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Novel Effect of Additives on the Quenching Mechanism of the Excited State of Copolymer-Pendant $[Ru(bpy)_3]^{2+}$ by Methylviologen in Methyl Alcohol

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The quenching of the excited state of acrylic acid copolymer-pendant $[Ru(bpy)_3]^{2+}$ by methylviologen (MV^{2+}) was studied in methyl alcohol. The Stern–Volmer plots for the quenching showed a line or a curve (downward or upward) depending on the additive such as acid, alkali, or neutral salt in methyl alcohol. This behavior in methyl alcohol is entirely different from that in water where only dynamic quenching occurs. The behaviors in alcohol were analyzed by assuming stepwise binding of MV^{2+} into the domains around the Ru complex formed by the dissociated carboxylates and by considering dynamic as well as static quenching models. The one kind of photochemical reaction system showed four different quenching mechanisms induced by the additives.

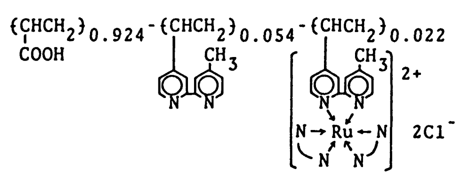
Photochemical reactions in polymer[1,2] and molecular assembly[3,4] systems are receiving intense interest as an approach to solar energy conversion.[5] Microenvironment of polymer systems very often affects remarkably photochemical reaction through electrostatic[6–8] or hydrophobic[9] interaction with quencher molecule. Tris(2,2′-bipyridine)ruthenium(II) complex ($[Ru(bpy)_3]^{2+}$) is attracting much attention as a sensitizer for visible light energy conversion.[2,4,5] Quenching of the excited state of $[Ru(bpy)_3]^{2+}$ by methylviologen (MV^{2+}) has been studied in the presence of anionic polymers[7,8] showing that an electrostatic interaction enhances the reaction rate. In such cases where polymer is present as a separate molecule in a sensitizer solution, the sensitizer should interact with the polymer in order that the polymer affects the sensitizing reaction. When a sensitizer is covalently attached to a polymer molecule, however, the microenvironmental effect of the polymer chain upon the photochemical reaction of the sensitizer can easily be studied independent of the interaction between sensitizer and polymer. The influencing factor is then only the interaction between polymer and quencher.

The present authors have prepared copolymer-pendant $[Ru(bpy)_3]^{2+}$, where copolymer is prepared from 4-methyl-4′-vinyl-2,2′-bipyridine and comonomer such as styrene, acrylic acid, etc.[10] These copolymer-pendant $[Ru(bpy)_3]^{2+}$ complexes have their characteristics in that the microenvironment around the Ru complex can drastically be changed by changing the comonomer compound. It means that the chemical as well as the physicochemical properties of the attached Ru complex can be changed with ease by choosing a proper comonomer. Taking solubility of a copolymer-pendant $[Ru(bpy)_3]^{2+}$, for example, a copolymer complex containing styrene comonomer is well soluble in many organic solvent such as benzene or chloroform, but entirely insoluble in water in contrast to the conventional low-molecular $[Ru(bpy)_3]^{2+}$ which is well soluble in water but insoluble in benzene or chloroform. This styrene-copolymer-pendant $[Ru(bpy)_3]^{2+}$ could be used as a stable membrane in water for fabricating photoresponsive graphite electrode[11,12] or stabilizing liquid-junction *n*-GaAs[13] and *n*-CdS[14].

When acrylic acid (AA) was used as a comonomer, the excited state of the water-soluble copolymer-pendant $[Ru(bpy)_3]^{2+}$ showed a remarkably pH-dependent activity toward MV^{2+} quencher due to the dissociation of the AA.[6] At neutral and alkaline regions in water, the quenching of the excited state of the AA-copolymer complex by MV^{2+} was remarkably enhanced due to the polyanionic domain formed around the Ru complex by the dissociation of the AA groups. It was concluded that electrostatic interaction brought about the enhancement of the quenching reaction, however, the linear relationship of the Stern–Volmer plots showed that the quenching is understood to occur via dynamic process in water.[6] Since the interaction is an electrostatic one, the reaction in a less polar solvent must present an aspect different from an aqueous system. It was found in the further study that static quenching occurs in methyl alcohol and that the mechanism is different depending on the additives such as base, acid, and neutral salt. This is the first example as far as the present authors know that one photochemical reaction system exhibits various quenching mechanisms as a function of additives. The mechanisms will be interpreted in terms of binding of MV^{2+} to polyanionic domain formed around Ru complex and of static quenching therein, and reported in this paper.

