shifts implies that the averaged conformational structure of the pyridinio group in 2 is the same as those in 3 and the other pyridinio-modified CD's; the pyridinio group is located on the rim of the CD torus and faces the glucose unit B.[8,9] Examination of the possible conformational structure of this compound on the CPK model reached the conclusion that the pyridine unit binding to rhenium must be expelled out from the CD cavity. The conclusion agrees well with the experimental results that no NOE was observed between protons in the CD unit and those in the Re-complex unit, and that the luminescence intensity did not change by the addition of typical 'good' guests for CD's such as 1-adamantanol or (–)-borneol.[15]

The Re-appended CD had a luminescence band at around 580 nm.[16] The luminescence was quenched by the addition of *N,N*-diethylaniline (DEA). Quenching of the luminescence by DEA has been reported for a Re complex, and the origin of the quenching has been attributed to the electron transfer from DEA to the photoexcited Re complex.[17] In the presence of DEA the decay curve for the luminescence was fitted to the two-exponential decay model.[18] The fractional amplitudes for the shorter-lived component increased with increasing concentration of DEA; but, that for the longer-lived component decreased with it. In Fig. 1 the fractional amplitudes were plotted against DEA concentration. The plot was well fitted by a quantitative model assuming the formation of an 1:1 inclusion compound. The binding constant K_b estimated through the fitting was $1.1 \times 10^3\ M^{-1}$. The shorter-lived component can be attributed to the luminescence from 2 with the cavity filled with DEA, and the longer-lived one to that from 2 free from DEA. This was confirmed by the fact that the amplitude for the shorter-lived component was negligibly small in the presence of a large excess of a competitive guest, 1-adamantanol.

Although the lifetime for the shorter-lived component stayed practically unchanged with increasing concentration of DEA, that for the longer-lived one decreased with it. The decrease in the lifetime can be attributed to the dynamic quenching by the free DEA molecule, which has been proved by the fact that a straight line was obtained on a Stern-Volmer plot of the lifetime (Fig. 2). The dynamic quenching by diffusional collision and the static quenching in the supramolecular species may occur at the same time.

The rate of ET in the supramolecular species was calculated from the lifetimes of the luminescence



Scheme 3. A schematic representation of the ET process in the supramolecular species.

by the equation:

$$k_{ET} = 1 / \tau_q - 1 / \tau_0$$

where τ_q and τ_0 are the lifetimes for the DEA-filled **2** (the shorter-lived component in the presence of DEA, 21 ns), and that for the DEA-free **2** in the absence of DEA (92 ns), respectively. The k_{ET} values was estimated to be 3.7×10^7 s^{-1}.

The above results indicate that electron was transferred from DEA which was trapped in the CD cavity to the Re complex which was fixed outside of the cavity through the non-covalent bonding between DEA and the host CD. In order to determine the mechanism of ET in the supramolecular species synthesis of a series of related compounds are necessary. This work is in progress in this labolatory.

REFERENCES AND NOTES

1. *Photoinduced Electron Transfers*, Parts A-D; Fox, M. A., Chanon, M. Eds.; Elsevier: Amsterdam, 1988.
2. Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440-447.
3. Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369-379.
4. (a) Beratan, D. N.; Onuchic, J. N.; Winkler, J. R.; Gray, H. B. *Science* **1992**, *258*, 1740-1741. (b) Beratan, D. N.; Onuchic, J. N.; Betts, J. N.; Bowler, B. E.; Gray, H. B. *J. Am. Chem. Soc.* **1990**, *112*, 7915-7921. (c) Onuchic, J. N.; Beratan, D. N. *J. Chem. Phys.* **1990**, *92*, 722-733.
5. Harriman, A.; Kubo, Y.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 388-390.
6. Kuroda, Y.; Ito, M.; Sera, T.; Ogoshi, H. *J. Am. Chem. Soc.* **1993**, *115*, 7003-7004.
7. MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 7470-7479.
8. Ikeda, H.; Moon, H. -T.; Du, Y. -Q.; Toda, F. *Supramol. Chem.* **1993**, *1*, 337-342.
9. Ikeda, H.; Du, Y. -Q.; Nakamura, A.; Toda, F. *Chem. Lett.* **1991**, 1495-1498.
10. Du, Y. -Q.; Nakamura, A.; Toda, F. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3351-3353.
11. Sullivan, B. P.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1244-1245.
12. Data for **2**: UV (H_2O) λ_{max} 306 nm (ε = 12500), 319 nm (ε = 13100), 343 nm (ε = 3900); ^{1}H-NMR (D_2O) δ 1.88–1.94 (m, 2H (H–β)), 2.54 (dd, J = 11.3 Hz, 2.5 Hz, 1H (H–B6b)), 2.62 (t, J = 7.7 Hz, 2H (H–γ)), 2.76 (dd, J = 11.3 Hz, ≤ 2 Hz, 1H (H–B6a)), 2.84 (t, J = 7.7 Hz, 2H (H–α)), 3.34–4.04 (total 37H), 4.15–4.19 (m, 1H (H–A5)), 4.61 (dd, J = 14.1 Hz, 10.0 Hz, 1H (H–A6b)), 4.89 (d, J = 4.0 Hz, 1H (H–B1)), 4.95 (d, J = 3.8 Hz, 1H (H–A1)), 5.01–5.04 (m, total 4H (H-1 protons of glucose units, C–F)), 5.09 (dd, J = 14.1 Hz, 2.0 Hz, 1H (H–A6a)), 5.10 (d, J = 4.0 Hz, 1H (H–G1)), 7.10 (d, J = 6.6 Hz, 2H (H–c)), 7.72–7.74 (m, 2H (H–f)), 7.83 (d, J = 6.6 Hz, 2H (H–b)), 8.14 (d, J = 6.6 Hz, 2H (H–d)), 8.18–8.22 (m, 2H (H–g)), 8.34 (d, J = 8.3Hz, 2H (H–h)), 8.62 (d, J = 6.6 Hz, 2H (H–a)), 9.25 (d, J = 5.4 Hz, 2H (H–e)). Anal. Calcd for $C_{68}H_{91}N_4O_{37}ReCl_2 \cdot 7H_2O$ C, 42.11; H, 5.46; N, 2.89. Found: C, 41.80; H, 5.14; N, 2.78.
13. Saka, W.; Yamamoto, Y.; Inoue, Y.; Chûjô, R.; Takahashi, K.; Hattori, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3175-3182.
14. This method has been applied to elucidate the 3D structures of modified CD's. See refs. 8 and 9, and also: Hamasaki, K.; Ikeda, H.; Nakamura, A.; Ueno, A.; Toda, F.;Suzuki, I.; Osa, T. *J. Am. Chem. Soc.* **1993**, *115*, 5035-5040.
15. Addition of the guests often induces change in the fluorescence intensity for fluorophore-appended CD's. A representative result has been reported in: Ueno, A.; Minato, S.; Suzuki, I.; Fukushima, M.; Ohkubo, M.; Osa, T.; Hamada, F.; Murai, K. *Chem. Lett.* **1990**, 605-608.
16. Sample solutions were made with aqueous phosphate buffer (pH 7.0; ionic strength, 0.1 M), which were used for luminescence measurements under air-saturation.
17. Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790-5795.
18. The lifetimes were, for example, 21.0 ns and 83.3 ns when DEA concentration was 0.8 mM.

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