Quenching kinetics of partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes with $C_{12}V^{2+}$ mediated by L-tyrosine esters

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The quenching kinetics of the 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 1,1′-didodecyl-4,4′-bipyridinium ($C_{12}V^{2+}$) in the presence of the L-tyrosine esters with hexyl (C_6Tyr), octyl (C_8Tyr) and dodecyl (C_{12}Tyr) groups has been investigated in methanol. A modified Stern–Volmer equation for the quenching reaction mediated by the L-tyrosine esters is proposed. In the absence of the L-tyrosine esters, the quenching reactions for the RuQPIm-19 and RuQPIm-44 systems take place through a static quenching process induced by a van der Waals interaction between the alkyl side chains on the polymers and $C_{12}V^{2+}$. In the presence of the L-tyrosine esters, the quenching reaction only takes place through a static process mediated by the L-tyrosine esters, and the kinetic parameters were calculated from the computed curve fitting using the modified Stern–Volmer equation. The second-order quenching constants, given by the product of the equilibrium constant and the first-order quenching constant, decrease for RuQPIm-19 and increase for RuQPIm-44 with increasing length of the alkyl group in the L-tyrosine esters. These results are attributed to the fact that the kinetic parameters are affected by the conformation of these polymers; RuQPIm-19 shrinks and RuQPIm-44 is partially bridged by addition of $C_{12}V^{2+}$ and the L-tyrosine esters.

In biological systems, long-range electron transfer in redox proteins involves electron tunneling through a polypeptide environment,[1–3] and their kinetics and reaction mechanisms have been extensively investigated.[4,5] Many investigations using modified proteins have suggested that the long-range electron transfer can be achieved because some amino acid residues in the proteins act as pathway molecules;[6–9] for example, photoinduced electron transfer in the photosynthesis of green plants takes place through a tyrosine residue.[10] Such modified proteins are difficult to modify, synthesize and characterize.

The pathway effect of 3-methylindole (used as a model compound for the tryptophan amino acid residue) on photoinduced electron transfer from tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, to methylviologen, MV^{2+}, in a synthetic polymer film has been recently investigated.[11] The electron transfer distance doubles because the 3-methylindole molecule acts as a pathway molecule between $Ru(bpy)_3^{2+}$ and MV^{2+}. Furthermore, for electrochemical water oxidation in a polymer membrane, the charge transfer distance is increased by the addition of *p*-cresol (a model compound for tyrosine amino acid) from 1.28 to 2.25 nm, showing that *p*-cresol functions as a mediator for the charge transport.[12]

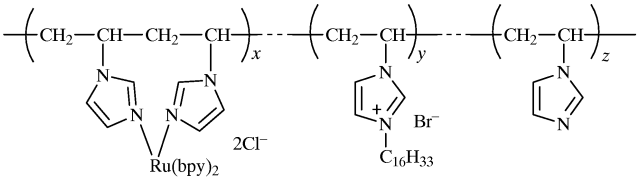
On the other hand, we have reported that the ruthenium(II) complex-containing polymers (RuQPIms), in which the bis(2,2′-bipyridine)ruthenium(II) complex is coordinated with the imidazolyl residues on the partially quaternized poly(1-vinylimidazole), have excellent photosensitizing abilities for photosensitized charge separation[13,14] and photoinduced hydrogen generation reactions.[15–17] Recently, the effects of L-tyrosine esters on the quenching of the RuQPIms with alkylviologens have been investigated in methanol.[18,19] By addition of L-tyrosine esters, the quenching efficiency is enhanced and the reaction mechanism changes because the L-tyrosine esters act as a mediator molecule. As far as we know, such investigations on the quenching reaction using the L-tyrosine esters are the first reported. Furthermore, there is little known on the kinetics of such quenching reactions. In this paper, the quenching kinetics of RuQPIms with 1,1′-didodecyl-4,4′-bipyridinium ($C_{12}V^{2+}$) mediated by L-tyrosine esters has been investigated in methanol.

