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Effect of Polymer on the Quenching of the Excited State of Copolymer–Pendant $Ru(bpy)_3^{2+}$ Containing Carboxylate Groups

M. Kaneko* and H. Nakamura

The Institute of Physical and Chemical Research, Wako, Saitama, 351-01 Japan.
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ABSTRACT: Quenching of the excited state of poly(acrylic acid-*co*-vinylbipyridine)–pendant $Ru(bpy)_3^{2+}$ by methylviologen (MV^{2+}) in alkaline aqueous medium was studied and the effect of polymer discussed. Higher molecular weight polymers gave much higher quenching rate constants. Among the three different molecular weight samples used (MW 2100, 4400, 13 300), the quenching of the lowest molecular weight polymer was explained to occur through a dynamic process, but the excited state of the higher molecular weight polymers (MW 4400 and 13 300) was quenched both by dynamic and static processes.

Tris(2,2′-bipyridine)ruthenium(II) complex (abbreviated to $Ru(bpy)_3^{2+}$) is attracting much attention as a sensitizer for visible light energy conversion.[1-4] The electron-transfer reactions between its excited state and various acceptors and donors have been studied intensively. Polymeric compounds present in the reaction medium affected much the photochemical reaction of $Ru(bpy)_3^{2+}$.[5] Such effect of polymer chains can better be studied by using polymer–pendant $Ru(bpy)_3^{2+}$.[6-10] One of the present authors has reported the electrostatic accelerating effect of the neighboring carboxylate anions on the quenching of the excited state of poly(acrylic acid-*co*-vinylbipyridine)–pendant $Ru(bpy)_3^{2+}$ by methylviologen (MV^{2+}) quencher.[6] In this paper the quenching mechanism of this polymer system depending on the molecular weight will be described.

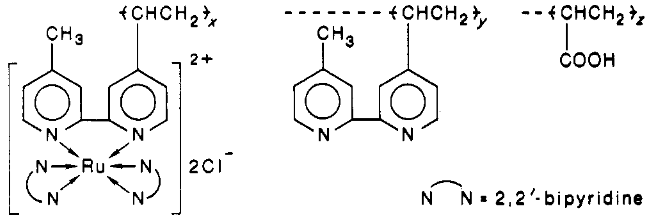
Experimental Section

Copolymer–pendant complexes were prepared from the reaction of the copolymer of acrylic acid and 4-methyl-4′-vinyl-2,2′-bipyridine with *cis*-$Ru(bpy)_2Cl_2$ as described earlier.[6,11] 1,1′-Dimethyl-4,4′-bipyridinium dichloride (methylviologen, MV^{2+}) was recrystallized twice from methyl alcohol/acetone mixture. The quenching of the excited state of the polymer complex by MV^{2+} was studied in an aqueous alkaline solution (usually at pH 11) where all the acrylic acid groups are dissociated to carboxylate anions. Emission decay was measured by a single-photon counting method with 1-ns pulsed light from a 12-atm hydrogen lamp. Laser flash photolysis was carried out by the third harmonic (355 nm) of Nd:YAG laser, Model HY500 from JK Laser Ltd. Emission was measured by the fluorimeter (Hitachi MPF-4). Laser flash experiments were done in vacuo and other experiments under argon atmosphere; the temperature was 25 °C.

Results and Discussion

The composition and the molecular weight of copolymer–pendant $Ru(bpy)_3^{2+}$ (**1**–**3**) are shown in Table I. The molar fraction of the pendant Ru complex group is 2.4–2.5%. The average numbers of Ru complex group per polymer chain are 0.6 (**1**), 1.2 (**2**), and 3.7 (**3**).

Table I
Copolymer–Pendant Ru Complexes



sample	MW	composition x	y	z
1	2 100	0.024	0.037	0.939
2	4 400	0.024	0.020	0.956
3	13 300	0.025	0.016	0.959

Table II
Stern–Volmer Constants for the Quenching of the Excited State of Polymer Complex with MV^{2+} Quencher[a]

complex	k_{sv}, 10^3 L mol^{-1}
monomeric $Ru(bpy)_3^{2+}$	0.15
1	2.86
2	10.3
3	51.0

[a] Ru complex, 10 μM. In 10 mM NaOH aqueous solution.

