March, 1985] © *1985 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 58, 1029—1032 (1985)* 1029

Comparative Studies of Anionic Molecular Assemblies as Mediums for Electron Transfer Quenching of Excited Ru[(bpy)$_3$]$^{2+}$ by Cationic Quenchers

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(Received November 5, 1984)

Behaviors of excited [Ru(bpy)$_3$]$^{2+}$ bound to anionic molecular assemblies such as polymer electrolytes, vesicles and micelles together with electron-acceptor quencher MV^{2+} have been investigated by measurements of [Ru(bpy)$_3$]$^{2+}$ luminescence quenching and radical yields in electron-transfer quenching using a dye laser photolysis apparatus. Quenching behavior characteristic to each molecular assembly has been observed. A remarkable enhancement of quenching was observed in the presence of poly(vinyl sulfate). Such an effect was observed also in sodium dihexadecyl phosphate solution though it is less pronounced. However, no such specific quenching behavior was observed in sodium dodecyl sulfate micellar solution.

The photochemical and photophysical properties of [Ru(bpy)$_3$]$^{2+}$ and related metal complexes are the subject under lively investigations from the viewpoint of solar energy conversion.[1] The electron-transfer and energy-transfer phenomena of these complexes in the excited state have been studied in some details both in bulk and heterogeneous systems.[2–4] In relation to the photoinduced electron transfer and excitation transfer in heterogeneous systems involving molecular assemblies, it is important to elucidate the nature of these systems as microenvironments on which those reaction processes take place. For example, luminescence quenching of ruthenium complex by Cu^{2+} and methylviologen cation (MV^{2+}) bound to anionic micelles was used as a probe to investigate the nature of the micelle as a microenvironment.[5]

However, our recent studies of excitation transfer among dye ions adsorbed on various molecular assemblies indicate clearly that the mode of excitation transfer and trapping is very characteristic to each kind of molecular assembly,[6,7] which seems to reflect the different adsorbed state of dyes characteristic to each molecular assembly. This result suggests the importance of the comparative studies of various molecular assemblies as mediums for photochemical reactions by using a common photochemical probe system. Along this line, we have examined the luminescence quenching reactions of excited [Ru(bpy)$_3$]$^{2+}$ due to electron transfer to MV^{2+} in solutions containing various anionic molecular assemblies such as polymer electrolyte, vesicles and micelles.

Results of these investigations shows very clearly the different microenvironmental characteristics of these molecular assemblies as the mediums for photochemical electron transfer reactions between cations.

Experimental

[Ru(bpy)$_3$]$^{2+}$ was synthesized according to the standard method[8] and was recrystallized several times from water. MV^{2+} (G. R. Grade, Tokyo Kasei) was purified by repeated recrystallization from methanol. Purified propylviologen sulfonate (PVS°) was kindly supplied by Dr. M. Furue of this University and used as received. *p*-Benzoquinone (BQ) was purified by recrystallization from ethanol and subsequent sublimation. CuCl$_2$·2H$_2$O (G. R. Grade, Nakarai) was used as received.

Sodium dodecyl sulfate (SDS) (S. U. Grade, Nakarai) and three kinds of polyelectrolyte; potassium poly(vinyl solfate) (PVSK) (G. R. Grade, Nakarai), poly(vinyl alcohol) (PVA) (E. P. Grade, Nakarai) and poly(methacrylic acid) sodium salt (PMAS) (Polysciences, Inc.) were used without further purification. Sodium dihexadecyl phosphate (NaDHP) was obtained by treating dihexadecyl hydrogen phosphate, which was synthesized according to Ref. 9, with NaOH in ethanol solution. To prepare the vesicle, NaDHP was sonicated in water at 60 °C for 30 min., using a sonifier set (Branson, model 185).

Water was purified by distillation with a nonboiling type distillation apparatus. All solutions for measurements were deoxygenated by flushing with N$_2$ gas for at least 20 min. All measurements were carried out at room temperature.

