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# Novel Effects of Polyelectrolytes on Fluorescence Quenching of Tris(2,2′-bipyridine)ruthenium(II) by Methyl Viologen and $Cu^{2+}$

**Joon Woo Park**† **and Young Hee Paik**

*Department of Chemistry, Ewha Womans University, Seoul 120, Korea* *(Received June 4, 1985)*

The addition of poly(styrenesulfonate) (PSS) to $Ru(bpy)_3^{2+}$ solutions shifted the emission peak by 3 nm to red, and increased emission intensity by 1.8 times. By contrast, poly(vinylsulfonate) (PVS) had little effect on the fluorescence spectrum. The effects of PSS on the spectral properties of $Ru(bpy)_3^{2+}$ were attributed to the presence of a hydrophobic phenyl group in PSS, which interact with $Ru(bpy)_3^{2+}$ by, at least in part, hydrophobic effect. The binding constant of $Ru(bpy)_3^{2+}$ to PSS in 0.1 M NaCl was $6\times10^4$ $M^{-1}$, and this value was about $10^3$ times higher than those of methyl viologen ($MV^{2+}$) and $Cu^{2+}$. The Stern-Volmer constants of emission quenching of $Ru(bpy)_3^{2+}$ by $MV^{2+}$ and $Cu^{2+}$ in 0.1 M NaCl solutions were 426 and 40 $M^{-1}$, which correspond to second order rate constants($k_q$) of $1.1\times10^9$ and $1.0\times10^8$ $M^{-1}s^{-1}$, respectively. The presence of PSS enhanced $K_{SV}$'s by ~50 times, whereas PVS increased the values only 1-4 times. The large enhancing effect of PSS, despite of lower charge density than PVS, was explained in terms of longer life-time of photoexcited $Ru(bpy)_3^{2+}$ bound to PSS and strong association of $Ru(bpy)_3^{2+}$ to PSS due to a specific interaction involving hydrophobic effect. The variation of $K_{SV}$'s on the concentrations of PVS and PSS were also investigated for $Ru(bpy)_3^{2+}-MV^{2+}$ and $Ru(bpy)_3^{2+}-Cu^{2+}$ photoredox systems.

## Introduction

The quenching of the excited triplet state of tris(2,2′-bipyridine)ruthenium(II) cation ($Ru(bpy)_3^{2+}$) via electron transfer reaction has been a subject of intense studies. These studies are mainly focused on the possibility of using the complex cation in conversion of solar energy into the stored chemical energy, and thus, on the enhancement of the efficiency of the conversion.[1] Methyl viologen ($MV^{2+}$: 1,1′-dimethyl-4,4′-bipyridinium) salts have been most widely used as an electron mediator, *i.e.*, fluorescence quencher. To accelerate the desired electron transfer reaction and/or to prevent back or side reactions, various microheterogeneous systems were extensively utilized.[1,2]

In view of large influences of polyelectrolytes on the rates and yields of many chemical reactions,[2] the effects of polyelectrolytes on the quenching of fluorescence of photoexcited $Ru(bpy)_3^{2+}$ by various quenchers have been investigated.[2-8] Similarly, the electron transfer reactions involving polymer-pendent $Ru(bpy)_3^{2+}$ or viologens were also studied.[9-11] The rates of electon transfer quenching of the excited $Ru(bpy)_3^{2+}$ by $Cu^{2+}$ and $Fe^{2+}$, for example, were increased up to 3 orders of magnitude by the addition of an anionic polyelectrolyte, poly(vinylsulfonate).[3-5] The remarkable enhancement of the quenching were attributed to the condensation of the $Ru(bpy)_3^{2+}$ and the cationic quenchers in the potential fields of the polyanion by the coulombic interaction.

In this paper, we describe our results of the studies on the fluorescence quenching of $Ru(bpy)_3^{2+}$ by $MV^{2+}$ and $Cu^{2+}$ in poly(styrenesulfonate) (PSS) and poly(vinylsulfonate) (PVS) solutions, which reveal that a specific interaction with polyelectrolytes also greatly affects the rates of the electron transfer reactions between the photoredox couples.

