Long-Range Triplet-Triplet Energy Transfer in Supramolecular Species in Fluid Aqueous Solutions

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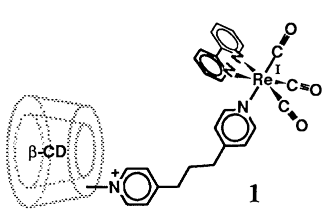
Excitation energy of a metal-to-ligand charge-transferred triplet state of a rhenium complex was transferred over a distance of 10 Å to 2-anthracenecarboxylate trapped in the hydrophobic cavity of the cyclodextrin unit which was linked covalently to one of the ligands of the complex.

Intramolecular triplet-triplet energy transfer (TT) by Dexter's electron-exchange mechanism is an old topic in photochemistry.[1] In recent years intramolecular TT is attracting much interests again in relation to intramolecular electron transfer (ET).[2-4] However, with one exception,[5] intramolecular TT in non-covalently assembled supramolecular species has never been reported. Tabushi et al.[5] have synthesized a benzophenone-capped cyclodextrin, and have observed efficient TT from the benzophenone moiety to naphthalene derivatives which were included in the cyclodextrin cavity. However, in this experiment, absolute rate of TT has not been measured.

We have reported[6] intramolecular ET in a supramolecular species composed of a rhenium complex bearing a cyclodextrin (CD) unit (**1**) and an electron-donor molecule trapped in the cavity of the CD unit. In the present paper we have measured the rate of intramolecular TT in supramolecular species of **1** and a new complex **2**.

The complex **2** was prepared by the following procedure: Mono-6-*O*-(*p*-tolylsulfonyl)-β-cyclodextrin was reacted with excess piperazine in DMF at 80 °C for 15 h. Reaction of the product with 3-(3-bromopropyl)pyridine in the presence of triethylamine in DMF at 80 °C for 12 h gave a pyridine derivative bearing a CD unit. The pyridine derivative was reacted with *fac*-[ClRe(bpy)(CO)$_3$] (bpy = 2,2'-bipyridyl) in the presence of AgPF$_6$ in DMF at 70 °C for 4 h. The crude product was purified by chromatography on a SP-Sephadex C-25 column to give **2**.[7] The present paper involves mainly the results obtained for **2**.



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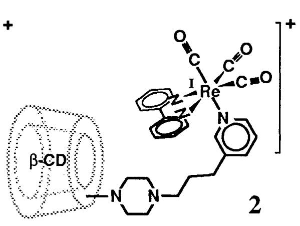

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The rhenium complex **2** has a luminescence band with a peak at 580 nm, which is due to a metal-to-ligand charge-transferred triplet state (^{3}MLCT).[8] Because the luminescence was intense even in the aerated aqueous solutions, the following experiments were done in air-saturated aqueous solutions at 25 °C (pH 7.0; ionic strength, 0.1 M; 1 M = 1 mol dm^{-3}).

The luminescence of **2** was quenched by 2-anthracenecarboxylate (2AC) (Figure 1). We can postulate that the quenching is caused by TT.[4] Differences in the quenching efficiencies for aromatic carboxylates and sulfonate (Table 1) also proves that the quenching is due to TT. Of the compounds listed 2-naphthalenesulfonate (2NS) associates most tightly to β-CD with a stability constant of about 10^5.[9] The triplet energy of 2NS, however, is so large that the compounds cannot accept excitation energy of the Re complex.[10] Anthracenes and pyrene have triplet energy smaller than that for the Re complex.

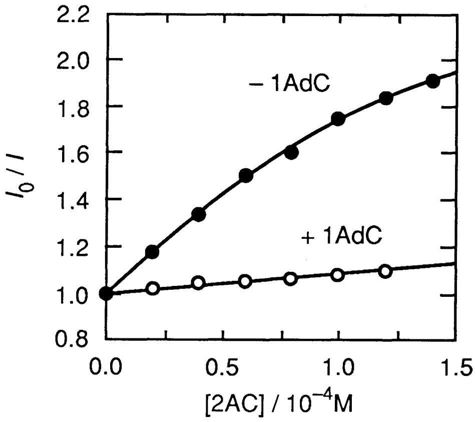

Figure 1. Stern-Volmer plots for the quenching of the luminescence of **2** by 2AC. [**2**] = 50 μM. Effect of the addition of a competitive guest (1AdC; 300 μM) is also shown.

That TT occurs by intramolecular process in an inclusion complex is supported by several lines of evidence. First, 2AC quenched the luminescence substantially, whereas 9-anthracenecarboxylate (9AC) did only slightly; The latter compound does not form the inclusion complex with β-CD.[11] Second, in the presence of 2AC, the luminescence was recovered by the addition of 1-adamantanecarboxylate (1AdC) (Figure 1); These compounds (2AC and 1AdC) are competing guests for β-CD. Third, the decay of the luminescence in the presence of 2AC could be analyzed by using a simple triple-exponential function (Table 2). The long-lived and middle-lived components were at-

Table 1. Quenching efficiency for the luminescence of **2** by aromatic carboxylates and sulfonate

Quencher	$(I_0 - I) / I_0$ [a]	Triplet energy / kJ mol^{-1} [b]
2-Anthracenecarboxylate	0.46	176
9-Anthracenecarboxylate	0.05	176
4-(1-Pyrenyl)butyrate	0.28	201
2-Naphthalenesulfonate	0	254

[a] I is the luminescence intensity for the solution containing 120 μM of the relevant quencher. I_0 is that for the solution without quencher. [**2**] = 50 μM.
[b] Triplet energy for **2** was estimated as 231 kJ mol^{-1}. For detail, see Ref. 10.