Results

The chemical structure of RuQPIms is shown in Scheme 1. During the luminescence quenching reactions, a change in the luminescence spectral profile was not observed, indicating the absence of an emitting excited state complex under these experimental conditions.

Absence of L-tyrosine esters

Fig. 1 shows the Stern–Volmer plots for the quenching of RuQPIm-19, RuQPIm-44, and $Ru(bpy)_2(MeIm)_2^{2+}$ with $C_{12}V^{2+}$ in methanol. The Stern–Volmer plot showed upward



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

Scheme 1

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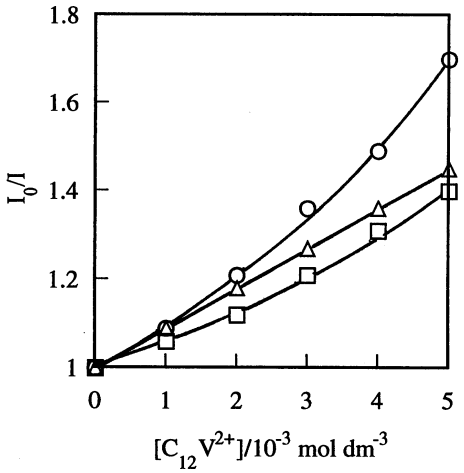


Fig. 1 Stern–Volmer plots for quenching of (○) RuQPIm-19, (□) RuQPIm-44 and (△) $Ru(bpy)_2(MeIm)_2^{2+}$ with $C_{12}V^{2+}$

deviating curves for RuQPIm-19 and RuQPIm-44, while it showed a straight line for $Ru(bpy)_2(MeIm)_2^{2+}$. In the $Ru(bpy)_2(MeIm)_2^{2+}$ system, the $C_{12}V^{2+}$ species have no interaction with $Ru(bpy)_2(MeIm)_2^{2+}$ and the quenching reaction proceeds through a dynamic quenching process, giving the Stern–Volmer plot as expressed by eqn. (1):[20]

$$I_0/I = 1 + K_{SV}[C_{12}V^{2+}] \quad \text{and} \quad K_{SV} = k_{q_2} \cdot \tau_0 \qquad (1)$$

where k_{q_2} represents the second-order quenching rate constant and τ_0 represents the luminescence lifetime in the absence of the $C_{12}V^{2+}$. This result is supported by the fact that the Stern–Volmer plot obtained from the luminescence measurements is also given by a straight line.[21] In contrast, the $C_{12}V^{2+}$ species undergo van der Waals interactions with RuQPIm-19 and RuQPIm-44,[13,22] consequently giving Stern–Volmer plots with upward deviating curves. We reported that the MV^{2+} species underwent a π–π interaction with RuQPIm-19, and that the quenching reaction only proceeded through a static quenching process; namely, only the MV^{2+} species undergoing a π–π interaction participated in the quenching reaction.[23] Considering this fact, it is presumed that the quenching reaction between these polymers and $C_{12}V^{2+}$ takes place only through a static quenching process. In order to prove this assumption, luminescence lifetime measurements were carried out. The luminescence decay curves showed multiexponential decays for all systems. Furthermore, the luminescence lifetimes for the longer lifetime components barely depended on the concentration of $C_{12}V^{2+}$. These facts support the assumption that the quenching reaction proceeds only through a static quenching process. Considering the experimental results, the Stern–Volmer plot for the static quenching process can be expressed by eqn. (2):[23–25]

$$I_0/I = \frac{1}{1 - k_{q_1}\tau_0 K_1[C_{12}V^{2+}]} \qquad (2)$$

where k_{q_1} represents the first-order quenching rate constant for the $C_{12}V^{2+}$ species undergoing a van der Waals interaction with these polymers and is proportional to the number of interacting $C_{12}V^{2+}$ molecules. K_1 represents the equilibrium constant incorporation of $C_{12}V^{2+}$ into the quenching sphere of the ruthenium(II) complex residue on these polymers. The observed Stern–Volmer plots for both systems can be fit using eqn. (2), and the reciprocal plots also give straight lines, therefore indicating that these quenching reactions only take place through the static quenching process. The kinetic parameters obtained from the theoretical curve fit are summarized in Table 1.

