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Enhancement of quenching of polymer-bound ruthenium(II) complexes with MV^{2+} using L-tyrosine esters

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Abstract

The effects of L-tyrosine esters with hexyl (C_6Tyr), octyl (C_8Tyr) and dodecyl (C_{12}Tyr) groups on quenching of partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes (RuQPIm-19 and RuQPIm-44: the numbers represent the degree of quaternization in molar percentage) with a 1,1′-dimethyl-4,4′-bipyridinium dication (MV^{2+}) have been investigated in methanol. The quenching efficiency was increased by the addition of L-tyrosine esters, and increased with decreasing the length of the alkyl groups in the L-tyrosine esters for RuQPIm-19 and RuQPIm-44. The Stern–Volmer plots for RuQPIm-19 significantly changed from an upward deviating curve to a downward deviating curve for C_6Tyr, a straight line for C_8Tyr, and a downward deviating curve for C_{12}Tyr. For RuQPIm-44, the Stern–Volmer plots gave downward deviating curves for all L-tyrosine esters. These facts indicated that the reaction mechanism of quenching was varied by the addition of L-tyrosine esters. Furthermore, viscosity studies showed that the RuQPIm-19 shrank on addition of MV^{2+} and L-tyrosine esters, but not RuQPIm-44, and that the L-tyrosine esters interacted with these polymers through van der Waals interaction. Consequently, it was suggested that the L-tyrosine esters mediated the quenching reaction.

1. Introduction

Long-range electron transfer in biological systems involving electron tunneling through polypeptides has been of considerable interest [1–4]. Many investigations have employed modified proteins [5, 6] and suggest that some amino acid residues in the proteins would participate in the electron transfer in biological systems [7–9]. In the photosynthesis of green plants, photoinduced electron transfer takes place through tyrosine residues [10]. In these electron transfer systems, however, modified enzyme systems and synthetic donor–acceptor systems, which are difficult to modify, synthesize, and characterize, have been mainly employed. For simple systems, the electron transfer reaction in a natural polymer matrix has been reported [11], and some polymer systems containing donors and acceptors have also been studied [12, 13]. The pathway effect in photoinduced electron transfer from $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) to methylviologen in a synthetic polymer film has been investigated, and the electron transfer distance was found to double in the presence of 3-methylindole as a tryptophan residue model [14]. Further, for electrochemical water oxidation in polymer membrane, the charge transfer distance is increased by the addition of *p*-cresol from 1.28 to 2.25 nm, showing that *p*-cresol functions as a mediator for the charge transport [15].

Partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes (RuQPIm) have been synthesized, and their photosensitizing abilities have been investigated [16–18]. In photosensitized charge separation, the efficiency of charge separation depends sig-

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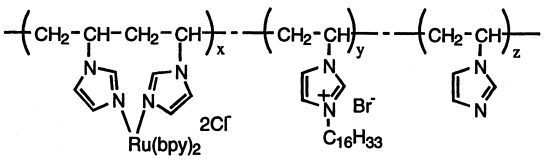
nificantly on the length of the alkyl group in alkylviologens as electron acceptors. In particular, van der Waals interaction between alkyl chains in the polymer backbone and alkylviologen causes a high efficiency of charge separation [16]. In the present paper, we report the effect of L-tyrosine esters on the quenching of partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes with MV^{2+}.

1.1. Experimental

1.1.1. Materials

L-tyrosine, alkyl alcohols, and other synthesis reagents (commercially available guaranteed reagents) were used without further purification. 1,1′-Dimethyl-4,4′-bipyridinium chloride (methylviologen; MV^{2+}) was purchased from TCI CO. Ltd, and recrystallized from methanol. Polymer-bound ruthenium(II) complexes (RuQPIm-19 and RuQPIm-44, the numbers represent the molar percentage of quaternized imidazolium residues) were prepared by the method described elsewhere [16, 19], and the chemical structures are shown in Fig. 1.