Experimental

Copolymer-pendant $[Ru(bpy)_3]^{2+}$ was prepared by reaction of a copolymer of 4-methyl-4′-vinyl-2,2′-bipyridine and acrylic acid (mol wt 4000) with *cis*-$[Ru(bpy)_2Cl_2]$ at the molar ratio of [bpy unit of the copolymer]/[Ru]=3.5 in *n*-BuOH under reflux for 2.5 h.[6] The polymer complex was purified by dialysis in water. The composition of the copolymer-pendant complex 1 was as follows.



1 N⌒N = 2,2′-bipyridine

Methylviologen (MV^{2+}) was purified by recrystallization in methyl alcohol–acetone mixture. The quenching of the excited state of the copolymer-pendant $[Ru(bpy)_3]^{2+}$ by methylviologen (MV^{2+}) was measured in methyl alcohol under the addition of various salts. Emission intensities were measured by the fluorimeter (Hitachi MPF-4). The emission decay was measured by a single-photon counting method with 1-ns pulsed light from a 12-atm hydrogen lamp.

Results and Discussion

The Stern–Volmer plots of the quenching of the excited state of the copolymer complex 1 by MV^{2+} in methyl alcohol were shown in Fig. 1. The plots without any additive show a downward curve. The plots of the quenching with the addition of HCl showed a linear relationship which almost coincides with those of conventional low molecular $[Ru(bpy)_3]^{2+}$. When neutral salt (Et_4NBr) is further added to this HCl-containing system, the quenching has become more efficient, and the slope of the plots is almost equal to the initial slope of the plots without additives. The solution in the presence of NaOH showed a very efficient quenching, and the plots gave a downward curve. The presence of thiourea in addition to HCl brought about an upward-curved plots.

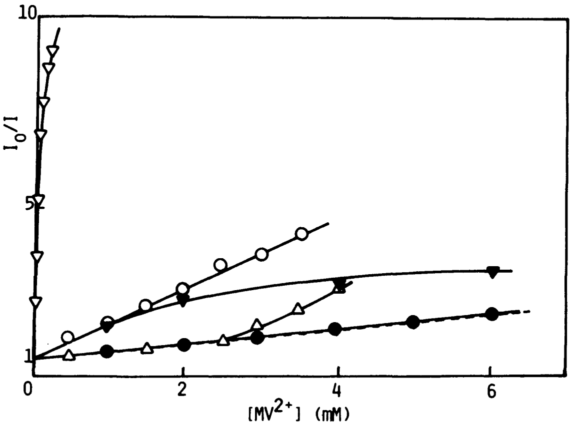


Fig. 1. Stern-Volmer plots for the quenching of excited 1 by MV^{2+} in methyl alcohol. Ru complex, 10^{-5} M (1 M=1 mol dm^{-3}). ▼, With no additive; ●, 0.5 mM HCl added; ○, 0.5 mM HCl and 0.1 M Et_4NBr added; ▽, 1 mM NaOH added; △, 0.5 mM HCl and 0.1 M H_2NCSNH_2 added; ------, $Ru(bpy)_3^{2+}$.

In the aqueous solution system reported before,[6] the quenching by MV^{2+} showed a remarkably pH-dependent behavior, indicating electrostatic interaction between carboxylate anions and MV^{2+}, but the linear Stern–Volmer plots showed a dynamic quenching. In the present system in methyl alcohol, the curved plots in Fig. 1 indicate the occurrence of static quenching. Since electrostatic interaction is enhanced in less polar medium as alcohol than in water, the behaviors of Fig. 1 are reasonable.

The polymer complex 1 contains both acid and base groups, i.e., carboxylic acid and free bpy pendant groups. These groups can interact and form hydrogen bonds as was reported.[6] Such interaction must be more enhanced in alcohol than in water and provide ionic environment around Ru complex. The much longer lifetime (843 ns) of the excited state of the polymer-pendant Ru complex in methyl alcohol than that of the monomeric complex (664 ns) supports a rigid and compact structure of the polymer complex which is possibly caused by such acid–base interactions between the pendant groups.