## Experimental

$Ru(bpy)_3(ClO_4)_2$ was prepared by modification of a precedure described in a literature[12] for the preparation of $Ru(bpy)_3(PF_3)_2$, *i.e.*, the reaction of $RuCl_3.xH_2O$ and 2,2′-bipyridine was followed by column chromatography on alumina and by precipitation with aqueous $NaClO_4$. PVS and PSS were obtained from Polyscience as sodium salts, and purified by precipitation from ethanol. All solutions were prepared with deionized distilled water. The concentration of $Ru(bpy)_3^{2+}$ was determined by using the value of $\varepsilon_{453} = 14000$ $M^{-1}cm^{-1}$ for the complex ion.[5] The concentrations of polyelectrolytes were calculated from dried weight and given in terms of monomer units.

Absorption spectra were taken on a Beckman DU-8B spectrophotometer, and fluorescence spectra were recorded on a Hitachi 650-10S fluorescence spectrophotometer at 25±0.5°C. The emission spectra were recorded in 550-660 nm range (slit width 5 nm) at excitation wavelength of 450 nm. For all experiments, air-saturated solutions were used, since the electron transfer rate expressed in terms of Stern-Volmer constant determined from an air-saturated solution is the same as that from a deaerated solution.[3] Unless otherwise specified, all solutions contained 0.1 M NaCl to maintain the nearly same ionic strength for all measurements, because the electron transfer rate under study strongly depends on the ionic strength[13] as expected from the interionic nature of the reactions.

## Results and Discussion

*Effects of PVS and PSS on the Emission Spectrum of Ru(bpy)$_3^{2+}$.* The emission intensity of Ru(bpy)$_3^{2+}$ solutions was greatly increased, up to 1.8 times, and the peak of emission spectrum shifted to longer wavelength by 3 nm by the addition of PSS. The typical spectra demonstrating the effects of PSS are shown in Figure 1. In contrast to PSS, the addition of PVS to solutions of Ru(bpy)$_3^{2+}$ had little or no effect on the intensity and peak position of the emission spectrum, which agreed well with a previous report.[4] The increased emission intensity in the presence of PSS reflects the longer life-time of a photoexcited Ru(bpy)$_3^{2+}$ associated with PSS than that of free Ru (bpy)$_3^{2+}$ or Ru(bpy)$_3^{2+}$ simply residing in the potential field of PVS. This suggests a specific interaction between PSS and Ru(bpy)$_3^{2+}$, and the specific interaction is supported by the change in the position of emission peak in PSS solutions. Since both PSS and PVS bear sulfonate groups in common, the observed effects on the spectral properties of Ru(bpy)$_3^{2+}$ stem from the presence of the hydrophobic phenyl group in PSS rather than the polar anionic group.

Meisel *et al.*[14] reported red shift (~20 nm) of emission peak of Ru(bpy)$_3^{2+}$ in SDS micellar solution and attributed the shift to the interaction of Ru(bpy)$_3^{2+}$ with hydrocarbon chains of the surfactant. DeGraff and coworkers[15,16] recently reported binding of $\alpha$-diimineruthenium(II) complexes with non-ionic surfactants and subsequent increases in life-time of the excited state. Their binding strength increases with hydrophobicity of ligands. These reports are in the same direction as the observed effects of PSS on the fluorescence spectra of Ru(bpy)$_3^{2+}$, and suggest that hydrophobic interaction between Ru(bpy)$_3^{2+}$ and PSS is, at least in part, responsible for the observed spectral change in PSS. However, little effect of SDS on emission intensity,[14] no direct relationship between position of emission peak and hydrophobicity of solvent media,[14] and no apparent interaction between Ru(bpy)$_3^{2+}$ with non-ionic surfactant Triton[15] imply that other factors might also be involved in the effects of PSS on the fluorescence spectra of Ru(bpy)$_3^{2+}$. The clarification of these factors is beyond the scope of present study.