L-tyrosine esters (C_6Tyr, C_8Tyr and C_{12}Tyr) were prepared by a modified version of the thionyl chloride method [20]. To an alkyl alcohol at 0°C, thionyl chloride (55 mmol) and then L-tyrosine (5 mmol) were added. The resulting suspension was stirred at 70°C for 12 h. After cooling to room temperature, 300 ml of ethyl ether was added. The white precipitate was collected by filtration, sufficiently washed with ethyl ether, and dried. These L-tyrosine esters were purified by recrystallization from methanol–ethyl ether. Identification was carried out by ^{1}H–NMR spectroscopy and elemental analysis. Calculated for C_6Tyr ($C_{15}H_{24}ClNO_3$): C, 59.69; H, 8.02; N, 4.64. Found: C, 59.50; H, 8.02; N, 4.74. Calculated for C_8Tyr ($C_{17}H_{26}ClNO_3$): C, 62.27; H, 8.00; N, 4.27. Found: C, 62.15; H, 8.19; N, 4.27. Calculated for C_{12}Tyr ($C_{21}H_{34}ClNO_3$): C, 65.68; H, 8.94; N, 3.65. Found: C, 65.60; H, 9.03; N, 3.71.



Polymers	x	y	z
RuQPIm-19	0.0035	0.1915	0.8050
RuQPIm-44	0.0035	0.4404	0.5561

Fig. 1. Chemical structure of RuQPIm.

1.1.2. Measurements

UV–VIS spectra were recorded on a JASCO V-570 UV/VIS/NIR spectrophotometer. Luminescence spectra were recorded on a Hitachi 650-10 S fluorescence spectrophotometer.

The quenching reaction was carried out at 25°C under an argon atmosphere in methanol. The luminescence at 648 nm from the triplet metal-to-ligand charge-transfer (MLCT) state [16, 21], which was excited at 488 nm, was monitored as a function of the concentration of viologen.

Viscosity measurements were carried out using an Ubbelhode viscometer in a thermostat adjusted to 25.0 ± 0.1°C. Sample solutions were adjusted to $[Ru^{II}] = 2.0 \times 10^{-5}$ mol dm^{-3}, $[MV^{2+}] = 5.0 \times 10^{-3}$ mol dm^{-3} and [L-tyrosine esters] $= 5.0 \times 10^{-2}$ mol dm^{-3}.

2. Results and discussion

2.1. Spectroscopic properties

For RuQPIm-19 and RuQPIm-44, no change was observed in the shapes of the absorption and luminescence spectra in the visible region and the absorbance and luminescence intensity at the maximum wavelength even when adding a large excess of L-tyrosine esters. However, the maximum wavelength of the luminescence spectra slightly shifted to the shorter wavelength from 652 nm to 650 nm for RuQPIm-19 and to 648 nm for RuQPIm-44. In the U.V. region, absorption spectra corresponding to electrical transitions of imidazolyl, quaternized imidazolium and L-tyrosine esters did not undergo interaction with the main chain of the polymers and ruthenium(II) complex residues. Therefore, the blue shift of the maximum wavelength of the luminescence spectra of the ruthenium(II) complex residue would be caused by a change in the physicochemical properties in the vicinity of the ruthenium(II) complex residues. Considering the fact that alkylviologen with a long alkyl group interacts with the alkyl side chains of the RuQPIm-19 and RuQPIm-44 through van der Waals interaction [16, 18], the L-tyrosine esters also have van der Waals interaction with the alkyl side chains on the polymers and are incorporated into the polymer domain. The interior of the polymer domain would become more hydrophobic, leading to the blue spectral shift. Further, it is spectroscopically confirmed that the L-tyrosine esters do not have π–π interaction with the MV^{2+} species.

2.2. Viscosity studies

In order to obtain information on the effect of L-tyrosine esters on the conformation of RuQPIm-19

Table 1
Specific viscosity of RuQPIms, MV^{2+} and L-tyrosine esters in methanol

	Specific viscosity ($\eta_{sp}/10^{-2}$)			
	RuQPIm-19		RuQPIm-44	
	—*	MV^{2+}	—*	MV^{2+}
—†	10.2	8.7	11.3	10.1
C_6Tyr	7.5	5.1	8.6	8.5
C_8Tyr	7.7	5.2	7.9	8.1
C_{12}Tyr	8.0	5.8	7.1	7.6

and RuQPIm-44, the viscosity was measured in methanol.