Presence of L-tyrosine esters

For $Ru(bpy)_2(MeIm)_2^{2+}$, the L-tyrosine esters did not affect the quenching reaction; the Stern–Volmer plot and the quenching efficiency did not change. This result indicates that these L-tyrosine esters completely disperse in methanol.

Fig. 2 shows the Stern–Volmer plots for the quenching of RuQPIm-19 and RuQPIm-44 with $C_{12}V^{2+}$ in the presence of L-tyrosine esters. The plots for RuQPIm-19 showed downward deviating curves, and the quenching efficiency increased only when C_6Tyr was added; it did not change when C_8Tyr and C_{12}Tyr were added at low concentrations of $C_{12}V^{2+}$ and

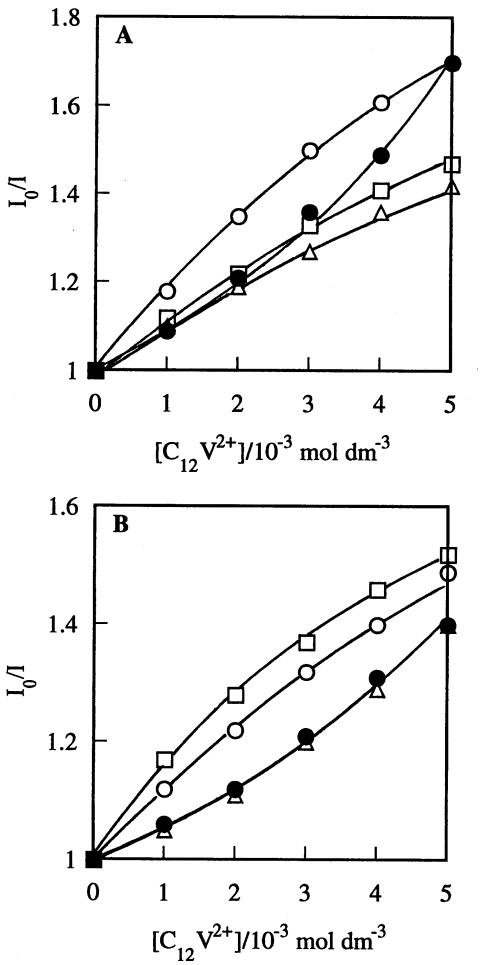


Fig. 2 Stern–Volmer plots for quenching of (A) RuQPIm-19 and (B) RuQPIm-44 with $C_{12}V^{2+}$ (●) in the absence and in the presence of the L-tyrosine esters (○) C_6Tyr, (□) C_8Tyr and (△) C_{12}Tyr. The concentration of the L-tyrosine esters was 0.05 mol dm^{-3}

Table 1 Kinetic parameters obtained from luminescence quenching data in the absence of L-tyrosine esters

	τ_0/ns	K_{SV}/mol^{-1} dm^3	k_{q_2}/mol^{-1} dm^3 s^{-1}	$K_1k_{q_1}$/mol^{-1} dm^3 s^{-1}
$Ru(bpy)_2(MeIm)_2^{2+}$	622	88.25	1.42×10^8	—
RuQPIm-19	628	—	—	1.32×10^8
RuQPIm-44	648	—	—	8.89×10^7

it decreased at high concentrations. On the other hand, the Stern–Volmer plot for RuQPIm-44 showed downward deviating curves for C_6Tyr and C_8Tyr and was not affected by C_{12}Tyr. The quenching efficiency was also increased by addition of C_6Tyr and C_8Tyr. These results indicate that the mechanism of the quenching reaction is varied by the addition of L-tyrosine esters, except for the RuQPIm-44–C_{12}Tyr system.