The variation of emission intensity of Ru(bpy)$_3^{2+}$ solution with concentrations of PSS is plotted in Figure 2. The observed fluorescence intensity ($I$) can be described by an average for the free and bound Ru(bpy)$_3^{2+}$, when self-quenching is negligible.

$$I = f_{\text{free}} I_{\text{free}} + f_{\text{bound}} I_{\text{bound}} \tag{1}$$

where $f$'s and $I$'s represent the fraction and emission intensity of each species present in solution, respectively. The emission intensity measured in the absence of PSS should be $I_{\text{free}}$, and the limiting intensity at high [PSS] can be assumed as $I_{\text{bound}}$. Using these values, the fractions of bound Ru(bpy)$_3^{2+}$ at different concentration of PSS are calculated.

The variation of $I$ with concentration of PSS reflects the equilibrium between free and bound Ru(bpy)$_3^{2+}$. If we assume that each Ru(bpy)$_3^{2+}$ binds to a pair of anionic sites of PSS,

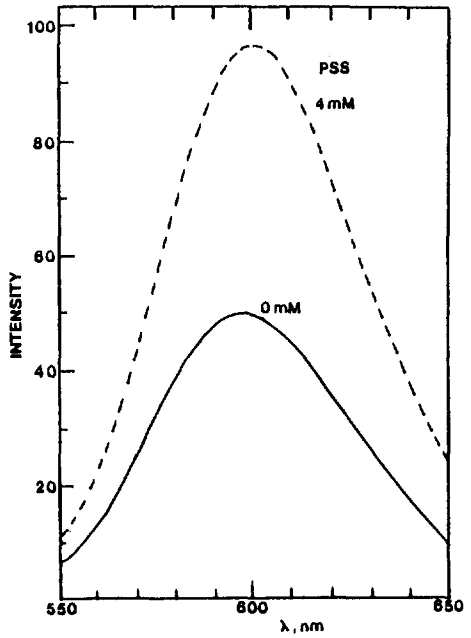

**Figure 1.** Fluorescence spectra of Ru(bpy)$_3^{2+}$ in the absence and presence of 4 m*M* PSS. Excitation wavelength was 450 nm.

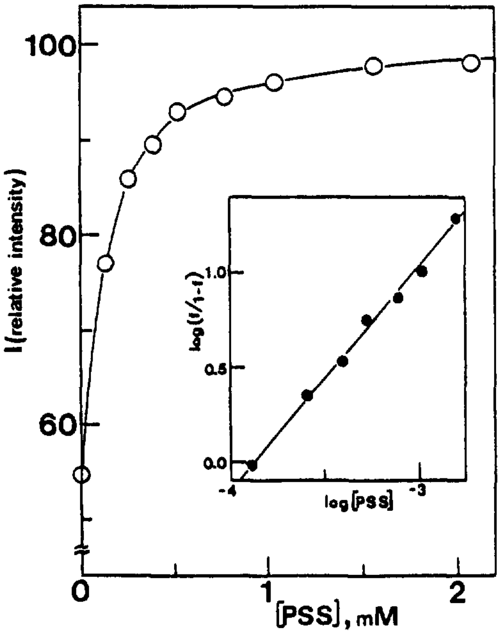

**Figure 2.** Variation of emission intensity of Ru(bpy)$_3^{2+}$ solutions at 600 nm with [PSS]. Inset is the plot of the emission data according to equation 4 to calculate the binding constant.

the equilibrium can be written as follows;

$$[\mathrm{Ru(bpy)_3^{2+}}]_{\mathrm{free}} + (\mathrm{PSS^-})_2 = [\mathrm{Ru(bpy)_3^{2+}}]_{\mathrm{bound}} \tag{2}$$

and the apparent equilibrium constant is expressed as;

$$K = \frac{f_{\mathrm{bound}}}{(1-f_{\mathrm{bound}})([\mathrm{PSS}]/2)} \tag{3}$$