The plots of the emission quenching in the absence of any additive in Fig. 1 shows the occurrence of static quenching. The ionic microenvironment formed by acid–base interaction described above would attract the cationic substrate (MV^{2+}), and cause static quenching. Hydrogen chloride added to this solution destroys such interaction by protonating free bpy groups, thus making the plots linear. The quenching efficiency in the presence of HCl for the polymer system is almost the same as the monomeric complex. The cationic protonated bpy groups as well as the divalent Ru complex species attached to the polymer chain would bring about expanded macromolecular structure due to electrostatic repulsion, which would make the reactivity of the pendant Ru complex almost the same as an isolated monomeric complex. The quenching rate constants (k_q) for the polymer complex with HCl additive as well as for the monomeric complex were shown in Table 1. They have almost the same k_q values.

The addition of Et_4NBr to the HCl-added system enhanced the quenching efficiency, the Stern-Volmer plots still being linear. The neutral salt not only weakens the electrostatic repulsion between the pendant cationic groups, but also can enhance the reaction between the cationic Ru complex and MV^{2+} through shielding effect. The result of Fig. 1 shows that the latter effect prevails to make the quenching more efficient in the presence of Et_4NBr than in its absence for the HCl-added polymer system. The k_q value was also shown in Table 1 for the Et_4NBr-added system which is five times as high as that without Et_4NBr.

The addition of NaOH remarkably enhanced the quenching efficiency. This is understood as due to the

Table 1. Quenching Parameters for the Systems That Can Be Analyzed by a Conventional Dynamic Model

Complex	Additive	k_{sv}/M^{-1}	τ/ns[a)]	$k_{q,2}/M^{-1}\,s^{-1}$
1	HCl	1.97×10^{2}	680	2.90×10^{8}
1	HCl+Et_4NBr	9.31×10^{2}	622	1.50×10^{9}
$[Ru(bpy)_3]^{2+}$	HCl	2.00×10^{2}	664	3.01×10^{8}

Ru; 10^{-5} M. a) Measured by a single photon counting method.

anionic domain formed around the Ru complex by the dissociation of the acrylic acid.[6)] The Stern–Volmer plots in methyl alcohol show a downward curve different from the behavior in water for which the plots show a linear relationship. Static quenching must occur in methyl alcohol. The Stern–Volmer plots with the addition of thiourea shows an upward-curve, also indicating static quenching. The quenching of the excited state of the polymer complex **1** by MV^{2+} in methyl alcohol is therefore entirely depending on the additives. Both the dynamic and static quenching mechanisms have to be considered. The quenching mechanisms were analyzed as follows.

The occurrence of static quenching in the present system shows that we should consider some specific microenvironment (called "domain") around the pendant Ru complex to which the substrate (MV^{2+}) is bound and quenches the excited Ru complex statically. Such a domain which affects specifically catalytic reactions of polymeric compounds have often been studied.[15)] The domain formed around pendant Ru complex is represented by [Ru]. Quencher molecule (MV^{2+}), Q is bound to this domain. Multistep reaction should be considered for such binding. It is assumed now that the rate constant of the forward binding reaction is equal for all the binding steps, but the backward rate constant of the binding is proportional to the number of Q bound to the domain. The stepwise bindings can then be expressed by Eqs. 1 to 3 where $[Ru\text{-}Q_i]$ represents the domain to which i molecules of Q are bound.

$$[Ru] + Q \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [Ru\text{-}Q_1] \qquad K_1 = k_a/k_{-a} \tag{1}$$

$$[Ru\text{-}Q_1] + Q \underset{2k_{-a}}{\overset{k_a}{\rightleftharpoons}} [Ru\text{-}Q_2] \qquad K_2 = K_1/2 \tag{2}$$

$$\vdots \qquad\qquad\qquad\qquad \vdots$$

$$[Ru\text{-}Q_{i-1}] + Q \underset{ik_{-a}}{\overset{k_a}{\rightleftharpoons}} [Ru\text{-}Q_i] \qquad K_i = K_1/i \tag{3}$$