Our previous report shows that both the L-tyrosine esters and $C_{12}V^{2+}$ undergo van der Waals interactions with the alkyl side chains on RuQPIm-19 and RuQPIm-44.[18,19,23] Therefore, the van der Waals interaction of the $C_{12}V^{2+}$ species would be restricted due to steric hindrance by the L-tyrosine esters, compared with the case in the absence of the L-tyrosine esters. In the latter case, the binding of the $C_{12}V^{2+}$ species into the quenching sphere of the ruthenium(II) complex residue would be a multistep process, and at least two $C_{12}V^{2+}$ species can bind to the quenching sphere. In the presence of the L-tyrosine esters, however, the binding of the $C_{12}V^{2+}$ species should be a one-step process due to the steric hindrance of the L-tyrosine esters, as expressed by eqns (3) and (4):

$$Ru^{II}QPIm\cdots n\text{Tyr} + C_{12}V^{2+} \overset{K}{\rightleftharpoons} Ru^{II}QPIm\cdots n\text{Tyr}\cdots C_{12}V^{2+} \quad (3)$$

$$K = \frac{[Ru^{II}QPIm\cdots n\text{Tyr}\cdots C_{12}V^{2+}]}{[Ru^{II}QPIm\cdots n\text{Tyr}][C_{12}V^{2+}]} \quad (4)$$

where K is the equilibrium constant for the incorporation of $C_{12}V^{2+}$ into the quenching sphere, and $Ru^{II}QPIm\cdots n$Tyr represents the RuQPIm to which n molecules of L-tyrosine ester are bound. These quenching reactions would proceed according to eqns (5)–(12):

$$Ru^{II}QPIm\cdots n\text{Tyr} \xrightarrow{h\nu} {}^*Ru^{II}QPIm\cdots n\text{Tyr} \quad (5)$$

$${}^*Ru^{II}QPIm\cdots n\text{Tyr} \xrightarrow{k_e} Ru^{II}QPIm\cdots n\text{Tyr} + h\nu' \quad (6)$$

$${}^*Ru^{II}QPIm\cdots n\text{Tyr} \xrightarrow{k_d} Ru^{II}QPIm\cdots n\text{Tyr} + \Delta \quad (7)$$

$${}^*Ru^{II}QPIm\cdots n\text{Tyr} + C_{12}V^{2+} \xrightarrow{k_{q2}[C_{12}V^{2+}]} Ru^{II}QPIm\cdots n\text{Tyr} + C_{12}V^{2+} \quad (8)$$

$$Ru^{II}QPIm\cdots n\text{Tyr}\cdots C_{12}V^{2+} \xrightarrow{h\nu} {}^*Ru^{II}QPIm\cdots n\text{Tyr}\cdots C_{12}V^{2+} \quad (9)$$

$${}^*Ru^{II}QPIm\cdots n\text{Tyr}\cdots C_{12}V^{2+} \xrightarrow{k_e} Ru^{II}QPIm\cdots n\text{Tyr}\cdots C_{12}V^{2+} + h\nu \quad (10)$$

$${}^*Ru^{II}QPIm\cdots n\text{Tyr}\cdots C_{12}V^{2+} \xrightarrow{k_d} Ru^{II}QPIm\cdots n\text{Tyr}\cdots C_{12}V^{2+} + \Delta \quad (11)$$

$${}^*Ru^{II}QPIm\cdots n\text{Tyr}\cdots C_{12}V^{2+} \xrightarrow{k'_{q1}} Ru^{II}QPIm\cdots n\text{Tyr}\cdots C_{12}V^{2+} \quad (12)$$

where k_e and k_d represent the rate constants of the luminescent and nonluminescent decays of the photoexcited ruthenium(II) complex, k_{q_2} is a second-order quenching constant, and k'_{q_1} is a first-order quenching constant for the quenching reaction by the $C_{12}V^{2+}$ species present within the quenching sphere. Eqns (5)–(8) are the dynamic quenching process and eqns (9)–(12) are the static quenching process. Based on eqns (3)–(12), the luminescence intensity (I_0/I) is represented by eqn. (13):

$$I_0/I = \frac{(1 + k_{q_2}\tau_0[C_{12}V^{2+}])(1 + K[C_{12}V^{2+}])}{1 + \dfrac{K[C_{12}V^{2+}]}{(1 + k'_{q_1}\tau_0)}(1 + k_{q_2}\tau_0[C_{12}V^{2+}])} \quad (13)$$