The binding constant $K$ is dependent on $f_{\mathrm{bound}}$ due to change in electrostatic potential of the polyanion upon ionic association. Considering this fact, the equation (3) can be rewritten in terms of semi-empirical relationship of Katchalsky-Spitinik.[17]

$$\log \frac{f_{\mathrm{bound}}}{(1-f_{\mathrm{bound}})} = \log K + n \log([\mathrm{PSS}]/2) \tag{4}$$

where $n$ is an empirical parameter. In the range of $[\mathrm{PSS}]_{\mathrm{total}} \gg [\mathrm{Ru(bpy)_3^{2+}}]_{\mathrm{total}}$, at which condition the self-quenching is also negligible, [PSS] is replaced by $[\mathrm{PSS}]_{\mathrm{total}}$. The plot of equation (4) is shown in inset of Figure 2. $K$ and $n$ values were $6\times10^4$ $M^{-1}$ and 1.2, respectively.

*Fluorescence Quenching in the Absence of Polyelectrolyte.* The addition of fluorescence quencher (Q), $\mathrm{MV^{2+}}$ or $\mathrm{Cu^{2+}}$, decreased the fluorescence intensity. The quenching data were analyzed by Stern-Volmer plot,

$$I_0/I = 1 + K_{sv}[\mathrm{Q}] \tag{5}$$

In this equation, $I_0$ and $I$ denote the emission intensities in the absence and presence of a quencher, respectively. The Stern-Volmer constant $K_{sv}$ is related to the second order rate constant ($k_q$) for the quenching and the fluorescence life-time ($\tau_F$) of a fluorescing species by $K_{sv} = k_q\, \tau_F$.

The fluorescence quenching data of $\mathrm{Ru(bpy)_3^{2+}}$ by $\mathrm{MV^{2+}}$ and $\mathrm{Cu^{2+}}$ are plotted in Figure 3 according to equation (5), and $K_{sv}$'s in the absence of polyelectrolyte were calculated as 426 $\mathrm{M^{-1}}$ for $\mathrm{MV^{2+}}$ and 40 $M^{-1}$ for $\mathrm{Cu^{2+}}$. These values correspond to $k_q$ values of $1.1\times10^9\,\mathrm{M^{-1}s^{-1}}$ (for $\mathrm{MV^{2+}}$) and $1.0\times10^8\,M^{-1}s^{-1}$ (for $\mathrm{Cu^{2+}}$) as $\tau_F$ of $\mathrm{Ru(bpy)_3^{2+}}$ in air saturated aqueous solution is 0.4 $\mu$sec.[13] The $k_q$ values are in fair agreement with those determined by life-time measurements.[13,18]

*Quenching in PSS and PVS Solutions.* The emission quenching of photoexcited $\mathrm{Ru(bpy)_3^{2+}}$ by cationic quenchers, $\mathrm{MV^{2+}}$ and $\mathrm{Cu^{2+}}$, were greatly enhanced by the addition of anionic polyelectrolytes, PSS and PVS. The Stern-Volmer plots in 8 mM PSS and PVS solutions are presented in Figure 3. Unlike the plots of data taken in the absence of polyelectrolytes, the Stern-Volmer plots in the presence of polyelectrolytes exhibited large curvature. Such quenching behavior is similar to those reported for similar photoredox systems in PVS[4,19] and SDS micellar[14] solutions. The curvature in Stern-Volmer plot represents, largely, the dependencies of the apparent bimolecular quenching constant, $k_q = K_{sv}/\tau_F$, on the concentration of quenchers, and mainly arises from competition of $\mathrm{Ru(bpy)_3^{2+}}$ and cationic quenchers for available anionic sites of polyanions. When quencher concentration is low, both $\mathrm{Ru(bpy)_3^{2+}}$ and quenchers condense in the potential field of polyanionic domain and the fluorescence quenching is very efficient. However, further addition of quenchers at given concentration of polyelectrolytes may displace some $\mathrm{Ru(bpy)_3^{2+}}$ from the polyanionic domain, resulting in less efficient electron transfer reaction. The $K_{sv}$ values extrapolated to $[\mathrm{Q}]=0$, *i.e.*, slopes at $[\mathrm{Q}]=0$ in Figure 3, are summarized in Table 1.