Spectra and relative yields of [Ru(bpy)$_3$]$^{2+}$ emission were measured with an Aminco-Bowman spectrophotofluorometer. Radical yields in electron-transfer quenching of excited [Ru(bpy)$_3$]$^{2+}$ were measured by using a dye laser photolysis apparatus:[10] the lasing dye was Coumarin 503 (Phase-R Company), whose lasing wavelength, output power and fwhm were 498 nm, 35 mJ and 250 ns, respectively. The luminescence decay curves were determined by exciting the sample with the second harmonic of a mode locked Nd^{3+}:YAG laser and by observing the decay curve with a highspeed microchannel plate photomultiplier (HTV R-1194UX)-fast storage oscilloscope (Tektronix 7834) combination.

Results and Discussion

Luminescence Quenching of [Ru(bpy)$_3$]$^{2+}$ in Molecular Assemblies. It is well-known that the luminescence of [Ru(bpy)$_3$]$^{2+}$ ($\lambda_{\max}$=610 nm, τ_0=650 ns) is quenched by MV^{2+} with a quenching rate constant of

$k_q \approx 5 \times 10^8\ M^{-1}\ s^{-1}$ (1 M=1 mol dm^{-3}) in water with a controlled ionic strength. However, when 0.01 M (in monomer unit) of PVSK was added to solution, a peculiar curves with a lump as shown in Figure 1 was obtained instead of the simple Stern-Volmer straight line. I_0/I shows a peak at 1.5×10^{-3} M of MV^{2+} where 98% of the $[Ru(bpy)_3]^{2+}$ emission is quenched, and the luminescence is restored with further addition of the quencher. When MV^{2+} concentration is higher than 5×10^{-3} M, the quenching is very similar to that in bulk solution.

Above results can be explained in terms of a limited capability of the anionic molecular assembly to adsorb cations. All $[Ru(bpy)_3]^{2+}$ cations may be adsorbed on PVSK when MV^{2+} concentration is low. Under these conditions, because both $[Ru(bpy)_3]^{2+}$ and MV^{2+} are concentrated by adsorption on PVSK, the luminescence is effectively quenched. With increase of the MV^{2+} concentration, all adsorption sites may be occupied by $[Ru(bpy)_3]^{2+}$ and MV^{2+}. With further increase of MV^{2+}, $[Ru(bpy)_3]^{2+}$ seems to be expelled into bulk solutions. Eventually, almost all of $[Ru(bpy)_3]^{2+}$ ions appear to be removed from the vicinity of PVSK, where the concentration of MV^{2+} is very high. The expelled $[Ru(bpy)_3]^{2+}$ ions undergo simple Stern-Volmer type of luminescence quenching quite similar to that in bulk solution.

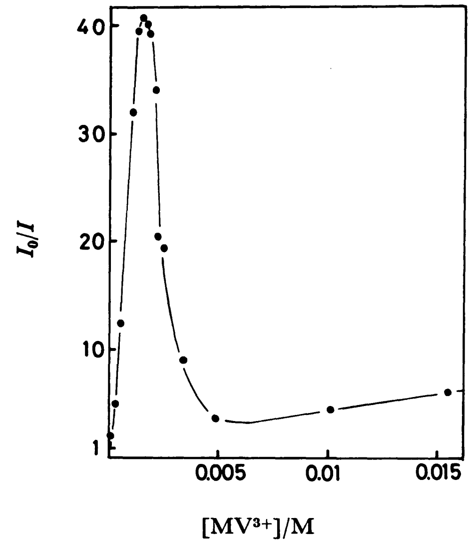

Fig. 1. (I_0/I)~[quencher] relation for the luminescence quenching of $[Ru(pby)_3]^{2+}$–MV^{2+} system in aqueous solution containing PVSK.
$[[Ru(bpy)_3]^{2+}] = 6 \times 10^{-5}$ M. [PVSK]$= 1 \times 10^{-2}$ M (in monomer unit)