where τ_0 (the lifetime in the absence of $C_{12}V^{2+}$) is equal to $1/(k_e + k_d)$. Because the dynamic quenching process does not occur due to steric hindrance of the polymer chains[19] and thus only static quenching takes place,[26] eqn. (14) is obtained by setting k_{q_2} in eqn. (13) equal to zero:

$$I_0/I = \frac{1 + K[C_{12}V^{2+}]}{1 + K[C_{12}V^{2+}]/(1 + k'_{q_1}\tau_0)} \quad (14)$$

Discussion

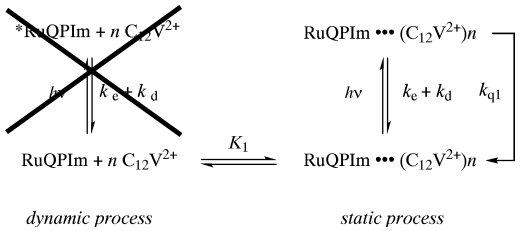
Absence of L-tyrosine esters

The observed Stern–Volmer plots for the quenching of RuQPIm-19 and RuQPIm-44 can be fit well using eqn. (2). In these systems, the reaction mechanism can be expressed as shown in Scheme 2. The n molecules of $C_{12}V^{2+}$ interact with RuQPIms through a van der Waals interaction, and the photoexcited ruthenium(II) complex residue is quenched only by the interacting $C_{12}V^{2+}$ species. The value of $K_1 \cdot k_{q_1}$ is larger for the RuQPIm-19 system than that for RuQPIm-44. RuQPIm-44 has more positive charges (the quaternized imidazolium residues); thus, the electrostatic repulsion is larger than that for RuQPIm-19. Furthermore, our previous paper reported that addition of $C_{12}V^{2+}$ caused shrinking of RuQPIm-19 and partial bridging of the RuQPIm-44 through the $C_{12}V^{2+}$.[19] The bridging decreases the degree of freedom of the $C_{12}V^{2+}$ species and restricts the reaction between RuQPIm-44 and $C_{12}V^{2+}$. Although the contribution of these conformational changes to K_1 or k_{q_1} is unclear, we reason as follows. The reactive species such as the ruthenium(II) complex residue and the interacting $C_{12}V^{2+}$ are concentrated by the shrinking of RuQPIm-19 into the polymer domain formed by the polymer backbone, which leads to an increase in the k_{q_1} value. In contrast, RuQPIm-44 with many quaternized imidazolium residues has a large K_1 value, while the k_{q_1} value is small due to fixation of the $C_{12}V^{2+}$ induced by partial bridging. Therefore, the contribution of the polymer conformation to the k_{q_1} value would be dominant.

Presence of L-tyrosine esters

In the presence of the L-tyrosine esters, the observed Stern–Volmer plots can be fit well using eqn. (14), and the kinetic parameters obtained are summarized in Table 2. The quenching reaction also takes place only through the static quenching process, regardless of the presence or absence of the L-tyrosine esters. However, it is clear that, in the absence and in the presence of the L-tyrosine esters, the two static quenching processes of the reaction mechanism differ substantially. The static quenching process in the absence of the L-tyrosine esters is the quenching reaction between RuQPIm-19 and $C_{12}V^{2+}$ species undergoing a van der Waals interaction. In the presence of the L-tyrosine esters, the static quenching of RuQPIm-19 with $C_{12}V^{2+}$ undergoing a van der Waals interaction takes place through the L-tyrosine esters; it is mediated by the L-tyrosine esters. Based on the results, the reaction mechanism can be expressed as shown in Scheme 3.

