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pH and Micellar Effects on the Quenching of Tris(2,2'-bipyridine)Ruthenium(II) Luminescence by 1-Alkyl-4,4'-bipyridinium: Evidence of Deep Embedment of the Quencher Cations in Sodium Dodecyl Sulfate Micelle

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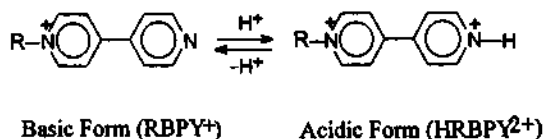
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The effects of pH and sodium dodecyl sulfate (SDS) micelle on the quenching of Ru(bpy)₃²⁺ luminescence by N-alkyl-4,4'-bipyridinium ions (RBPY⁺; R=methyl, octyl, dodecyl, benzyl) were investigated. In the absence of SDS, the quenching rate at pH 2 is similar to that of the corresponding methylalkyl viologens and much greater than that in pH 8 solution due to greater reducibility of the protonated form of RBPY⁺ (HRBPY²⁺). The quenching rate at pH 2 is strongly enhanced by the presence of SDS, while that at basic pH is greatly retarded. These observations are explained by deep embedment of RBPY⁺ into the hydrophobic hydrocarbon region of the micelle, whereas Ru(bpy)₃²⁺ and HRBPY²⁺ locate in the Stern layer of the micelle.

Introduction

The electron transfer quenching of luminescence from tris(α,α'-diimine)ruthenium(II) complexes by viologens has been extensively investigated in relation to the development of light to chemical energy conversion schemes¹⁻⁹ and photosensitized reductive transformation of organic compounds^{10,11} where viologens behave as electron mediators. The rate of the quenching reactions is greatly enhanced by the presence of anionic micelles such as sodium dodecyl sulfate (SDS), largely due to condensation of the electron donor and acceptor pairs in the potential field of the anionic microparticles by electrostatic interaction.³⁻⁹ However, different degree of embedment of viologens into micellar interface depending on the alkyl chain length also influences the surface diffusion of the viologens in micelles and thus the quenching rate.^{4,6,7}

1-alkyl-4,4'-bipyridinium ions (RBPY⁺) undergo the following acid-base equilibrium. The acidic form (HRBPY²⁺) has structural similarity to viologens, while the basic form is a substituted pyridinium ion which can be considered as an analog of coenzyme NAD⁺.¹² Because of these interesting characteristics, the pH-dependent electrochemical¹³⁻¹⁶ and spectroscopic^{14,15,17} behaviors of the compounds as well as the ability of the compounds as electron mediators in redox reactions in homogeneous media have been investigated.¹⁸⁻²⁰ An nmr study indicated that the bipyridine moiety of RBPY⁺ intercalates between the hydrocarbon chains of the SDS micelle.²¹ In this paper, we have studied the emission quenching of Ru(bpy)₃²⁺ by various RBPY⁺ in acidic and basic solutions. The opposite effect of SDS on the quenching reaction rate depending on pH is discussed in terms of difference of the locations of HRBPY²⁺ and RBPY⁺ in the micelle.



Experimental Section

Sodium dodecyl sulfate was obtained from Fluka and was purified by recrystallization from ethyl alcohol after washing with diethyl ether. Chloride salts of 1-alkyl-4,4'-bi-

pyridinium (RBPY⁺Cl⁻) were prepared by reacting 4,4'-bipyridine with the corresponding alkyl (R=methyl (C₁), octyl (C₈), dodecyl (C₁₂) and benzyl (Bz)) halides according to a literature procedure,¹⁸ followed by anion exchange to chloride by stirring the RBPY⁺X⁻ solution in the presence of AgCl. Other chemicals were obtained from Aldrich and used without further purification. Water was deionized and then distilled in glass. Unless otherwise specified, all solutions contained 0.10 M NaCl and were adjusted either to pH 8.0 with 0.01 M phosphate buffer or to pH 2.0 with HCl. All spectral and electrochemical measurements were performed at 25±0.5 °C.