The decay of the excited state of the copolymer–pendant $Ru(bpy)_3^{2+}$ is shown in Figure 1. Almost single-exponential decay was observed for the excited state of the copolymer complex. The emission from the excited state of the copolymer complex (610 nm)[6] is quenched by MV^{2+} in an aqueous solution. The decay of the excited state of the copolymer complex and the formation of MV^+ were studied by laser flash photolysis in a 10 mM NaOH aqueous solution in the presence of MV^{2+}. The emission decay was monitored at 610 nm and the MV^+ formation at 605 nm. The rate constants for the MV^+ formation (1.37×10^9 M^{-1} s^{-1}) and for the decay of the excited state (1.44×10^9 M^{-1} s^{-1}) are almost the same, indicating that the quenching of the excited state of the copolymer complex by MV^{2+} is caused by the electron transfer from its excited state to MV^{2+} as is the case for the monomeric $Ru(bpy)_3^{2+}$.

The Stern–Volmer plots for the emission quenching with MV^{2+} quencher in an alkaline aqueous solution are shown in Figure 2 for complexes **1**–**3** as well as for the monomeric $Ru(bpy)_3^{2+}$. In this figure, I_0/I denotes the ratio of relative emission intensities in the absence and the presence of the quencher. The polymer complexes show much more efficient quenching than the monomeric one. The Stern–Volmer constants (k_{sv}, slope of the plots) are shown in Table II, where the k_{sv} values for the curved plots were calculated from the initial slope of the curve. Among the polymer complexes, higher molecular weight complex shows more efficient quenching. From the linearity of the Stern–Volmer plots, the quenching of the excited state of the monomeric complex and the polymer complex **1** can be understood to occur by a dynamic mechanism in which the reaction of the excited Ru complex and MV^{2+} occurs by a diffusional process. However, the curved plots for polymer complexes **2** and **3** indicate the occurrence of a static process in which some interaction of the excited Ru complex and MV^{2+} must be presumed.

In order to study the quenching of the excited state of polymer complexes **2** and **3** by MV^{2+}, the emission decays of both of the complexes in the absence and the presence of MV^{2+} were measured and are shown in Figures 3 and

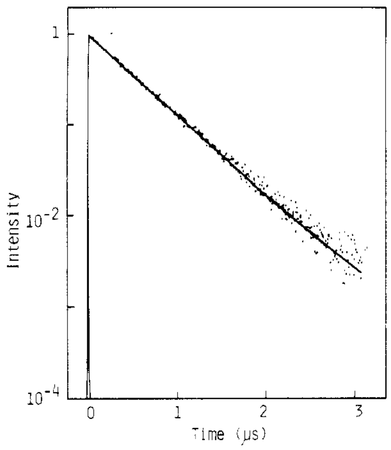


Figure 1. Emission decay of the excited state of copolymer complex 1.

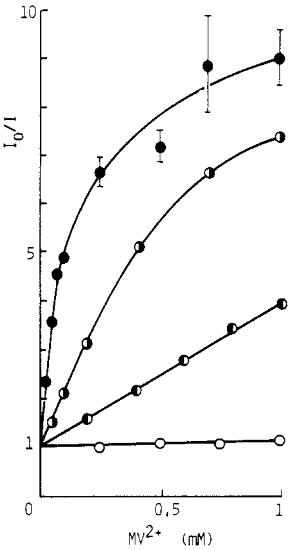


Figure 2. Stern–Volmer plots for the quenching of the excited state of copolymer complexes 1 (◐), 2 (◑), and 3 (●) and of the monomeric complex (○): Ru complex, 10 μM in 10 mM NaOH aqueous solution.