Here, the equilibrium reaction between RuQPIms and the L-tyrosine esters, which shifts to the formation reaction with a large excess of L-tyrosine, is neglected. As mentioned above,



Scheme 2

Table 2 Kinetic parameters obtained from luminescence quenching data in the presence of L-tyrosine esters

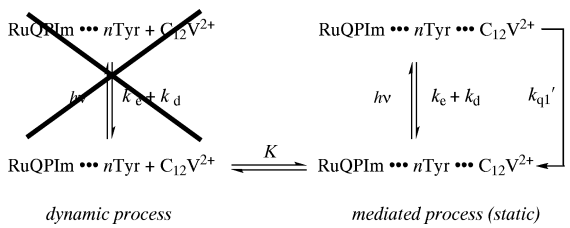
L-Tyrosine ester	τ_0/ns	K/mol^{-1} dm^3	k'_{q_1}/mol^{-1} dm^3 s^{-1}	$K \cdot k'_{1_1}$/mol^{-1} dm^3 s^{-1}
RuQPIm-19				
C_6Tyr	628	308.8	3.42×10^6	1.06×10^9
C_8Tyr	628	209.3	2.72×10^6	5.69×10^8
C_{12}Tyr	628	176.7	2.80×10^6	4.95×10^8
RuQPIm-44				
C_6Tyr	648	195.1	2.99×10^6	5.83×10^8
C_8Tyr	648	346.4	1.79×10^6	6.20×10^8
C_{12}Tyr[a]	648	—	—	—

[a] This system behaves the same as in the absence of L-tyrosine esters, given in Table 1.

only one $C_{12}V^{2+}$ molecule among the many interacting $C_{12}V^{2+}$ molecules can be incorporated into the quenching sphere of the ruthenium(II) complex due to steric hindrance.

RuQPIm-19 system. For the RuQPIm-19 systems, the quenching efficiency, corresponding to the liability of quenching, is increased by addition of C_6Tyr; while it does not particularly change with C_8Tyr and C_{12}Tyr, it is smaller than that in the absence of the L-tyrosine esters at high concentrations of $C_{12}V^{2+}$. Furthermore, the quenching efficiency decreases with increasing length of the alkyl group in the L-tyrosine esters, C_6Tyr > C_8Tyr > C_{12}Tyr, as this increases the distance between the L-tyrosine esters and the ruthenium(II) complex residue. With longer alkyl groups such as C_8Tyr and C_{12}Tyr, however, the quenching efficiency is only slightly affected. This suggests a contribution of other factors to the quenching efficiency; just as it is with the conformation of RuQPIm-19. We reported that the viscosity of the RuQPIm-19 was decreased by addition of $C_{12}V^{2+}$ and L-tyrosine esters in the order of C_6Tyr > C_8Tyr > C_{12}Tyr.[18] This result led us to conclude that RuQPIm-19 shrank. This shrinkage would shorten the distance between C_{12}Tyr and the ruthenium(II) complex residue. Therefore, the decrease in the quenching efficiency is counterbalanced by the shortened distance induced by shrinking.

As summarized in Table 2, the kinetic parameters also depend on the L-tyrosine esters for the RuQPIm-19 systems. Considering the Fuoss equation,[27] $K \cdot k'_{q_1}$ can be regarded as the second-order rate constant for the quenching reaction mediated by the L-tyrosine esters, and its value decreases with increasing length of the alkyl group in the L-tyrosine esters. Similarly, the K value decreases. In contrast, the k'_{q_1} values are independent of the length of the alkyl group in the C_8Tyr and C_{12}Tyr systems. These facts suggest that the effects of the L-tyrosine esters on the quenching reaction are determined by at least two factors, length of the alkyl group and the conformational change. The K value is decreased by steric hindrance of the alkyl group in the L-tyrosine esters. The k'_{q_1} value is also decreased by the steric hindrance, while it is increased by the shrinking of RuQPIm-19, particularly for the C_{12}Tyr system. Further, it is found that the conformational change induced by addition of the L-tyrosine esters and $C_{12}V^{2+}$ hardly affects the K value. Compared with the second-order rate constant ($K_1 \cdot k_{q_1}$) in the absence of the L-tyrosine esters, the $K \cdot k'_{q_1}$ values are clearly larger, indicating that the quenching reaction mediated by the L-tyrosine esters is faster than non-mediated quenching.