The specific viscosity (η_{sp}) for methanol solutions of RuQPIm-19, RuQPIm-44, RuQPIm-19/L-tyrosine esters, RuQPIm-44/L-tyrosine esters and those containing MV^{2+} is summarized in Table 1. The specific viscosity was decreased by the addition of L-tyrosine esters. With increasing length of the alkyl group in the L-tyrosine ester, the specific viscosity slightly increased for RuQPIm-19. The results indicate that the polymer shrank with the addition of L-tyrosine esters, which was mainly induced by van der Waals interaction between the alkyl side chains on the polymers and the alkyl groups of the L-tyrosine esters[2]. This can be explained as follows. The number of alkyl side chains on the RuQPIm-19 is relatively small, and the van der Waals interaction would be weak. With increasing length of the alkyl group in the L-tyrosine esters, the viscosity of the L-tyrosine ester itself increases, thus leading to an increase in the viscosity of a mixture of RuQPIm-19 and L-tyrosine esters. In contrast, the RuQPIm-44 having many alkyl side chains has strong van der Waals interaction with L-tyrosine esters; in addition, the interaction increases with increasing length of the alkyl group in the L-tyrosine esters. Because RuQPIm-44 also has many positive charges on the polymer, however, it is difficult to undergo shrinkage due to electrostatic repulsion. Therefore, the viscosity would be mainly decreased by the decrease in flexibility of the alkyl side chains on the polymer induced by strong van der Waals interaction with the L-tyrosine esters. The increase in the viscosity of the L-tyrosine ester itself with increasing length would be counterbalanced by the decrease in the viscosity of the mixed solution induced by restriction of the flexibility of the alkyl side chains, therefore leading to the decrease in the viscosity of the mixture of the polymer and L-tyrosine ester. Further, the specific viscosity is also decreased by the addition of MV^{2+}; in particular, the decrease was significantly large for RuQPIm-19/MV^{2+}. This is attributed to π–π interaction for MV^{2+} as mentioned above [16–18]. For RuQPIm-44/MV^{2+}, the effect of MV^{2+} on the viscosity is not remarkable because the MV^{2+} species have no interaction with the polymer.

On the other hand, the specific viscosity of methanol containing RuQPIm, MV^{2+} and L-tyrosine esters, which corresponds to sample solutions used in quenching studies, shows interesting behavior. On the addition of L-tyrosine esters, the specific viscosity significantly decreases. Furthermore, with increasing length of the alkyl group in the L-tyrosine ester, the specific viscosity increases for RuQPIm-19/MV^{2+}/L-Tyr and decreases for RuQPIm-44/MV^{2+}/L-Tyr. These facts indicate that the polymer is shrunk by the L-tyrosine ester. For RuQPIm-19/MV^{2+}/L-Tyr, although the shrinking of the polymer induced by π–π interaction with the MV^{2+} species is accelerated by van der Waals interaction with the L-tyrosine ester, the total viscosity of the solution increases with increasing length of the alkyl group in the L-tyrosine ester. This is attributed to the fact that the viscosity of the L-tyrosine ester itself increases. It is likely that the shrinking of RuQPIm-19 by L-tyrosine esters is independent of the alkyl group in the L-tyrosine ester due to the small amount of alkyl side chains on the polymer. In contrast, for the RuQPIm-44/MV^{2+}/L-Tyr system, the decrease in the specific viscosity with increasing length of the alkyl group in the L-tyrosine ester is attributed to the strength of the van der Waals interaction between the L-tyrosine ester and the polymer. The increase in the viscosity of the L-tyrosine ester itself is counterbalanced by the decrease in viscosity of the polymer by strong van der Waals interaction with the L-tyrosine ester; therefore, the viscosity of the mixed solution decreases. Compared with the RuQPIm-19 system, however, the effect of L-tyrosine esters on the specific viscosity is small. This is attributed to the decrease in the viscosity of the RuQPIm-19 system caused by shrinking of the polymer, while that for RuQPIm-44 is caused by a decrease in flexibility of the alkyl side chain on the polymer induced by strong van der Waals interaction. The decrease in the specific viscosity of a mixture of RuQPIm-44 and L-tyrosine esters is larger than that of RuQPIm-19; whereas, in the presence of MV^{2+}, that of RuQPIm-19 is very large. The main chain of the RuQPIm-19 shrinks through π–π interaction with MV^{2+}; at this moment, the alkyl side chains would aggregate to some extent. Consequently, the L-tyrosine esters interact with the aggregated alkyl side chains on the RuQPIm-19, leading to further shrinking.