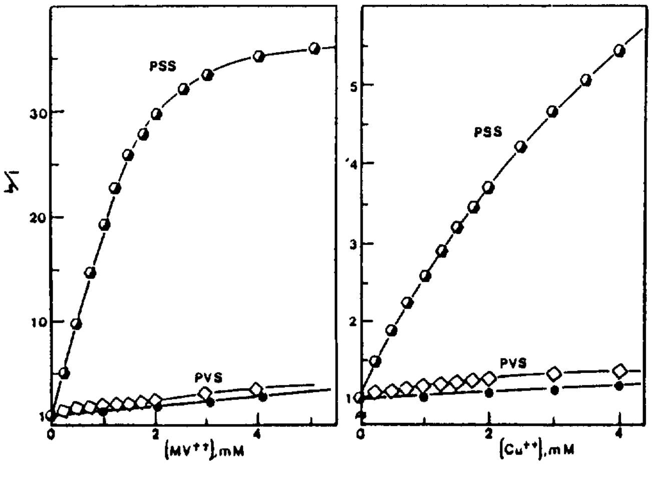

**Figure 3.** Stern-Volmer plots of emission quenching of $\mathrm{Ru(bpy)_3^{2+}}$ by $\mathrm{MV^{2+}}$ and $\mathrm{Cu^{2+}}$ in 8 mM PSS and PVS solutions. Filled circles are data taken in the absence of polyelectrolytes.

As can be seen in Figure 3 and Table 1, the presence of PSS enhanced $K_{sv}$ about 50 times, while the value increased only 1-4 times by PVS.[20] Despite of large difference in the intrinsic quenching constants of $\mathrm{MV^{2+}}$ and $\mathrm{Cu^{2+}}$, the enhancement of quenching produced by the polyelectrolytes is similar for both quenchers. Thus, the large difference in the enhancing effects between PSS and PVS should be attributed to the difference in the interacting properties of $\mathrm{Ru(bpy)_3^{2+}}$ with PSS and PVS. From the structural point of view, the negative charge density of PSS is expected to be lower than that of PVS. If one considers only electrostatic effect of polyelectrolytes on the quenching rate, the PSS should have less enhancing effect than PVS, but this is not the case observed in this investigation. The specific interaction, at least in part due to hydrophobic effect, between $\mathrm{Ru(bpy)_3^{2+}}$ and PSS seems to be responsible for the higher $K_{sv}$'s in PSS solutions. This interaction is also manifested in changes of the spectral properties of $\mathrm{Ru(bpy)_3^{2+}}$ as shown in Figures 1 and 2.

The increased emission intensity of $\mathrm{Ru(bpy)_3^{2+}}$ solution in the presence of PSS (Figure 1) reflects higher fluorescence quantum yield and, thus longer life-time of the photoexcited $\mathrm{Ru(bpy)_3^{2+}}$ bound to PSS than the free $\mathrm{Ru(bpy)_3^{2+}}$. Since the half-widths of emission spectra are virtually unchanged with the presence of PSS, the ratio of emission intensities of bound and free $\mathrm{Ru(bpy)_3^{2+}}$, 1.8, is approximated as the ratio of life-times of bound and free $\mathrm{Ru(bpy)_3^{2+}}$. The increased life-time of $\mathrm{Ru(bpy)_3^{2+}}$ bound to PSS contributes to the enhanced $K_{sv}$ in PSS