Scheme 3

RuQPIm-44 system. For the C_{12}Tyr system, the quenching reaction is not affected; the quenching mechanism does not change and the kinetic parameters are almost the same as in the absence of L-tyrosine ester. The quenching efficiency is increased by addition of C_6Tyr and C_8Tyr in the order of C_6Tyr < C_8Tyr, indicating that the C_8Tyr species mediates more effectively the electron transfer from the photoexcited ruthenium(II) complex to the $C_{12}V^{2+}$. We reported that the viscosity of RuQPIm-44 was decreased by addition of the $C_{12}V^{2+}$, and a further decrease was observed on addition of the L-tyrosine esters. This result led us to conclude that RuQPIm-44 was partially bridged by $C_{12}V^{2+}$ through a van der Waals interaction because it was difficult for the RuQPIm-44, with many positive charges, to undergo a large conformational change, as seen for RuQPIm-19. Probably, the L-tyrosine esters are incorporated into the bridged RuQPIm-44 through a van der Waals interaction. The mediated quenching is barely inhibited by the bridging of RuQPIm-44 because the steric hindrance of the polymer backbone is small, although the alkyl side chains and alkyl groups in the L-tyrosine esters and $C_{12}V^{2+}$ species are close.

On the other hand, the alkyl length dependence of the kinetic parameters is also unique; the second-order quenching constants ($K \cdot k'_{q_1}$) in the mediated quenching reaction increase with increasing length of the alkyl groups in the L-tyrosine esters. Furthermore, the K values increase and k'_{q_1} values decrease with increasing alkyl length; incorporation of the $C_{12}V^{2+}$ molecule into the quenching sphere is accelerated and the electron transfer from the photoexcited ruthenium(II) complex to $C_{12}V^{2+}$ is restricted. For the mediated quenching, the distance between the ruthenium(II) complex residue and $C_{12}V^{2+}$ molecule, that is, between the ruthenium(II) complex residue and the L-tyrosine esters as well as between the L-tyrosine esters and $C_{12}V^{2+}$ molecule, is very important. The $C_{12}V^{2+}$ species interact with RuQPIm-44 through a van der Waals interaction; therefore, the distance between the ruthenium(II) complex residue and the $C_{12}V^{2+}$ molecule does not depend on the L-tyrosine esters. The L-tyrosine esters, which interact with RuQPIm-44 through a van der Waals interaction, but not by hydrogen bonding or π–π interactions,[18] are incorporated from the side of the alkyl group into the polymer domain. It is necessary that the L-tyrosine esters are incorporated in-between the ruthenium(II) complex residue and the $C_{12}V^{2+}$ molecule, in which the mediated quenching is feasible. Lengthening of the alkyl group in the L-tyrosine esters produces a strong van der Waals interaction, which enhances incorporation, yet it also increases the steric hindrance, which inhibits incorporation. The two effects affect the K value and the k'_{q_1} value, respectively; in addition, the balance between them determines the second-order quenching constant. The $C_{12}V^{2+}$ having the longest alkyl group undergoes the strongest van der Waals interaction, while the steric hindrance is largest; consequently, C_{12}Tyr has no mediated

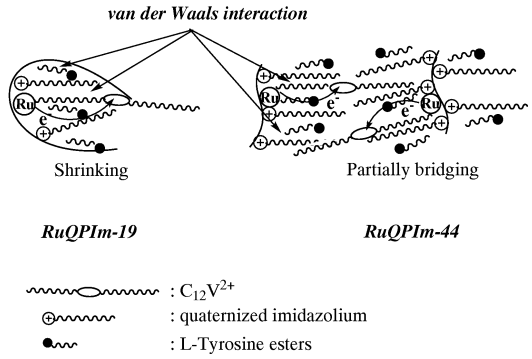


Fig. 3 Tentative representation of the mechanism of the quenching reaction between RuQPIm and $C_{12}V^{2+}$

effect. C_6Tyr, which has the shortest alkyl group, undergoes a weak van der Waals interaction and the steric hindrance is relatively small, leading to large k'_{q_1} and small K values. In contrast, C_8Tyr with an intermediate alkyl group length has a good balance of the two effects, leading to a large second-order quenching constant.