According to this assumption, the number of Q molecule bound to the domain obeys the Poisson distribution. Such a Poisson distribution of quencher molecule to the microenvironment around sensitizer has often been considered for micellar[16,17)] or polymeric[9)] systems. The total concentration of the domain, $[Ru]_t$, is expressed by Eq. 4. The concentration of the Q bound to the domain, $[Q]_b$, is:

$$[Ru]_t = \sum_{i=0}^{\infty} [Ru\text{-}Q_i] = [Ru] \sum_{i=0}^{\infty} \frac{(K_1[Q])^i}{i!} = [Ru] \exp(K_1[Q]) \tag{4}$$

$$[Q]_b = \sum_{i=0}^{\infty} i[Ru\text{-}Q_i] = [Ru]K_1[Q] \exp(K_1[Q]) = [Ru]_t K_1[Q] \tag{5}$$

where [Q] is the concentration of the free Q and expressed by the following Eq.

$$[Q] = [Q]_t/(K_1[Ru]_t + 1) \tag{6}$$

Under these situations the next four quenching models were considered where dynamic and static quenchings are concerned.

In model 1 are considered both the dynamic quenching of [Ru*] by the bulk Q and the static quenching in the domain, in the latter of which the quenching rate is independent of the number of the Q in the domain.

Model 1

$$[Ru] \xrightarrow{h\nu} [Ru^*] \xrightarrow{k_{q,2}[Q]} [Ru] \tag{7}$$

$$[Ru^*] \xrightarrow{k_d} [Ru] \tag{8}$$

$$[Ru^*] \xrightarrow{k_f} [Ru] \tag{9}$$

$$[Ru\text{-}Q_i] \xrightarrow{h\nu} [Ru^*\text{-}Q_i] \xrightarrow{k_{q,1}} [Ru\text{-}Q_i] \tag{10}$$

$$[Ru^*\text{-}Q_i] \xrightarrow{k_d} [Ru\text{-}Q_i] \tag{11}$$

$$[Ru^*\text{-}Q_i] \xrightarrow{k_f} [Ru\text{-}Q_i] \tag{12}$$

In these equations k_d and k_f are the rate constants of the nonluminescent and luminescent decays of the excited state of the Ru complex, respectively. It should be reasonable to assume that these photochemical processes of Eqs. 7 to 12 are much faster than the binding processes of Eqs. 1 to 3. It means that the equilibrium processes of Eqs. 1 to 3 etc. should be kept constant during the time period when the photochemical processes of Eqs. 7 to 12 occur. The total rate of light absorption at the excitation of the Ru complex, I_t is expressed by the following equation, when steady state is assmued for the Reactions 7 to 12.

$$I_t = [Ru^*](k_d + k_f + k_{q,2}[Q]) + \sum_{i=1}^{\infty} [Ru^*\text{-}Q_i](k_d + k_f + k_{q,1}) \tag{13}$$

The rate of light absorption by [Ru] is,

$$I_t \times \frac{[\mathrm{Ru}]}{[\mathrm{Ru}]_t} = [\mathrm{Ru}^*](k_\mathrm{d}+k_\mathrm{f}+k_{\mathrm{q},2}[\mathrm{Q}])\,. \tag{14}$$

The relative emission intensity, I_o/I, from the excited state of the Ru complex in the absence and the presence of Q is,

$$I_0/I = (k_\mathrm{f}/(k_\mathrm{d}+k_\mathrm{f})) \div (k_\mathrm{f}\sum_{i=0}^{\infty}[\mathrm{Ru}^*\text{-}\mathrm{Q}_i]/I_t)\,. \tag{15}$$

From Eq. 13,

$$\sum_{i=0}^{\infty}[\mathrm{Ru}^*\text{-}\mathrm{Q}_i] = \frac{I_t+[\mathrm{Ru}^*](k_{q,1}-k_{\mathrm{q},2}[\mathrm{Q}])}{k_\mathrm{d}+k_\mathrm{f}+k_{\mathrm{q},1}}, \tag{16}$$

and from Eq. 14,

$$[\mathrm{Ru}^*] = \frac{I_t}{k_\mathrm{d}+k_\mathrm{f}+k_{\mathrm{q},2}[\mathrm{Q}]}\cdot\frac{[\mathrm{Ru}]}{[\mathrm{Ru}]_t}\,. \tag{17}$$