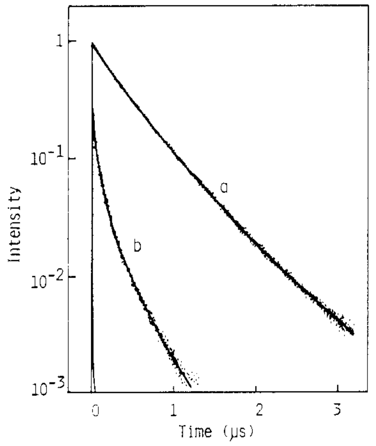


Figure 3. Emission decays for copolymer complex 2 in the absence (a) and the presence (b) of MV^{2+}: Ru complex, 10 μM; MV^{2+}, 0.1 mM.

4, respectively. The multiexponential decays for both of the polymer complexes (**2** and **3**) in the presence of MV^{2+} indicate unambiguously that static mechanism is involved in the quenching of the excited state.

The dissociated carboxylate groups of the polymer complex are considered to form anionic domains around the pendant Ru complex.[6] Such anionic domains would bind the cationic quencher (MV^{2+}) electrostatically.[6] Such binding is expressed by multistep processes. When assuming that the forward rate constant (k_a) of the binding of the quencher (Q) is constant for each binding step but that the backward rate constant (k_{-a}) is proportional to the number of bound Q's the profile of the binding is represented by eq 1–3 where [Ru] denotes the domain around Ru complex. Under these conditions, the number of Q molecules bound to a domain obeys the Poisson distribution.

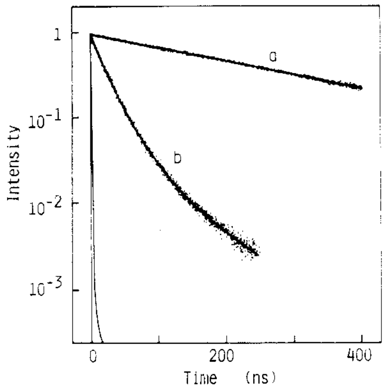


Figure 4. Emission decays for copolymer complex 3 in the absence (a) and the presence (b) of MV^{2+}: Ru complex, 0.1 mM; MV^{2+}, 10 mM.

Table III
Summary of the Quenching Mechanism for the Various Models

model	dynamic quenching by bulk Q	static quenching by bound Q
conventional dynamic model	$k_{q,2}[Q]$	none
model 1	$k_{q,2}[Q]$	$k_{q,1}$
model 2	none	$k_{q,1}$
model 3	$k_{q,2}[Q]$	$ik_{q,1}$
model 4	none	$ik_{q,1}$

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

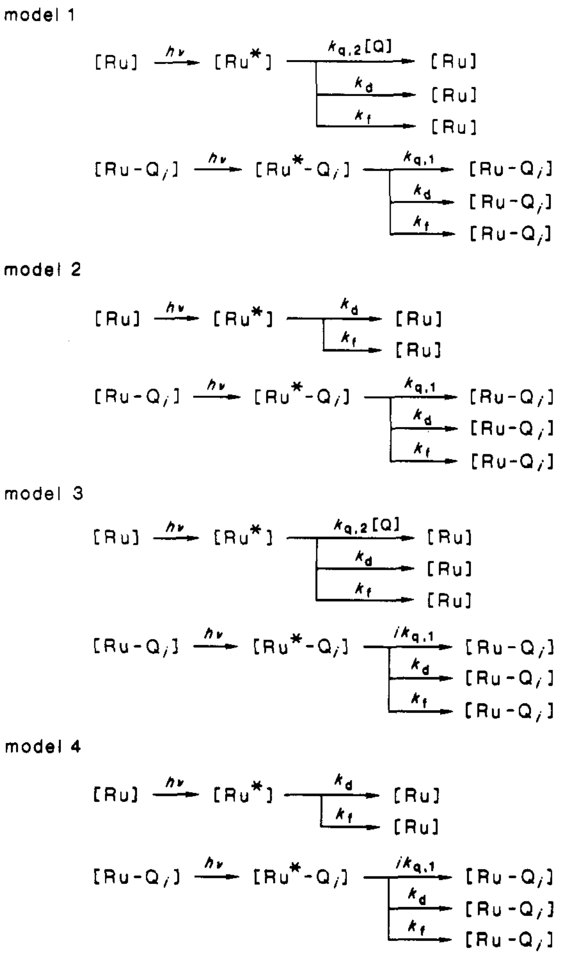
$$[\mathrm{Ru{-}Q_1}] + \mathrm{Q} \underset{2k_{-a}}{\overset{k_a}{\rightleftharpoons}} [\mathrm{Ru{-}Q_2}] \quad K_2 = K_1/2 \tag{2}$$

$$[\mathrm{Ru{-}Q}_{i-1}] + \mathrm{Q} \underset{ik_{-a}}{\overset{k_a}{\rightleftharpoons}} [\mathrm{Ru{-}Q}_i] \quad K_i = K_1/i \tag{3}$$