Comparing the two systems, a difference in the conformation contributes to the quenching reaction, by shrinking of the RuQPIm19 and partial bridging of the RuQPIm-44. Such conformational changes, which are induced by addition of $C_{12}V^{2+}$ and the L-tyrosine esters, affect the kinetics parameters differently; in particular, the alkyl length dependence of the K value is typical. The shrinking of RuQPIm-19 restricts the incorporation of $C_{12}V^{2+}$ into the quenching sphere through the L-tyrosine esters by the steric hindrance of the polymer backbone and the alkyl groups in the L-tyrosine esters. In contrast, the bridging of RuQPIm-44 accelerates the van der Waals interaction of the L-tyrosine esters and incorporation of $C_{12}V^{2+}$ into the quenching sphere because the steric hindrance is small. Based on these results, we propose the reaction mechanism of quenching of RuQPIm-19 and RuQPIm-44 with $C_{12}V^{2+}$ shown schematically in Fig. 3.

Conclusions

We kinetically analyzed the quenching reactions between RuQPIms and $C_{12}V^{2+}$ in the presence of L-tyrosine esters. The quenching reaction in the absence of the L-tyrosine esters takes place through a static quenching process induced by a van der Waals interaction of the $C_{12}V^{2+}$ with these polymers. The reaction mechanism for quenching is varied by addition of the L-tyrosine esters; namely, the quenching reaction takes place through a static quenching process mediated by the L-tyrosine esters. Furthermore, the kinetics parameters for the mediated quenching process are calculated from the computed curve fitting using the modified Stern–Volmer equation as expressed by eqn. (14). With increasing length of the alkyl group in the L-tyrosine esters, the second-order quenching constant for the mediated process, given by the product of the equilibrium constant for the incorporation of $C_{12}V^{2+}$ into the quenching sphere through the L-tyrosine esters and the first-order quenching constant, decreases for RuQPIm-19 and increases for RuQPIm-44. This is attributed to the conformational changes in which RuQPIm-19 is shrunk and RuQPIm-44 is partially bridged by addition of $C_{12}V^{2+}$ and the L-tyrosine esters.

Experimental

Materials

L-Tyrosine, alkyl alcohols, and other reagents, which were commercially available and of guaranteed purity, were used without further purification. 1,1′-Didodecyl-4,4′-bipyridinium dibromide (laurylviologen, $C_{12}V^{2+}$) was prepared by refluxing a methanol solution containing 4,4′-bipyridine and 1-bromododecane for 8 h. Poly(1-vinylimidazole)-bound ruthenium(II) complex (RuPIm) and *cis*-bis(2,2′-bipyridine) di(1-methylimidazole)ruthenium(II) hexafluorophosphate, $[Ru(bpy)_2(MeIm)_2](PF_6)_2$, as the low molecular weight model complex, were prepared according to a method described elsewhere.[28] Partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes were prepared by quaternization of the RuPIm with 1-bromohexadecane. L-Tyrosine esters with hexyl (C_6Tyr), octyl (C_8Tyr) and dodecyl (C_{12}Tyr) groups were prepared by a method reported previously.[18,19]

Measurements

UV/VIS absorption spectra were recorded on a JASCO V-570 UV/VIS/NIR spectrophotometer. Luminescence spectra were measured using a Hitachi 650-10S fluorescence spectrophotometer. Luminescence lifetime measurements were carried out using a Horiba NAES-550 nanosecond fluorometer.

The quenching reaction was carried out at 25 °C under an argon atmosphere in methanol. The luminescence intensity at 648 nm from the triplet metal-to-ligand charge transfer (MLCT) state,[13,29] which was excited at 488 nm, was monitored as a function of the $C_{12}V^{2+}$ concentration. The computed curve fittings of the observed Stern–Volmer plots were carried out using the curve-fit program in DeltaGraph 4.0, version 4.0.3 (Delta Point Inc.).

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