Therefore, from Eqs. 16 and 17,

$$\sum_{i=0}^{\infty}[\mathrm{Ru}^*\text{-}\mathrm{Q}_i] = I_t\cdot\frac{(k_1+k_{\mathrm{q},2}[\mathrm{Q}])+(k_{\mathrm{q},1}-k_{\mathrm{q},2}[\mathrm{Q}])[\mathrm{Ru}]/[\mathrm{Ru}]_t}{(k_1+k_{\mathrm{q},2}[\mathrm{Q}])(k_1+k_{\mathrm{q},1})}, \tag{18}$$

where

$$k_\mathrm{d}+k_\mathrm{f}=k_1,\quad \text{Lifetime } \tau_0=1/k_1\,. \tag{19}$$

Since the lifetime in the absence of Q (τ_o) equals $1/k_1$, Eq. 15 becomes as Eq. 20.

$$I_0/I = \frac{\tau_0 I_t}{\sum_{i=0}^{\infty}[\mathrm{Ru}^*\text{-}\mathrm{Q}_i]} = \frac{(1+\tau_0 k_{\mathrm{q},1})(X+Y[\mathrm{Q}]_t)}{X+Y[\mathrm{Q}]_t+\tau_0(Xk_{\mathrm{q},1}-k_{\mathrm{q},2}[\mathrm{Q}]_t)\exp(-K_1[\mathrm{Q}]_t/X)} \tag{20}$$

$$X = K_1[\mathrm{Ru}]_t + 1 \tag{21}$$

$$Y = \tau_0 k_{\mathrm{q},2} \tag{22}$$

Although Eq. 20 contains too many parameters to be determined, it is shown by differentiation that the I_o/I vs. [Q] plots fall on a downward curve.

In model 2, no dynamic quenching by the bulk Q is considered, so that the reactions can be expressed by Eqs. 23 to 27.

Model 2

$$[\mathrm{Ru}] \xrightarrow{h\nu} [\mathrm{Ru}^*] \begin{cases} \xrightarrow{k_\mathrm{d}} [\mathrm{Ru}] & (23)\\ \xrightarrow{k_\mathrm{f}} [\mathrm{Ru}] & (24)\end{cases}$$

$$[\mathrm{Ru}\text{-}\mathrm{Q}_i] \xrightarrow{h\nu} [\mathrm{Ru}^*\text{-}\mathrm{Q}_i] \begin{cases} \xrightarrow{k_{\mathrm{q},1}} [\mathrm{Ru}\text{-}\mathrm{Q}_i] & (25)\\ \xrightarrow{k_\mathrm{d}} [\mathrm{Ru}\text{-}\mathrm{Q}_i] & (26)\\ \xrightarrow{k_\mathrm{f}} [\mathrm{Ru}\text{-}\mathrm{Q}_i] & (27)\end{cases}$$

In this model, $k_{\mathrm{q},2}=0$ and $Y=0$ in comparison to the model 1, so Eq. 28 can be derived from Eq. 20.

$$I_0/I = \frac{(1+\tau_0 k_{\mathrm{q},1})}{1+\tau_0 k_{\mathrm{q},1}\exp(-K_1[\mathrm{Q}]_t/\mathrm{X})} \tag{28}$$

According to this model, the I_o/I vs. $[\mathrm{Q}]_t$ plots show a downward curve as the model 1. The method to distinguish between the models 1 and 2 is described later.

In the next model 3 both the dynamic and the static quenchings were considered, but the rate of the static quenching in the domain is proportional to the number of the Q molecule bound to the domain. This is different from the model 1 where the rate of the static quenching is independent of the number of the Q molecule bound. The reactions are expressed by the Eqs. 29 to 34.

Model 3

$$[\mathrm{Ru}] \xrightarrow{h\nu} [\mathrm{Ru}^*] \begin{cases} \xrightarrow{k_{\mathrm{q},2}[\mathrm{Q}]} [\mathrm{Ru}] & (29)\\ \xrightarrow{k_\mathrm{d}} [\mathrm{Ru}] & (30)\\ \xrightarrow{k_\mathrm{f}} [\mathrm{Ru}] & (31)\end{cases}$$

$$[\mathrm{Ru}\text{-}\mathrm{Q}_i] \xrightarrow{h\nu} [\mathrm{Ru}^*\text{-}\mathrm{Q}_i] \begin{cases} \xrightarrow{ik_{\mathrm{q},1}} [\mathrm{Ru}\text{-}\mathrm{Q}_i] & (32)\\ \xrightarrow{k_\mathrm{d}} [\mathrm{Ru}\text{-}\mathrm{Q}_i] & (33)\\ \xrightarrow{k_\mathrm{f}} [\mathrm{Ru}\text{-}\mathrm{Q}_i] & (34)\end{cases}$$