Luminescence spectrum was recorded with a Hitachi F-3010 fluorescence spectrophotometer equipped with a thermostatic cell holder. The excitation wavelength was 450 nm. The quenching data were analyzed by Stern-Volmer Eq. (1).

$$I_0/I = 1 + K_{sv} [Q] \quad (1)$$

where I_0 and I denote the luminescence intensity in the absence and presence of the quencher.

Redox potentials of RBPY⁺ were determined either from differential pulse polarograms taken with a Solea-Tacussel PRG 5 at scan rate of 2 mV/s with pulse height of 20 mV or from cyclic voltammograms recorded with a BAS 100B electrochemical analyzer using a glassy-carbon electrode at scan rate of 100 mV/s.

Results and Discussion

pH-Dependent Electrochemical Behavior of RBPY⁺. Since the rate of electron-transfer quenching reaction with oxidative quenchers depends on the reduction potential of the quenchers, we summarize the electrochemical behavior of RBPY⁺ briefly. Previously, we reported the pH-dependent electrochemical behavior of RBPY⁺ cations.¹⁶ At acidic condition where RBPY⁺ is protonated as HRBPY²⁺, the cations are reduced by two-consecutive 1-*e*⁻ processes similar to dialkyl viologens. The reduction potentials of both steps shift to more negative direction by increasing pH of medium due to preceding acid-base equilibria of the electroactive species. As pH of the medium increased, the two redox peaks merged into a single peak and RBPY⁺ is reduced by one-step 2-*e*⁻ transfer process above pH 7. The reduction potential is further shifted to more negative value as the 2-*e*⁻ reduction products undergo chemical reactions with H⁺. The reduction potential of RBPY⁺ at pH ≥ 11 is similar to that of NAD⁺ analogs. We summarized the reduction potentials in Table 1: only the first reduction potentials are listed for pH 2 solutions. We also measured the reduction potential of 1-methyl-4-cyanopyridinium ion CC₁(NP⁺) whose value is included in the Table.

pH-Dependent Quenching Behavior and Acid-base Properties of RBPY⁺. Luminescence quenching of Ru(bpy)₃²⁺ by RBPY⁺ depends on pH of the solutions. The pH dependence of luminescence intensity of a Ru(bpy)₃²⁺ solution in the presence of RBPY⁺ gave a typical titration curve, where relative change of the intensity was parallel to the relative change of absorbance of RBPY⁺ with pH (see Figure 2 in Ref. 17). Above pH 5 in homogeneous solutions and above pH 6 in 10 mM SDS micellar solutions, no further change in the luminescence intensity is observed

Table 1. The Reduction Potentials (E) of 1-Alkyl-4,4'-bipyridinium Ions (RBPY⁺) and the Stern-Volmer Constants (K_{sv}) for Luminescence Quenching of Ru(bpy)₃²⁺ by RBPY⁺ at 25 °C^{a,b}

Quencher	-E/V (vs SCE)				K_{sv}/M^{-1}			
	pH 2.0		pH 11.0		pH 2.0		pH 8.0	
	H ₂ O	10mM SDS	H ₂ O	10mM SDS	H ₂ O	10mM SDS	H ₂ O	10mM SDS
C ₁ BPY ⁺	0.70	0.66	1.08	1.07	360	2600	110	55
C ₈ BPY ⁺	0.70	0.60	0.96	1.05	400	3050	135	106
C ₁₂ BPY ⁺	0.59	0.67	0.89	0.97	630	2500	245	170
BzBPY ⁺	0.65	0.63	1.01	1.01	490	3300	390	160
C ₁ CNP ⁺	0.77	0.79	1.02	1.01	^c	^c	730	2050

^aAt pH 2, only the first reduction potentials are listed. ^b K_{sv} values in SDS solutions are apparent values calculated at 0.5 mM quencher concentration except that for C₁₂BPY⁺ which was taken at 0.2 mM. ^cNot significantly different from the values taken at pH 8.