[2] It was confirmed by ^{1}HNMR spectroscopy that there was no hydrogen bonding between an amino group or a phenolic hydroxyl group and imidazolyl residues.

2.3. Quenching studies

Fig. 2 shows Stern–Volmer plots for the quenching of RuQPIm with MV^{2+}. In the absence of L-tyrosine esters, the Stern–Volmer plots were an upward deviating curve for RuQPIm-19 and a straight line for RuQPIm-44, which agreed with the results reported in our paper [16]. With the addition of L-tyrosine esters, the quenching efficiency increased and the degree of the increase increased with decreasing length of the alkyl groups in the L-tyrosine esters for RuQPIm-19 and RuQPIm-44. Furthermore, the Stern–Volmer plots differed from those in the absence of the L-tyrosine esters. These results suggest that the quenching reactions are mediated and the mechanism of the quenching reaction is varied by L-tyrosine esters. In the RuQPIm-19 systems, the quenching reaction would take place through three processes: (1) quenching by the MV^{2+} species having π–π interaction with the polymer (Stern–Volmer plot of the upward deviating curve); (2) quenching by the MV^{2+} species having no interaction (straight line); and (3) quenching mediated by L-tyrosine esters (downward deviating curve). On the other hand, in the RuQPIm-44 systems, the quenching reaction proceeds through processes (2) and (3) because RuQPIm-44 has no interaction with the MV^{2+}. Here, these processes respectively are abbreviated as (1) the interactive process; (2) the direct process; and (3) the mediated process. The Stern–Volmer plot would be given by the sum of these quenching processes. Because the direct process barely depends on the L-tyrosine esters, however, the Stern–Volmer plot and quenching efficiency are mainly affected by the interactive and mediated processes for RuQPIm-19 and only the mediated process for RuQPIm-44.

The Stern–Volmer plots for RuQPIm-19 give a downward deviating curve for C_6Tyr, a straight line for C_8Tyr, an upward deviating curve for C_{12}Tyr and the quenching efficiency is increased. These are induced by shrinking of the polymer; namely, the shrinking of the polymer increases the interactive part of the mediated process. In the case of C_6Tyr, although the quenching reaction proceeds through the three quenching processes, the mediated process is mainly dominant, giving a Stern–Volmer plot with a downward deviating curve. With increasing length of the alkyl group in the L-tyrosine esters, the mediated process is restricted by steric hindrance of the alkyl groups; namely, it is difficult for C_8Tyr and C_{12}Tyr to approach the vicinity of the ruthenium(II) complex residue due to the long alkyl group. In particular, the C_{12}Tyr shows little mediation, and the interactive process is dominant, supported by the fact that the Stern–Volmer plot gives an upward deviating curve. Furthermore, although the van der Waals interaction between the L-tyrosine ester and RuQPIm-19 is strong with the increasing length of the alkyl group in the L-tyrosine esters, the viscosity of RuQPIm-19 increases slightly. This indicates that shrinking of the polymer is barely independent of the length of the alkyl group in the L-tyrosine esters; consequently, the contribution of the interactive process to the quenching reaction is constant regardless of the length of the alkyl group. Considering this fact, the change in the Stern–Volmer plot and quenching efficiency with increasing length of the alkyl group would be caused by the decrease in the contribution of the mediated process to the quenching reaction.