In this model, the total rate of light absorption is expressed by Eq. 35 when steady state is assumed for the Reactions 29 to 34.

$$\begin{aligned} I_t &= [\mathrm{Ru}^*](k_1+k_{\mathrm{q},2}[\mathrm{Q}]) + \sum_{i=1}^{\infty}[\mathrm{Ru}^*\text{-}\mathrm{Q}_i](k_1+ik_{\mathrm{q},1})\\ &= k_1\sum_{i=0}^{\infty}[\mathrm{Ru}^*\text{-}\mathrm{Q}_i] + k_{\mathrm{q},2}[\mathrm{Q}][\mathrm{Ru}^*]\\ &\qquad + k_{\mathrm{q},1}\sum_{i=0}^{\infty}i[\mathrm{Ru}^*\text{-}\mathrm{Q}_i] \end{aligned} \tag{35}$$

The rate of light absorption by [Ru] is,

$$I_t \times \frac{[\mathrm{Ru}]}{[\mathrm{Ru}]_t} = [\mathrm{Ru}^*](k_1+k_{\mathrm{q},2}[\mathrm{Q}])\,. \tag{36}$$

Therefore,

$$[\mathrm{Ru}^*] = \frac{I_t[\mathrm{Ru}]}{(k_1+k_{\mathrm{q},2}[\mathrm{Q}])[\mathrm{Ru}]_t}\,. \tag{37}$$

The relative emission intensity, I_o/I, is,

$$I_0/I = (k_\mathrm{f}/k_1) \div (k_\mathrm{f}\sum_{i=0}^{\infty}[\mathrm{Ru}^*\text{-}\mathrm{Q}_i]/I_t) = \frac{\tau_0 I_t}{\sum_{i=0}^{\infty}[\mathrm{Ru}^*\text{-}\mathrm{Q}_i]}\,. \tag{38}$$

From Eq. 35,

$$\sum_{i=0}^{\infty}[\mathrm{Ru}^*\text{-}\mathrm{Q}_i] = \frac{I_t-k_{\mathrm{q},2}[\mathrm{Q}][\mathrm{Ru}^*]-k_{\mathrm{q},1}\sum_{i=0}^{\infty}i[\mathrm{Ru}^*\text{-}\mathrm{Q}_i]}{k_1} \tag{39}$$

From Eq. 5,

$$\sum_{i=0}^{\infty}i[\mathrm{Ru}^*\text{-}\mathrm{Q}_i] = [\mathrm{Ru}^*]K_1[\mathrm{Q}]\exp(K_1[\mathrm{Q}]) \tag{40}$$

Therefore Eq. 39 becomes

$$\sum_{i=0}^{\infty}[\mathrm{Ru^*\text{-}Q}_i] = \frac{1}{k_1}[I_t-(k_{\mathrm{q},2}[\mathrm{Q}] + k_{q,1}K_1[\mathrm{Q}]\exp(K_1[\mathrm{Q}))[\mathrm{Ru^*}]]. \tag{41}$$

By using Eqs. 14 and 4, Eq. 41 becomes Eq. 42

$$\begin{aligned}\sum_{i=0}^{\infty}[\mathrm{Ru^*\text{-}Q}_i] &= \frac{I_t}{k_1}\left[1-\frac{1}{k_1+k_{\mathrm{q},2}[\mathrm{Q}]}\cdot\frac{[\mathrm{Ru}]}{[\mathrm{Ru}]_t}\right.\\ &\qquad\left.\times\,(k_{\mathrm{q},2}[\mathrm{Q}]+k_{\mathrm{q},1}K_1[\mathrm{Q}]\exp(K_1[\mathrm{Q}]))\right]\\ &= \frac{I_t}{k_1}\cdot\frac{k_1+k_{\mathrm{q},2}[\mathrm{Q}](1-\exp(-K_1[\mathrm{Q}]))-k_{\mathrm{q},1}K_1[\mathrm{Q}]}{k_1+k_{\mathrm{q},2}[\mathrm{Q}]}.\end{aligned} \tag{42}$$