though the reduction potentials of the quenchers depend on pH. Since the luminescence spectrum of Ru(bpy)₃²⁺ in the absence of a quencher does not depend on pH, the pH dependence of the intensity in the presence of a quencher should be ascribed to the pH dependence of the quenching efficiency of the quencher.¹⁷ The parallelism between the change of luminescence intensity of Ru(bpy)₃²⁺ in the presence of RBPY⁺ and absorbance change of the quencher, which reflect the acid-base equilibrium of the quencher molecule, indicate that the pH-dependent quenching arises from different quenching efficiency of the acidic and basic forms of RBPY⁺ for Ru(bpy)₃²⁺ luminescence and the subsequent reactions of the reduced quenchers do not affect the quenching efficiency. The pK_a values of HRBPY²⁺ were calculated from the pH-dependency of the quenching: they are about 3.6 in homogeneous aqueous solutions and 4.5 in 10 mM SDS solutions containing 0.1 M NaCl.¹⁷ The pK_a values predict that the quencher molecules are present mostly as protonated form (HRBPY²⁺) below pH 2 and as deprotonated (RBPY⁺) above pH 7. Thus we followed the quenching behavior of HRBPY²⁺ and RBPY⁺ at pH 2 and pH 8, respectively.

Quenching in Homogeneous Aqueous Solutions.

Figures 1 and 2 show the Stern-Volmer plots of the luminescence quenching of Ru(bpy)₃²⁺ by RBPY⁺ in homogeneous aqueous media at pH 2 and 8, respectively. The plots gave good linearity except C₁₂BPY⁺ in pH 8 solution, which shows negative deviation from linearity above 0.25 mM, presumably due to self-association of the quencher to form micelles: the critical micelle concentrations (cmc) of C₁₂BPY⁺Cl⁻ (pH 8) and HC₁₂BPY²⁺Cl⁻ (pH 2) in the media of ionic strength 0.1 M are estimated to be 0.4 and 4.5 mM, respectively, from surface tension measurements. The Stern-Volmer constants (K_{sv}) of the quenching reactions are determined from the slopes of plots and summarized in Table 1.

The redox potentials of RBPY⁺ as well as the K_{sv} values for the quenching at pH 2 are very similar to those of the corresponding methylalkyl viologens given in a previous report.⁸ Also, the order of K_{sv} values in pH 2 solutions, HC₁BPY²⁺ < HC₈BPY²⁺ < HBzBPY²⁺ < HC₁₂BPY²⁺, agrees well

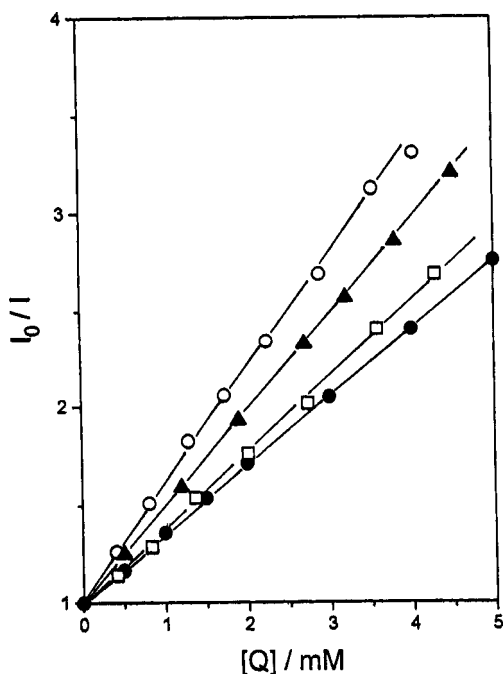


Figure 1. Stern-Volmer plots for the emission quenching of 5.0×10^{-6} M $\text{Ru}(\text{bpy})_3^{2+}$ by RBPY^+ in aqueous 0.1 M NaCl solutions at pH 2.0. Note that the quenchers are protonated to HRBPY^{2+} , $\text{HC}_1\text{BPY}^{2+}$; (\square), $\text{HC}_8\text{BPY}^{2+}$; (\circ), $\text{HC}_{12}\text{BPY}^{2+}$; (\triangle), HBzBPY^{2+} .