On the other hand, the Stern–Volmer plots for the RuQPIm-44 systems are varied by addition of the L-tyrosine esters from a straight line to downward

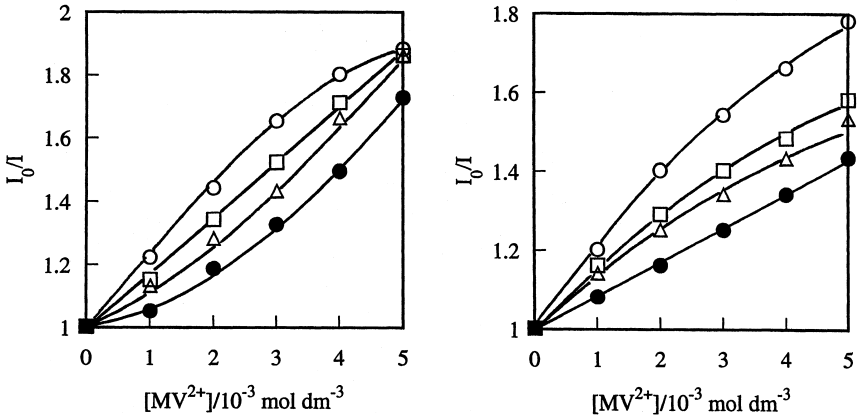


Fig. 2. Stern–Volmer plots for quenching of RuQPIm with MV^{2+} in the absence and the presence of L-tyrosine esters for RuQPIm-19 (A) and RuQPIm-44 (B). Absence of L-tyrosine esters (●), C_6Tyr (○), C_8Tyr (□), and C_{12}Tyr (△).

deviating curves and the quenching efficiency increases. With increasing length of the alkyl group in the L-tyrosine ester, the quenching efficiency decreases. As mentioned above, because the contribution of the direct process to the changes in the Stern–Volmer plot and the quenching efficiency is small, only the mediated process influences those characteristics. Although the van der Waals interaction increases with increasing length of the alkyl group, the steric hindrance restricts the approach of the L-tyrosine esters, particularly the aromatic segment, in the vicinity of the ruthenium(II) complex residue, consequently leading to the decrease in the quenching efficiency.

Compared with the RuQPIm-19 systems, the contribution of the mediated process to the quenching reaction is large, particularly for C_6Tyr. Furthermore, it is surprising that the mediated process contributes to the quenching reaction even when adding C_{12}Tyr. This would be attributed to little shrinking of the RuQPIm-44 induced by addition of the L-tyrosine ester. The L-tyrosine esters are readily incorporated in the vicinity of the ruthenium(II) complex residue on the RuQPIm-44, but not readily for RuQPIm-19, due to shrinking of the polymer. In particular, it is necessary for the aromatic segment of the L-tyrosine esters, which would function as a mediator, to enter the quenching sphere of the ruthenium(II) complex residue [14]. Therefore, the steric hindrance of the RuQPIm-19 induced by shrinking restricts the entrance of the aromatic segment of L-tyrosine esters into the quenching sphere, while that of RuQPIm-44 is relatively easy due to little shrinking.

3. Conclusions

We reveal the effect of L-tyrosine esters on the quenching reaction of RuQPIm with MV^{2+}. The spectroscopic properties of the ruthenium(II) complex residue are slightly affected by L-tyrosine esters. In viscosity measurements, the specific viscosity of the RuQPIm-19 is decreased by addition of MV^{2+} and L-tyrosine esters; the decrease is particularly remarkable for the RuQPIm-19/MV^{2+}/L-tyrosine ester, indicating shrinking of the polymer induced by π–π interaction with MV^{2+} and van der Waals interaction with the L-tyrosine esters as shown in Fig. 3. In contrast, because the RuQPIm-44 has many positive charges, quaternized imidazolium residues, on the polymer backbone, it barely shrinks due to electrostatic repulsion. The decrease in the viscosity of RuQPIm-44 comes from the decrease in flexibility of the alkyl side chain on the polymer induced by strong van der Waals interaction with the L-tyrosine esters.

