Enhanced Electron-Transfer Quenching of Excited Ruthenium-Trisbipyridine by Viologen-Carbazole Linked Compounds in Aqueous Solutions[1]

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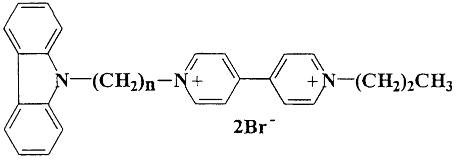
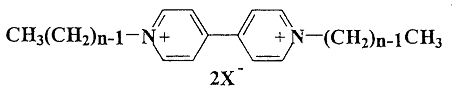
Viologen-carbazole linked compounds quenched photoexcited tris(2,2'-bipyridine)ruthenium(II), abbreviated to Ru-trisbpy, much more efficiently than simple viologen in aqueous solutions. The observation was ascribed to enhanced electron-transfer to partially dehydrated viologen as deduced from spectroscopic- and electeochemical evidences.

Molecular environments around donor-acceptor pairs play extremely important roles in electron-transfer reaction dynamics, as they have been observed in various biological systems.[2,3] Mechanistic details of these microenvironmental effects remain to be elucidated in terms of molecular structures. In this paper, we investigated the role of hydrophobic environment around an electron acceptor (viologen unit) in electron-transfer from a well known photoexcited electron donor (Ru-trisbpy). The viologen unit was covalently linked to carbazole moiety via polymethylene group, as a spacer, as shown by the following molecular formulae (CzC10V and CzC6V):



CzCnV: n=6,10



2C6V: n=6, X=Br ; 2MV: n=1, X=Cl

The electron-transfer quenching efficiency with CzC10V was higher than that with simple viologen (2C6V) in water, but the reaction could be strongly suppressed by the formation of extremely stable "through-ring cyclodextrin(CD) complexes" with CzC10V. The results will be discussed in terms of intramolecular interactions between the carbazole- and viologen moieties.

Preparation and spectroscopic properties of the carbazole-viologen linked compounds have previously been reported.[4] The linked compound, with appropriate spacer-chain length, forms through-ring CD complexes, which afford distinguished NMR signals apart from uncomplexed species in D_2O. Aqueous solutions containing Ru-trisbpy (20 μM;M=mol dm^{-3}) and various viologen derivatives were deoxygenated by freeze-pump and thaw cycles, and Ru-trisbpy luminescence decay was followed at 600 nm. In order to prevent micellization of the amphiphilic viologen derivatives, dilute solutions (less than 1 mM) were used in our experiments. Photoexcitation of Ru-trisbpy was carried out by the use of the second harmonics (532 nm) of a Nd;YAG laser (28 mJ per a pulse with 14 ns duration, and 10 Hz repetition rate).

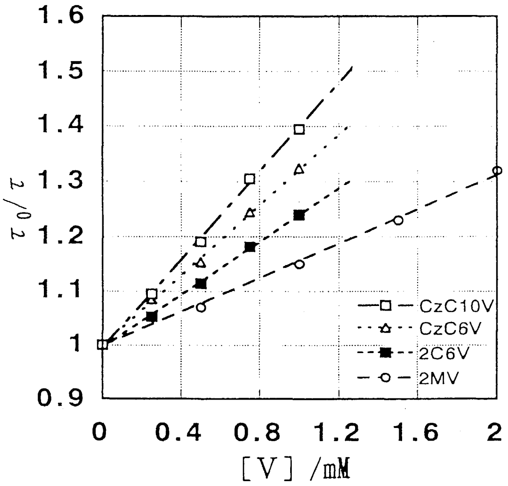


Figure 1. Stern-Volmer plots for decrease in Ru-trisbpy luminescence lifetime (τ) in the presence of various viologen as the quencher.

Stern-Volmer plots for decrease in Ru-trisbpy luminescence lifetime (τ) with viologen concentration are shown in Figure 1, where the data for the linked compounds with a longer spacer (n=10) and a shorter spacer (n=6) are compared with those for simpler viologen molecules (2C6V and 2MV). The quenching efficiencies for the two linked compounds are certainly higher than those for the simpler viologens.

An important feature of the carbazole-linked compound is the presence of intramolecular charge-transfer spectra (λmax at ca. 420 nm for CzC10V in the aqueous solutions), which disappear on the formation of stable "through-ring α-CD complex".[4] Effects of complexation between the viologen derivatives (up to 1 mM) and α-CD (10 mM) on the quenching rate constant (kq) were then examined. The data, as summarized in Table 1, indicate that the kq-value for the linked compound with a longer spacer (n=10) was remarkably reduced by the complexation. The corresponding value for the linked compound with shorter spacer (n=6), which does not form stable "through-ring α-CD complex", was slightly affected by the presence of α-CD. Essentially, no effect was observed with dimethylviologen (2MV).