We have examined the effect of PVSK concentration as indicated in Table 1. The MV^{2+} concentration that gives the peak value of I_0/I is proportional to the concentration of PVSK. This result suggests that PVSK is able to bind MV^{2+} at a ratio of *ca.* one MV^{2+} for 6 monomer units of PVSK. Another cationic quencher Cu^{2+} also causes the similar effect, but the extent of the quenching (the peak value of I_0/I) in this case is much smaller. The neutral quencher BQ or PVS°, however, does not give such a peculiar quenching. Moreover, when the anionic PVSK is replaced by neutral PVA, the lump in I_0/I *vs.* [quencher] relation disappears. After the completion of the present work we found similar report[11] on $[Ru(bpy)_3]^{2+}$-Cu^{2+}-PVSK system. However, the object of the present work is the comparative studies of various anionic molecular assemblies as microenvironment for the photochemical electron transfer quenching reaction between adsorbed cations. For this purpose, MV^{2+} which shows far greater quenching ability than Cu^{2+} in the ad-

TABLE 1. PEAK VALUE $(I_0/I)_{peak}$ OF THE LUMP IN I_0/I *vs.* $[MV^{2+}]$ RELATION AS A FUNCTION OF ADDED PVSK CONCENTRATION

[PVSK]/M	$[Ru(bpy)_3]^{2+}$/M	$[MV^{2+}]$ which gives $(I_0/I)_{peak}$/M	$(I_0/I)_{peak}$
1×10^{-3}	6×10^{-5}	1.5×10^{-4}	≈40
5×10^{-3}	6×10^{-5}	7×10^{-4}	≈50
1×10^{-2}	6×10^{-5}	1.5×10^{-3}	≈40
1×10^{-2}	3×10^{-5}	1.5×10^{-3}	≈55

TABLE 2. RESULTS FOR VARIOUS MOLECULAR ASSEMBLY-QUENCHER SYSTEMS

Molecular assembly	[molecular assembly]/M[a)]	Quencher	[quencher] which gives $(I_0/I)_{peak}$/M	$(I_0/I)_{peak}$
PVSK	1×10^{-2}	MV^{2+}	1.5×10^{-3}	≈40
PVSK	1×10^{-2}	Cu^{2+}	2.2×10^{-3}	≈10
PVSK	1×10^{-2}	BQ	— [b)]	—
PVSK	1×10^{-2}	PVS°	— [b)]	—
PVA	1×10^{-2}	MV^{2+}	— [b)]	—
PMAS	2×10^{-3}	MV^{2+}	2.5×10^{-5}	≈1.4
SDS	8×10^{-2}	MV^{2+}	— [b)]	—
NaDHP	2.6×10^{-4}	MV^{2+}	3.4×10^{-5}	≈3
NaDHP	1.3×10^{-3}	MV^{2+}	4.1×10^{-4}	≈5

a) Concentrations are given in monomer unit. b) No lump was observed in I_0/I *vs.* [quencher] plot.

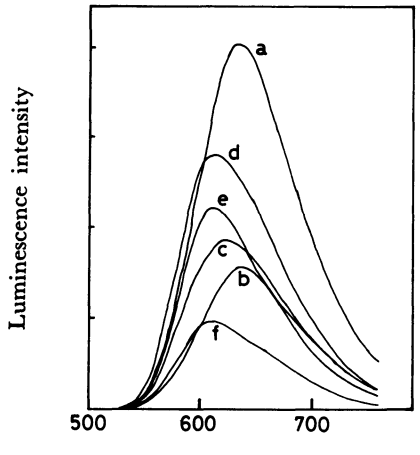

Fig. 2. Effect of the addition of MV^{2+} upon the luminescence spectrum of $[Ru(bpy)_3]^{2+}$ in aqueous solution containing NaDHP.
[NaDHP]=2.6×10^{-4} M.
[MV^{2+}]: a; 0, b; 1.0×10^{-5}, c; 6.1×10^{-5}, d; 1.3×10^{-4}, e; 5.4×10^{-3}, f; 1.1×10^{-2} M.