In quenching studies, the quenching efficiency is increased and the Stern–Volmer plots are varied by the addition of L-tyrosine esters, indicating that the quenching reaction is varied by addition of the L-tyrosine esters. In the presence of the L-tyrosine esters, the quenching reaction proceeds through three processes,

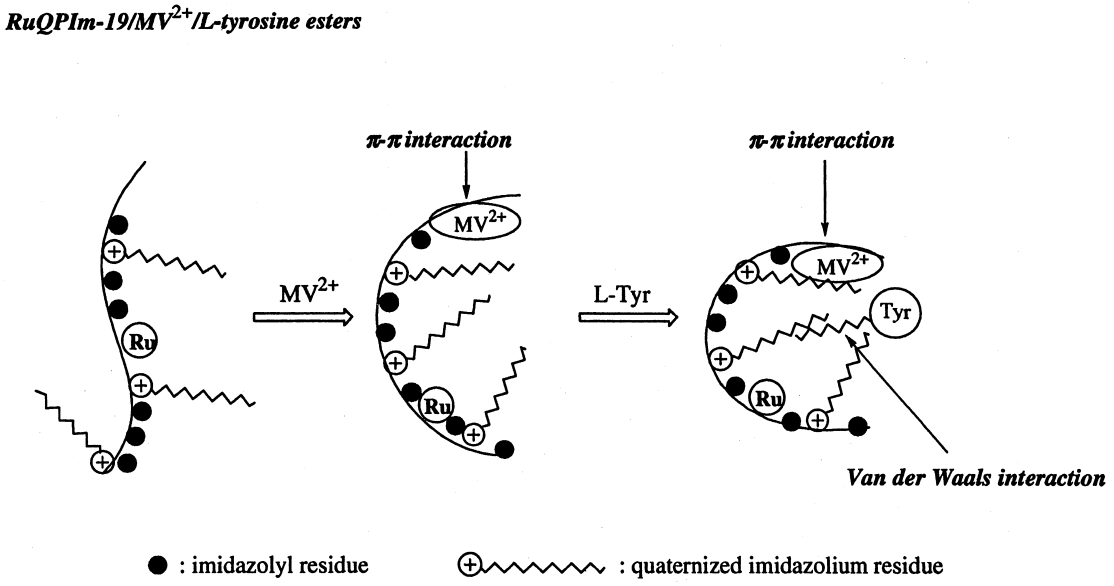


Fig. 3. Tentative illustration of shrinking of RuQPIm-19 induced by addition of MV^{2+} and L-tyrosine esters.

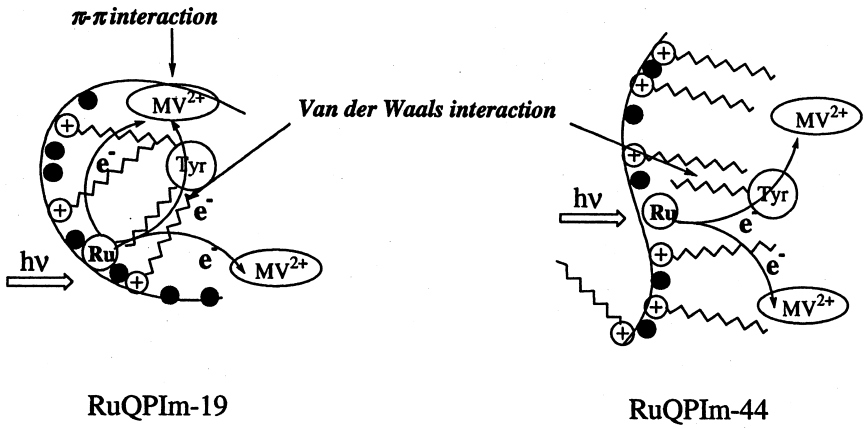


Fig. 4. Tentative illustration of reaction mechanism of quenching of RuQPIm-19 and RuQPIm-44 with MV^{2+} mediated by L-tyrosine esters.

an interactive process, a direct one and a mediated one for RuQPIm-19 and through a direct process and a mediated one for RuQPIm-44. The quenching efficiency and the Stern–Volmer plot is given by the sum of these processes. Furthermore, these quenching reactions are also affected by the conformation of the polymers. Based on these results, we propose the reaction mechanism of quenching for RuQPIm-19 and RuQPIm-44 systems as shown in Fig. 4.

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