**TABLE 1: Stern-Volmer and Apparent Second Order Rate Constants of Fluorescence Quenching of Photoexcited $\mathrm{Ru(bpy)_3^{2+}}$ by $\mathrm{MV^{2+}}$ and $\mathrm{Cu^{2+}}$ in Polyelectrolytes solutions.**[a]

| Polyelectrolyte | [P], m$M$ | $K_{sv}$, $M^{-1}$ | | $k_q$, $10^9 M^{-1}s^{-1}$ | | $(k_q)_p/(k_q)_w$[b] | |
|---|---|---|---|---|---|---|---|
| | | $\mathrm{MV^{2+}}$ | $\mathrm{Cu^{2+}}$ | $\mathrm{MV^{2+}}$ | $\mathrm{Cu^{2+}}$ | $\mathrm{MV^{2+}}$ | $\mathrm{Cu^{2+}}$ |
| none | 0 | 426 | 40 | 1.1 | 0.1 | — | — |
| PSS | 4 | 23800 | 1920 | 35 | 2.7 | 31 | 27 |
| | 8 | 17000 | 1680 | 24 | 2.3 | 22 | 23 |
| PVS | 4 | 640 | 90 | 1.7 | 0.23 | 1.5 | 2.3 |
| | 8 | 790 | 140 | 2.1 | 0.35 | 1.9 | 3.5 |

[a] These values were taken at $[\mathrm{Q}]\to0$ in 0.1 M NaCl solutions at 25°C. $[\mathrm{Ru(bpy)_3^{2+}}]$ was $1\times10^{-5}M$. [b] $(k_q)_p/(k_q)_w$ stands for the enhancement of $k_q$ by the presence of polyelectrolytes.

solutions by $K_{sv}=k_q\tau_F$. Using the equation of $k_q=K_{sv}/\tau_F$, the bimolecular quenching constants $k_q$ are calculated and included in Table 1.

Assuming that the increased $k_q$ in the presence of PSS is due to the increased local concentrations of the interacting pair, Ru$(bpy)_3^{2+}$ and a quencher, the "effective local concentrations" introduced by Tara and Morawetz[19] and the association constants of quenchers with PSS are estimated. The volume fraction of a polymer in the polymer concentration of $n$ mole/l is given by $N_0vn/1000$, where $N_0$ is Avogadro's number and v (in cm$^3$) denotes the volume of one monomer unit of the polymer. The fraction of a quencher residing in the volume fraction of the polymer becomes $C_{eff}N_0vn/(C_{bulk}1000)$, where $C_{eff}$ and $C_{bulk}$ stand for the effective local concentration in the polyanion domain and the bulk concentration of a quencher, respectively. If one assumes that PSS exists in an extended rod-like conformation of radius 14 Å and of monomer length 2.5 Å,[21] the volume fraction of PSS in 8 mM solution becomes $7.4\times10^{-3}$. In this concentration of PSS, the fraction of bound Ru$(bpy)_3^{2+}$ is virtually 1 (Figure 2), and thus the enhancement in $k_q$ is proportional to the increase of local concentration of a quencher in the domain of the polyanion. The 22 times increase in $k_q$, for example, in case of $MV^{2+}$ in 8 mM PSS solution, is equivalent to $C_{eff}/C_{bulk}=22$. This value corresponds to the fraction of bound $MV^{2+}$ of 0.16, and the apparent binding constant of $MV^{2+}$ to PSS is calculated as 47 $M^{-1}$ $(K=0.16/((1-0.16)\times(8\times0.16)\times(8\times10^{-3}/2)))$.[22] By the same method, $K$ of $Cu^{2+}$ to PSS in 8 mM PSS solution is estimated to be 49 $M^{-1}$. Also, the $K$ values in 4 mM PSS solutions are calculated as 63 and 56 $M^{-1}$ for $MV^{2+}$ and $Cu^{2+}$, respectively. The above estimation of $K$ values is very crude.[21] But it points that the binding constants of the quenchers with PSS are about 3 orders of magnitude less than that of Ru$(bpy)_3^{2+}$ with the same polyelectrolyte.[22]