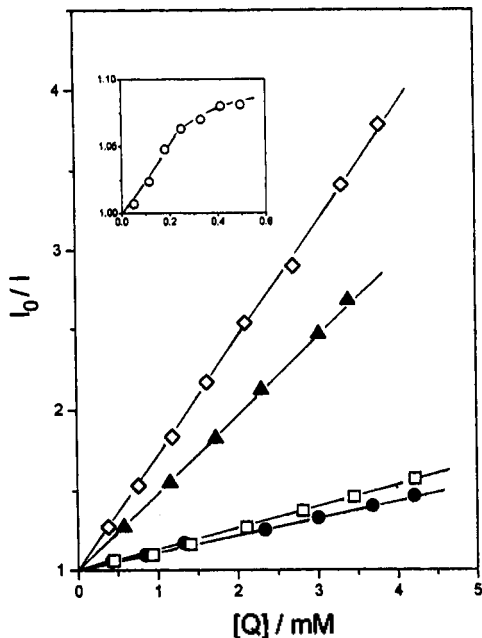


Figure 2. Stern-Volmer plots for the emission quenching of 5.0×10^{-6} M $\text{Ru}(\text{bpy})_3^{2+}$ by RBPY^+ and 1-methyl-4-cyanopyridinium ion in aqueous 0.1 M NaCl solutions at pH 8.0. Inset is the results of $\text{C}_{12}\text{BPY}^+$; (\bullet), C_1BPY^+ ; (\square), C_8BPY^+ ; (\circ), $\text{C}_{12}\text{BPY}^+$; (\blacktriangle), BzBPY^{2+} ; (\diamond), C_1CNP^+ .

with that observed with methylalkyl viologens.⁸ One possible explanation for this order is the difference in reduction potentials of HRBPY^{2+} . Table 1 shows good correlation between the reduction potential and K_{sv} values. The other ex-

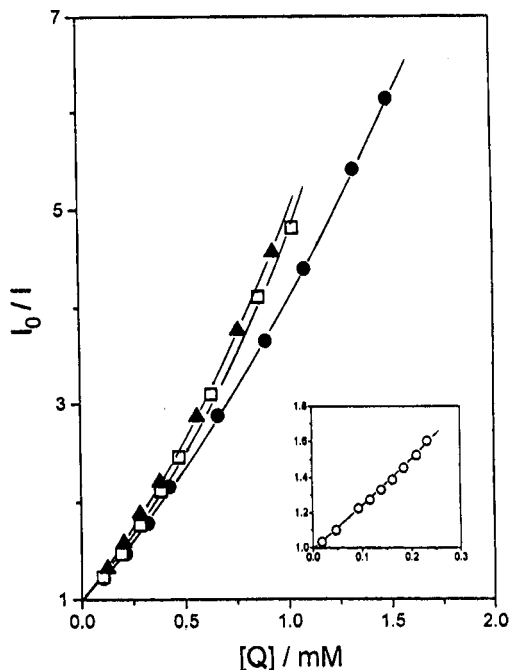


Figure 3. Stern-Volmer plots for the emission quenching of 5.0×10^{-6} M $\text{Ru}(\text{bpy})_3^{2+}$ by RBPY^+ in aqueous 10 mM SDS solutions at pH 2.0. The quenchers are protonated to HRBPY^{2+} . Inset is the result of $\text{C}_{12}\text{BPY}^+$; (\bullet), $\text{HC}_1\text{BPY}^{2+}$; (\square), $\text{HC}_8\text{BPY}^{2+}$; (\circ), $\text{HC}_{12}\text{BPY}^{2+}$; (\blacktriangle), HBzBPY^{2+} .