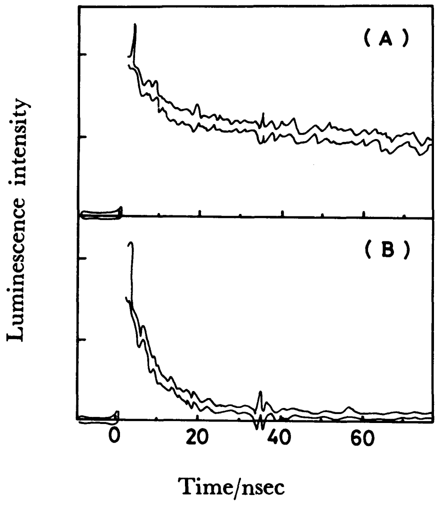

Fig. 3. Decay curves of $[Ru(bpy)_3]^{2+}$ emission in aqueous solution containing PVSK.
[$[Ru(bpy)_3]^{2+}$]=6×10^{-5} M. [PVSK]=1×10^{-2} M (in monomer unit). [MV^{2+}]: A; 4×10^{-3}, B; 2×10^{-3} M.

sorbed state is much better system.

Above experimental results are summarized in Table 2, which suggests that the electrostatic force plays an important role for the adsorption of $[Ru(bpy)_3]^{2+}$ and MV^{2+} onto the molecular assemblies. Table 2 also indicates that each anionic molecular assembly shows characteristic behavior in the adsorption of cations. Not only the MV^{2+} concentration at $(I_0/I)_{peak}$ but also the luminescence quenching itself is characteristic to each kind of molecular assembly. Moreover, SDS micellar solution does not show such a peculiar behavior in luminescence quenching as observed in PVSK solution in the present experimental conditions. However, it should be noted here that there is some kind of specific interaction between SDS micelle and $[Ru(bpy)_3]^{2+}$ because a slight broadening of the absorption spectrum and a bathochromic shift of *ca.* 20 nm of the luminescence spectrum occurs by adsorption. We have observed similar spectral shift also in the case of NaDHP vesicle solution. As shown in Figure 2, the emission maximum of $[Ru(bpy)_3]^{2+}$ without MV^{2+} or with low concentration MV^{2+} lies at *ca.* 630 nm, in which case $[Ru(bpy)_3]^{2+}$ is supposed to be adsorbed on the NaDHP vesicle.

By adding more MV^{2+}, the emission intensity is a little recovered and the peak wavelength becomes the same as in pure water solution. Further increase of MV^{2+} concentration results in the simple Stern-Volmer type quenching in bulk solution. Contrary to these spectral shifts in SDS and NaDHP solutions which indicate more or less specific interaction between $[Ru(bpy)_3]^{2+}$ and detergent molecules, no such shift caused by adsorption was observed in the case of PVSK solution, where, although the adsorption due to electrostatic attraction is the strongest among the molecular assemblies used here, the environmental state for $[Ru(bpy)_3]^{2+}$ is very close to that in pure aqueous solution.

Emission Decay Curve. Figure 3 shows that the emission of $[Ru(bpy)_3]^{2+}$ -MV^{2+} system in PVSK solution does not show single exponential decay; the decay curves are composed of at least two components. The fast decay component corresponds to the quenching of excited $[Ru(bpy)_3]^{2+}$ on PVSK chain by the MV^{2+} which is also adsorbed on PVSK chain in the vicinity of the quencher. The slow one corresponds to the decay of $[Ru(bpy)_3]^{2+}$ in the bulk. The intensity of the slow component emission of sample A is higher than that of sample B, since the large part of $[Ru(bpy)_3]^{2+}$ of the former is expelled into bulk.