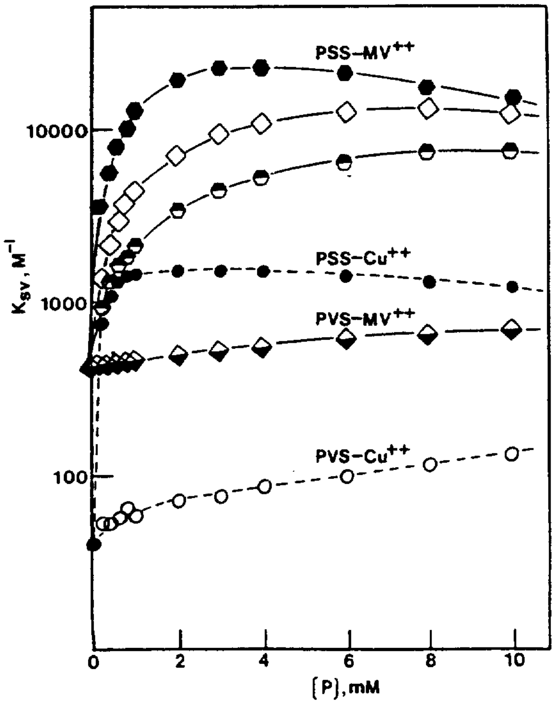

**Figure 4.** Variation of $K_{sv}$'s on the concentrations of polyelectrolytes shown. The concentrations of $MV^{2+}$ in PSS solutions were 0.75(●), 2(◇) and 4(⊖) mM. [Q] of other solutions were 2 mM.

The large difference between binding constants ($K$) of Ru$(bpy)_3^{2+}$ and of $MV^{2+}$ or $Cu^{2+}$ with PSS is quite contrast to that with PVS: Meisel and Matheson[3] reported that $K_{Ru(bpy)_3^{2+}}/K_{Cu^{2+}}$ to PVS is only 3.4. The much smaller enhancement of $K_{sv}$ and $k_q$ by PVS than by PSS, despite of higher charge density, can be regarded as an evidence that the binding constant of Ru$(bpy)_3^{2+}$ to PVS is much smaller than the same to PSS. We account this to a specific interaction between Ru$(bpy)_3^{2+}$ and PSS, which is also responsible for the longer excited state life-time and shift in the emission peak of Ru$(bpy)_3^{2+}$.

The enhancement of the bimolecular quenching constant of $Cu^{2+}$ is about 2 times greater than that of $MV^{2+}$ in PVS solutions. This reflects the higher charge density of $Cu^{2+}$, compared to that of $MV^{2+}$, which may appear as higher local concentration of the cation in the potential field of PVS. However, the $k_q$ enhancing efficiency of PSS is almost same for both quenchers. This seems due to hydrophobicity of $MV^{2+}$, which counteracts the smaller charge density of the cation in binding with the hydrophobic PSS macroanion.

As expected, the fluorescence intensity of Ru$(bpy)_3^{2+}$ solutions at constant concentrations of the fluorescing species and quencher was stronly dependent on the concentration of polyelectrolytes. The apparent Stern-Volmer constant ($K_{sv}$) were calculated at various concentrations of polyelectrolytes and graphed in Figure 4. This figure also demonstrates the remarkably different effects of PSS and PVS on the fluorescence quenching of Ru$(bpy)_3^{2+}$ by $MV^{2+}$ and $Cu^{2+}$.

In contrast to PVS, the effects of PSS on $K_{sv}$'s exhibit maxima. Even though the concentration of Ru$(bpy)_3^{2+}$ $(1\times10^{-5}$ M) is much lower, compared to those of quenchers, the much higher binding constant of Ru$(bpy)_3^{2+}$ to PSS leads to higher local concentration of the fluorescing species in the polyanion domain. When [PSS] is low, the Ru$(bpy)_3^{2+}$-quencher pairs increase sharply with increasing concentration of PSS, resulting in higher $K_{sv}$. However, as the concentration of PSS is further increased, the average number of Ru$(bpy)_3^{2+}$-quencher pair, and thus, $K_{sv}$'s are rather decreased. On the other hand, the binding affinity of Ru$(bpy)_3^{2+}$ and quenchers to PVS are close and small. The coulombic effect of PVS increases the average number of the interacting pairs up to much higher concentration of PVS as [PVS] increases. Thus, the effect of PVS on $K_{sv}$'s is rather similar to the effects of simple salts on equilibrium or rate constants of reactions involving charged species.