In the absence of Q, the excited state of the complex decays by both nonradiative process (rate constant, k_d) and emission of fluorescence (rate constant, k_f). When Q is present, quenching by Q is added to these two processes. As for the quenching, both the dynamic quenching of the excited Ru complex containing no bound Q ([Ru*]) by the bulk Q (second-order rate constant, $k_{q,2}$) and the static quenching by the bound Q (first-order rate constant, $k_{q,1}$) are possible. The rate of the static quenching by the bound Q is either independent of the number of the bound Q or proportional to the number (i) of the bound Q. By the combination of these processes, the four models in Chart I are proposed for the quenching of the excited state of the polymer complex.

In model 1, both dynamic and static quenchings are considered, where the static quenching rate is independent of the number (i) of bound Q's. In model 2, only static quenching is considered for which the rate is independent of i. In model 3, both dynamic and static quenchings are considered, where the static quenching rate is proportional to i. In model 4, only static quenching is considered for

Chart I



which the rate is proportional to i. These are summarized in Table III.

These models can be discriminated by the profiles of Stern–Volmer plots and emission decay. According to the calculations based on these models reported earlier,[8] the profiles of the Stern–Volmer plots of these models are typically represented by Figure 5a. For models 1 and 2, the Stern–Volmer plots should show downward curve, while for models 3 and 4 they should show upward curve. The emission decay profiles of these four models in the presence of Q are shown in Figure 5b. Since for models 1 and 3 both the dynamic and static quenchings occur, the emission decay should be multiexponential and the longer lifetime component decays faster than that without Q. For models 2 and 4, since only the static quenching is considered, the emission from [Ru*] which contains no Q remains as it is without Q, so that the decay of the longer lifetime component should be parallel to the decay without Q.

The downward-curved Stern–Volmer plots for the quenching of the excited state of the polymer complexes **2** and **3** (Figure 2) as well as the emission decays shown in Figures 3 and 4 indicate that the quenching occurs according to model 1 for which both the dynamic and static quenchings are involved and that the static quenching rate is independent of the number of bound Q. The quenching for the lowest molecular weight polymer complex **1** is understood to occur only by a conventional dynamic process. The much higher quenching rate for this polymer complex (**1**) than the monomeric complex can then be explained simply by a so-called concentration effect[13] which is often observed for the reactions by polymers.

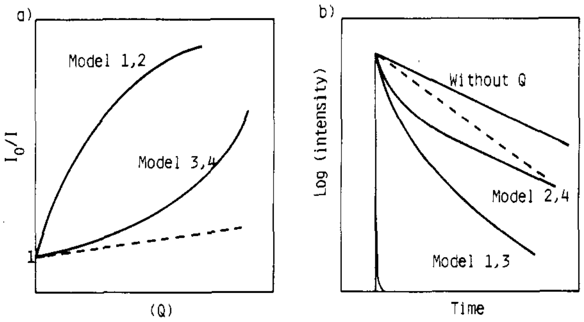


Figure 5. Profiles of the Stern–Volmer plots (a) and the emission decays (b) for quenching models 1–4 and for the conventional dynamic quenching model (- - -).

The quenching mechanism of the excited state of polymer–pendant $Ru(bpy)_3^{2+}$ thus depends on the molecular weight of the polymer. For the lower molecular weight complex, a dynamic quenching model is still applicable although the rate is markedly higher than the monomeric complex, while for the higher molecular weight complex, static quenching by the bound quencher also is involved along with the conventional dynamic quenching.

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Registry No. Methylviologen, 1910-42-5.

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