Therefore, from Eqs. 15 and 42,

$$\begin{aligned}I_0/I &= \frac{I_t\tau_0}{\sum_{i=0}^{\infty}[\mathrm{Ru^*\text{-}Q}_i]}\\ &= \frac{k_1+k_{\mathrm{q}.2}[\mathrm{Q}]}{k_1+k_{\mathrm{q},2}[\mathrm{Q}](1-\exp(-K_1[\mathrm{Q}]))-k_{\mathrm{q},1}K_1[\mathrm{Q}]}.\end{aligned} \tag{43}$$

Since

$$[\mathrm{Q}] = [\mathrm{Q}]_t/(K_1[\mathrm{Ru}]_t+1) = [\mathrm{Q}]_t/X, \tag{44}$$

Eq. 45 is concluded.

$$I_0/I = \frac{k_1+k_{\mathrm{q},2}[\mathrm{Q}]_t/X}{k_1+k_{\mathrm{q},2}[\mathrm{Q}]_t(1-\exp(-K_1[\mathrm{Q}]_t/X)/X)-k_{\mathrm{q},1}K_1[\mathrm{Q}]_t/X}. \tag{45}$$

The I_0/I vs. $[\mathrm{Q}]_t$ plots of the model 3 thus show a downward curve.

In model 4, no dynamic quenching by the bulk Q is considered, and only the static quenching in the domain is assumed whose rate constant is proportional to the number of the bound Q (see Eqs. 46 to 50).

Model 4

$$[\mathrm{Ru}] \xrightarrow{h\nu} [\mathrm{Ru^*}] \xrightarrow{k_\mathrm{d}} [\mathrm{Ru}] \tag{46}$$

$$[\mathrm{Ru^*}] \xrightarrow{k_\mathrm{f}} [\mathrm{Ru}] \tag{47}$$

$$[\mathrm{Ru\text{-}Q}_i] \xrightarrow{h\nu} [\mathrm{Ru^*\text{-}Q}_i] \xrightarrow{ik_{\mathrm{q},1}} [\mathrm{Ru\text{-}Q}_i] \tag{48}$$

$$[\mathrm{Ru^*\text{-}Q}_i] \xrightarrow{k_\mathrm{d}} [\mathrm{Ru\text{-}Q}_i] \tag{49}$$

$$[\mathrm{Ru^*\text{-}Q}_i] \xrightarrow{k_\mathrm{f}} [\mathrm{Ru\text{-}Q}_i] \tag{50}$$

By substituting $k_{\mathrm{q},2}=0$ in the Eq. 45 (model 3), the next relation is obtained.

$$I_0/I = \frac{k_1}{k_1-k_{\mathrm{q},1}K_1[\mathrm{Q}]_t/X} = \frac{1}{1-k_{\mathrm{q},1}\tau_0K_1[\mathrm{Q}]_t/X} \tag{51}$$

The I_0/I vs. $[\mathrm{Q}]_t$ plots should show an upward curve, and the I/I_0 vs. $[\mathrm{Q}]_t$ plots be linear.

The models 1 and 2 can be distinguished by emission decay profile. The patterns of the emission decay for the models 1 and 2 are illustrated as Fig. 2. Since in the model 1 both dynamic and static quenching occur, the emission decay should be nonexponential, and both the shorter and the longer lifetime components should decay faster than the system without Q. In the model 2 only static quenching occurs, indicating that the emission decay is also nonexponential, but that the [Ru] which does not bind Q even in the presence of Q in the system emits just as the system without Q. It means that the longer lifetime components in the presence of Q decay at the same rate as the decay in the absence of Q. The decay profile of the model 2 can therefore be shown as Fig. 2.

In Fig. 1 the quenchings in the absence of additive as well as in the presence of NaOH showed downward curves, so that they should obey either the model 1 or 2. The emission decay in the absence of any additive was studied and shown in Fig. 3. The relative emission decays in the absence and the presence of $\mathrm{MV^{2+}}$ shown in Fig. 3 are corresponding to the decay profile of the model 1 shown in Fig. 2. The quenching with no additive should therefore obey the model 1. The emission decay in the presence of NaOH was shown in Fig. 4. This shows the same

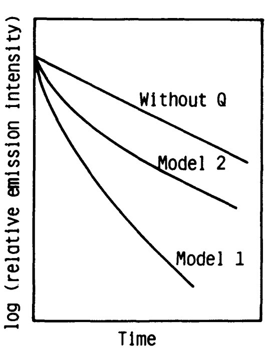


Fig. 2. Profiles of emission decay in the models 1 and 2.