Laser Photolysis Experiments. In Table 3, the absorbances of transient MV^+ radical obtained with a dye laser photolysis system are listed. In simple aqueous solution, the absorbance of the transient radical observed in the samples with different quencher concentrations was proportional to the degree of quenching. This is in agreement with the result in our previous report.[10]

In the case of PVSK solution, however, the radical formation is strongly suppressed at the MV^{2+} concentration of 1.5×10^{-3} M, where I_0/I shows the peak of lump. In general, the radical yield is determined by the competition between the dissociation into free radicals and deactivation by back electron transfer in the geminate radical pair formed by the photoinduced electron transfer. When both radical ions are bound to PVSK in close proximity to each other, the back electron transfer will dominate in

TABLE 3. TRANSIENT ABSORBANCE OF MV^+ GENERATED BY AN ELECTRON TRANSFER FROM EXCITED $[Ru(bpy)_3]^{2+}$ TO MV^{2+}

Solvent	$[MV^{2+}]$/M	Degree of quenching /%	Transient absorbance of MV^+ observed at 603 nm
H_2O	0.0015	22	0.064
H_2O	0.007	66	0.177
H_2O	0.012	78	0.216
H_2O with 0.01 M PVSK	0.0015	98	0.026
H_2O with 0.01 M PVSK	0.007	71	0.076
H_2O with 0.01 M PVSK	0.012	80	0.150

TABLE 4. CHANGE OF $(I_0/I)_{peak}$ VALUE AND $[MV^{2+}]$ WHICH GIVES $(I_0/I)_{peak}$ DEPENDING UPON THE IONIC STRENGTH OF SOLUTION[a)]

Ionic strength	$(I_0/I)_{peak}$	$[MV^{2+}]$ which gives $(I_0/I)_{peak}$ /M
0.0045	40	0.0015
0.01	25	0.0013
0.023	9.5	0.0010
0.045	4.5	0.0009

a) In each measurement of $(I_0/I)_{peak}$, the ionic strength was kept constant by adjusting the NaCl concentration.

the pair leading to a very small free radical yield. With increase of MV^{2+} concentration, $[Ru(bpy)_3]^{2+}$ may be expelled into bulk solutions, where the free radical yield is considerably higher than in adsorbed state. We have observed analogous effect of adsorption upon free radical yield also in the case of NaDHP solution.

Effect of the Addition of Salt upon the Luminescence Quenching Behavior in PVSK Solution. In order to examine in a more detail the adsoprtion on molecular assembly and the luminescence quenching behaviors of $[Ru(bpy)_3]^{2+}$-MV^{2+} system, we have investigated the effect of addition of NaCl on the luminescence of PVSK solution. The results are summarized in Table 4, which shows that the MV^{2+} concentration that gives $(I_0/I)_{peak}$ and the $(I_0/I)_{peak}$ value itself decrease with increase of the ionic strength of the solution. This result means that, when NaCl is added into the solution, Na^+ may be attracted to the polymer electrolyte, shielding its electrostatic fields and preventing adsorption of $[Ru(bpy)_3]^{2+}$ and MV^{2+} on polymer electrolyte.

Concluding Remarks. In the present work, we have demonstrated the luminescence-quenching behaviors of $[Ru(bpy)_3]^{2+}$-MV^{2+} system adsorbed on anionic molecular assemblies. The remarkable enhancement of quenching observed when both $[Ru(bpy)_3]^{2+}$ and quencher cations are adsorbed on anionic moelcular assembly was the largest in PVSK solution. Such effect was observed also in NaDHP vesicle solution though it is less pronounced compared with PVSK solution. However, no such specific quenching behavior was observed in SDS micellar soluton. These results show clearly the difference among these anionic molecular assemblies in the capability to keep $[Ru(bpy)_3]^{2+}$-cationinc quencher pair in sufficiently close proximity to undergo photoinduced electron transfer. In this respect, SDS micelle seems to have the most disordered structure among these three molecular assemblies, which can be concluded also from several other experimental results.[6,7,12,13)]

The present work was partly supported by the Grant-in-Aid from the Japanese Ministry of Education, Science and Culture to NM (58045097).

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