Table 2. Lifetimes and amplitudes recovered by lifetime analyses for the luminescence of **2** using a triple-exponential function [a]

Quencher	A_1	τ_1 / ns	A_2	τ_2 / ns	A_3	τ_3 / ns
none	1.0	101.4				
2AC [b]	0.225	99.5	0.910	24.8	−0.135	6.5

[a] [**2**] = 20 µM. Excitation beam was passed through filters of Hoya UV32 and U360. The resultant beam contains light of the wavelengths between 320 and 380 nm. Luminescence was led into a photomultiplier through a Hoya O58 filter. [b] [2AC] = 50 µM.

tributed to the luminescence of the quencher-free **2** and that of the quencher-loaded **2** (**2** $\supset$ 2AC), respectively. The short-lived rising component was due to the singlet-singlet energy transfer from 2AC to the rhenium complex.[12] Even in the presence of 2AC, lifetime for free **2** is almost the same as that in the absence of 2AC. This means that intermolecular TT by a dynamic process does not work when the quencher concentration is 50 µM.[13]

By the decay analysis the rate for TT (k_{TT}) from the rhenium complex to 2AC in the supramolecular species (**2** $\supset$ 2AC) was estimated as 3.7×10^7 s^{-1}.[14] In the system with host **1** (**1** $\supset$ 2AC), k_{TT} was estimated as 2.9×10^7 s^{-1}. These values are very similar to each other. On the basis of ^{1}H-NMR spectroscopy we have concluded that the spacer bonds in **1** lie in the fully-extended conformation.[6] When the extended conformation was assumed to be the most stable conformation of **1**, the distance between rhenium metal and the rim of the CD cavity would be estimated as about 12 Å. Although we have not done ^{1}H-NMR study for **2** extensively enough to discuss the conformation, the distance for **2** would be about 10 Å in the extended conformation. These values of the distance are so large that electron can not get over the distance by through-space tunnelling. Onuchic, Beratan, and coworkers have examined the electron tunneling pathway in proteins.[15] The pathway contains σ-bonds, hydrogen bonds, and spaces between non-covalently interacting atoms. In our supramolecular systems the environment of the chromophores is very much like that of the donors and acceptors in proteins. Thus we suppose that the most probable pathway for TT (i.e. electron exchange) may consist of some covalent bonds in the spacer unit, the covalent bonds in some part of the CD unit, and the space between the surface of the quencher molecule and the inner wall of the CD cavity. Through this pathway the electron exchange over the distance of 10 Å might be possible by the aid of through-bond coupling mechanism. However, there is another possibility that the energy transfer takes place at the conformations other than the fully-extended one. This point is being investigated.

References and Notes

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7 Data for **2**: UV (phosphate buffer soln.; pH 7.0; ionic strength, 0.1 M) λ_{max} 304 nm (ε = 10,900), 319 nm (ε = 11,100), 343 nm (ε = 3500); ^{1}H-NMR (D_2O) δ 1.87–1.94 (m, 2H), 2.6–3.5 (broad, total 10H), 2.91 (dd, J = 15, 8.5 Hz, 1H), 2.98–3.05 (m, total 3H), 3.55–4.10 (total 40H), 5.12 (d, J = 3.0 Hz, 1H), 5.13–5.18 (m, total 6H), 7.30 (dd, J = 6.0, 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.89 (dd, J = 6.0, 7.0 Hz, 2H), 8.18 (d, J = 6.0 Hz, 1H), 8.26 (s, 1H), 8.35 (dd, J = 8.0, 7,0 Hz, 2H), 8.48 (d, J = 8.0 Hz, 2H), 9.40 (d, J = 6.0 Hz, 2H).

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12 In steady-state luminescence measurements we have used an excitation wavelength of 420 nm in order to excite the rhenium-complex moiety without exciting 2AC directly. However, with this excitation wavelength, we could not get luminescence with an enough intensity to be used for the lifetime analysis. Then instead we used uv light of the wavelengths between 320 and 380 nm as an exciting light. When we excite the system with the uv light, the Re complex was excited not only directly but also through the singlet-singlet energy transfer from excited 2AC to the Re complex.

13 In fact the quenching by an intermolecular process is effective at higher concentrations of 2AC. A major cause of the weak quenching by the non-guest quencher 9AC and by 2AC in the presence of 1AdC is also the intermolecular energy transfer by a dynamic bimolecular process.

14 The rate of TT in the supramolecular species was calculated by the equation: $k_{TT} = 1 / \tau_q - 1 / \tau_0$, where τ_q and τ_0 are the lifetimes for the quencher-loaded rhenium complex (the middle-lived component in the presence of 2AC), and that for the quencher-free host (the lifetime in the absence of 2AC), respectively.

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