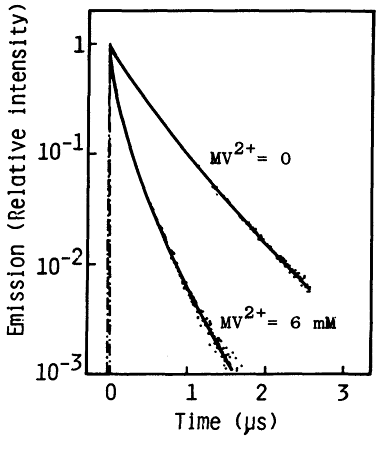


Fig. 3. Emission decay of excited **1** in MeOH with no additive under Ar at 25 °C.

Table 2. Quenching Mechanism of the Excited Copolymer-Pendent $[Ru(bpy)_3]^{2+}$ (**1**) by MV^{2+} in Methyl Alcohol

Model	Rates of quenching by		Stern–Volmer plot based on emission intensity	Additive
	Bulk Q	Bound Q		
1	$k_{q,2}[Q]$	$k_{q,1}$	Downward curve	None
2	—	$k_{q,1}$	Downward curve	NaOH
3	$k_{q,2}[Q]$	$ik_{q,1}$	Upward curve	$HCl + H_2NCSNH_2$
4	—	$ik_{q,1}$	Upward curve	
Conventional dynamic model	$k_{q,2}[Q]$	—	Linear relationship	HCl or $HCl + Et_4NBr$

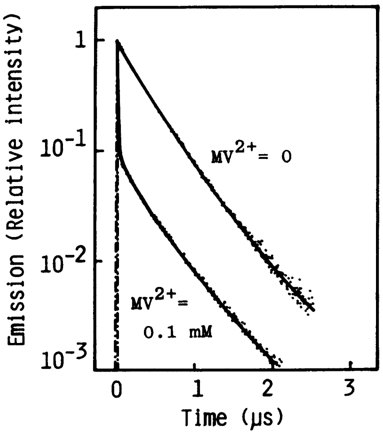


Fig. 4. Emission decay of excited **1** in MeOH containing 1 mM NaOH measured under Ar at 25 °C.

decay profile as the model 2 (see Fig. 2). The quenching in the presence of NaOH should therefore obey the model 2.

The quenching in the presence of HCl and H_2NCSNH_2 showed an upward curve (Fig. 1), indicating that it should obey either the model 3 or 4. Since the I/I_0 vs. $[Q]_t$ plots did not give a straight line, this should not obey the model 4, but the model 3.

The quenching mechanism of the systems shown in Fig. 1 can therefore be summarized as Table 2. It was already described that the quenching of the system containing HCl or both HCl and Et_4NBr is explained by a conventional dynamic model. In the system with no additive, both the dynamic quenching by the bulk Q and the static quenching in the domain occur, the rate of the latter being independent of the number of the bound Q.

In the presence of NaOH, no dynamic quenching occurs and only static quenching is involved whose rate is independent of the number of the bound Q. This situation is entirely different from the alkaline aqueous system[6] for which the Stern–Volmer plots showed a linear relationship indicating that the quenching in water can be explained by a dynamic model even in the presence of NaOH. In the present MeOH system, the quenching specificity of the NaOH-added system would be due to the less polarity of the medium than water. In MeOH the binding of MV^{2+} to the anionic domain composed by the dissociated carboxylato groups would be much stronger than in water, which would make the quenching static.

In the system containing HCl and H_2NCSNH_2, both the dynamic quenching by the bulk Q and the static quenching in the domain occur, the rate of the latter being proportional to the number of the bound Q. Some specific anionic domain formation might be suggested to occur due to acid-base interaction between carboxylic groups of the polymer chain and H_2NCSNH_2.

The quenching mechanism of the acrylic acid-copolymer pendant $[Ru(bpy)_3]^{2+}$ by MV^{2+} is thus strongly dependent on the conditions of the MeOH medium. This is the first example in which one photochemical reaction system exhibits different quenching mechanisms depending on the additives.

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