As to dihexylviologen (2C6V), rapid exchange between the α-CD complexes and free species was indicated by the NMR studies. The α-CD molecules are considered to be loosely bound around the polymethylene chain. Formation of similar CD complexes with diheptylviologen was also suggested by Kodaka and Fukaya on the basis of quenching experiments with Ru-trisbpy luminescence intensity.[5] In the present experiment, the kq-value for 2C6V decreased by 60% on the formation of α-CD complex. The kq-value for 2C6V decreased by 60% on the formation of α-CD complex. The kq-value for 2C6V in the

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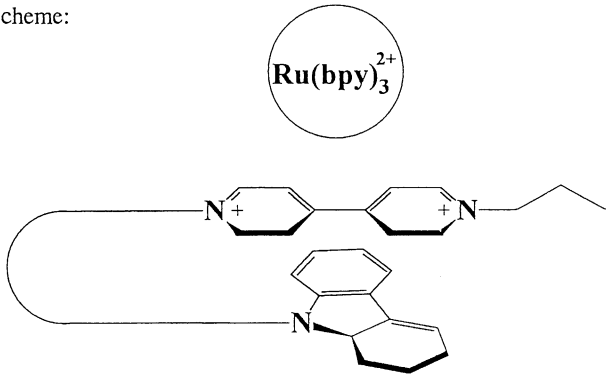
Table 1. Effects of α-CD on the Ru-trisbpy luminescence quenching rate constants (kq / 10^8 $M^{-1}s^{-1}$) for various viologens

[α-CD]	2MV	2C6V	CzC6V	CzC10V
none	3.1	4.0	5.4	6.6
10mM	3.0	1.6	4.6	1.6

presence of α-CD agreed with that for CzC10V under the same conditions. Formation of through-ring CD complexes forces the spacer of CzC10V to take extended conformation.[4] As a consequence, the viologen unit of CzC10V may be exposed to the excited Ru-trisbpy to the same extent as that of 2C6V in the presence of α-CD. The agreement of the kq-value between 2C6V and CzC10V under this circumstance is a reasonable result.

In the absence of α-CD, on the other hand, the kq-values for CzC10V and CzC6V are clearly larger than those for simple viologens with small alkyl substituents. Direct involvement of carbazole moiety itself in the quenching process should be disregarded, because Ru-trisbpy luminescence is unaffected by the presence of amphiphilic carbazole derivative with a trimethylammonium group. The presence of intramolecular charge-transfer absorption in the aqueous solution indicates that carbazole moiety is located very close to the viologen unit in the same molecule. Detailed NMR studies[4] also indicated the presence of face-to-face interaction of the terminal groups (carbazole- and viologen units) as shown by the following scheme:



Scheme 1.

As an electronic effect of contribution from charge-transfer configurations, one might expect decrease in electron affinity of the viologen unit in the linked compounds. The larger kq-vaues for CzC10V and CzC6V suggest, on the contrary, considerable increase in electron affinity of the viologen unit as compared with the simpler viologens. The reason is ascribed to entropy change, rather than enthalpy, on the formation of charge-transfer complexes in aqueous solutions as discussed below.

In order to assure better contact between the π donor-acceptor pair, water molecules in the complexing site must be partly removed. As to intra-molecular charge-transfer complexes of anthracene-viologen linked compound in aqueous solutions, the entropy change has actually been found negative (-14/cal mol^{-1} K^{-1}).[6] The value may represent effects of dehydrating lower -/ or upper surface of viologen molecule, which is in contact with the anthracene moiety. The situation must be true also with carbazole-viologen linked compounds. Since water molecules should be released on going from V^{2+} to V^{+} , free energy change in reducing partially dehydrated viologen will be less than otherwise. On the basis of the above reasoning, solvent effects on redox potential of the relevant viologen derivatives (CzC6V and 2MV) were examined.[7] In aqueous solutions, the redox potential for CzC6V was higher than that for 2MV by 0.1 V: (-0.33 and -0.44 V *vs*. NHE) for CzC6V and 2MV, respectively. The redox potential for CzC6V was exactly the same with that for 2MV (-0.27 V *vs*. NHE) in acetonitrile. The charge-transfer absorption for CzC6V in acetonitrile appears only as a weak shoulder on the absorption edge. The considerable blue shift and decrease in intensity, as compared with those in water, indicate that the interaction between viologen- and carbazole moieties becomes considerably small in acetonitrile. These results are in perfect agreement with the above reasoning.

If the quenching experiment is carried out with polar organic solvents, instead of water, the difference in kq-value between carbazole-viololgen linked compounds and simpler viologen is also expected to disappear. The difference in Ru-trisbpy luminescence quenching between the amphiphilic- and simpler viologens was carefully examined by the use of the ethanol solutions (spectro grade). The kq-value for CzC6V (3.2×10^8 $M^{-1}s^{-1}$) became fairly close to that for 2C6V (2.7×10^8 $M^{-1}s^{-1}$). In addition, the charge-transfer absorption of CzC6V (λmax , 420 nm in the aqueous solution) could be hardly observed in the ethanol solution. These results are in excellent agreement with the above discussions.

Enhanced quenching of the photoexcited Ru-trisbpy by the linked compounds was thus concluded to come from partial dehydration of the viologen unit, which is interacting with carbazole moiety in face-to-face configuration in aqueous solutions. The charge-transfer absorption band served as an excellent probe for estimating proximity of the two terminal groups in the linked compounds.

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References and Notes

1 Contribution No.1029 from the Department of Chemical Science and Technology, Kyushu University.

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7 Cyclic voltammograms were obtained with the following reference electrodes and supporting electrolytes (0.1M): Ag/AgCl and KCl in water, and Ag/Ag^{+} and TBAP in acetonitrile.