## Conclusions

Studies on the fluorescence behaviors of Ru$(bpy)_3^{2+}$ in PSS solutions reveal a specific interaction, which arises, at least in part, by hydrophobic interaction between the fluorescing species and the polyanion. This interaction leads to longer life-time of the excited state of Ru$(bpy)_3^{2+}$ and high binding constant of Ru$(bpy)_3^{2+}$ to PSS. The binding constant was found to be $6\times10^4$ $M^{-1}$, and about $10^3$ higher than the same of $MV^{2+}$ or $Cu^{2+}$. Such specific interaction was not revealed in PVS. The combined effects of specific and coulombic interactions of Ru$(bpy)_3^{2+}$ with PSS resulted in remarkably high $K_{sv}$ values for the emission quenching reactions between Ru$(bpy)_3^{2+}$ and cationic quenchers, $MV^{2+}$ and $Cu^{2+}$, compared to $K_{sv}$'s in PVS solutions. The novel effects of PSS on the enhancement of the rates of electron transfer reactions due to longer excited lifetime and higher binding constant of a reacting species might lead to improvement of the efficiency of photoenergy conversion by proper choice of hydrophobic polyelectrolytes.

*Acknowledgements.* This work was supported by the Korea Science and Engineering Foundation. Y.H. Paik is a recipient of the Graduate Fellowship from KOSEF. We thank to KOSEF for the supports.

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(20) In the absence of added salts, the addition of PVS enhanced $K_{sv}$ by about $10^3$ times,[3] while we observed only 1-4 times enhancement of $K_{sv}$ by PVS in 0.1 M NaCl solutions presumably due to masking of potential field of the polyanion by $Na^+$.

(21) The radius and length of monomer unit of PVS were estimated as 10 Å and 2.5 Å, respectively.[4] We assumed the length of phenyl group in PSS is 4 Å. In our experimental condition of 0.1 M NaCl, PSS may not exist as extended rod-like polyanion due to reduced charge repulsion. Thus, volume fraction of the polyanion and binding constants of quenchers with PSS correspond to their upper limits.

(22) There is good possibility that the quenchers, especially $MV^{2+}$, are associated with only one anionic site of polyelectrolytes. In this case, the binding constants of quenchers with PSS are reduced by half, and our argument on $K$'s is strengthened.

# Methyl Linoleate Oxidation via Electron Transfer in Competition with $^1O_2$ Formation Photosensitized by N-Acetyl-L-Tryptophan and 3-Methyl Indole

**Minjoong Yoon†, Moon Young Song and Dae Won Cho**

*Department of Chemistry, College of Science, Chungnam National University Daejon 300-31, Korea*

*(Received June 7, 1985)*

The efficiency of photosensitization of methyl linoleate (ML) oxidation by N-acetyl-L-trypophan(NAT) and 3-methyl indole(scatole) was markedly enhanced by increased concentration of ML in ethanol solution. The fluorescence intensities of sensitizers were observed to be quenched by ML, indicating that ML interacts with the indole excited singlet state. The inhibition of photosensitization by azide demonstrated a possible role of singlet oxygen in the photosensitization. The steady state kinetic treatment of azide inhibition of photosensitization was expected to show linear increase of reciprocal yield of ML oxidation product vs. reciprocal ML concentration at constant azide concentration, but the actual slope was nonlinear. This indicates another competing reaction involved in the photosensitization. As a possible competing reaction, electron transfer from ML to the excited sensitizer was proposed, since the measured fluorescence quenching rate constant closely resembled electron transfer rate constant determined from ML concentration dependence of oxidation product formation.