planation is hydrophobic interaction between the quenchers and $\text{Ru}(\text{bpy})_3^{2+}$. As a quencher has greater hydrophobic character, it forms a stabler encounter complex with $\text{Ru}(\text{bpy})_3^{2+}$ and the electron-transfer reaction in the encounter complex becomes more efficient.^{22,23}

The quenching rate at pH 8 is slower than that at pH 2, presumably due to more negative redox potential of the deprotonated quenchers, RBPY^+ . Because of $2e^- + \text{H}^+$ transfer nature of the electrochemical reduction,¹⁶ direct correlation between the reduction potential and the rate of the quenching reaction which is single electron transfer from $^*\text{Ru}(\text{bpy})_3^{2+}$ to the quencher is not feasible. However, fairly good correlation between them still holds except BzBPY^+ which causes the most efficient quenching among RBPY^+ investigated. The alkyl chain dependence of the quenching rate is much stronger in pH 8 solution than in pH 2 solution. This, together with the high quenching rate of BzBPY^+ , can be attributed to the greater contribution of hydrophobic interaction as the deprotonated form interacts more strongly with the luminescer.

Quenching in SDS Micellar Solutions. The Stern-Volmer plots of emission quenching data in SDS micellar solutions show positive deviation from linearity (Figures 3 and 4). This is a common feature for quenching reaction in micellar media.^{8,9} A simple model to explain this was suggested by Atik and Singer assuming multi-step equilibria for binding a quencher with micelles and intramicellar quenching.²⁴ Another cause for the positive deviation was suggested by this group in terms of difference in the binding sites of the micelles for quenchers and difference in quenching efficiency of the bound quenchers.^{8,9} The apparent K_{sv} values are calculated from the quenching data at

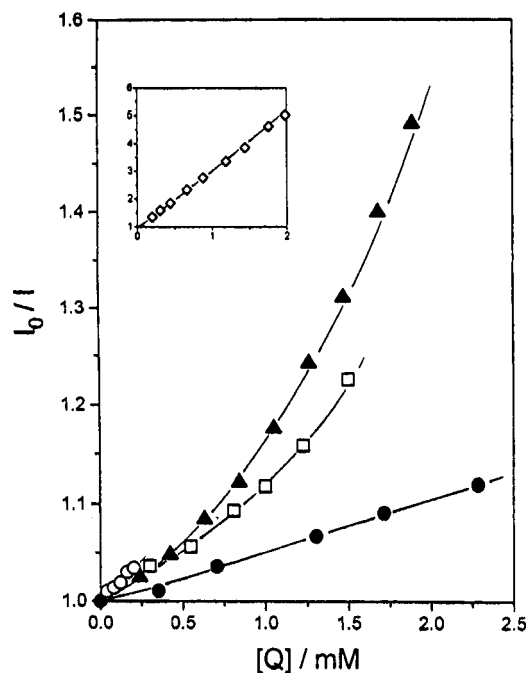


Figure 4. Stern-Volmer plots for the emission quenching of 5.0×10^{-6} M $\text{Ru}(\text{bpy})_3^{2+}$ by RBPY^+ and 1-methyl-4-cyanopyridinium ion in aqueous 10 mM SDS solutions at pH 8.0. Inset is the results of C_1CNP^+ : (●), C_1BPY^+ ; (□), C_8BPY^+ ; (○), $\text{C}_{12}\text{BPY}^+$; (▲), BzBPY^{2+} ; (◇), C_1CNP^+ .

$[\text{RBPY}^+] = 0.5$ mM and the results are included in Table 1: the results of $\text{C}_{12}\text{BPY}^+$ were obtained at 0.2 mM due to precipitation of $\text{C}_{12}\text{BPY}^+$ /dodecyl sulfate ion pair.

The quenching rate in pH 2 media increases greatly by the presence of SDS micelle. Again, the order of the quenching rate among quenchers and the rate enhancement by SDS is similar to that found with methylalkyl viologens.⁸ This indicates that the solubilization site and reducibility of HRBPY^{2+} in SDS micelle as well as surface diffusion coefficients for HRBPY^{2+} on the micelle are similar to those of the corresponding methylalkyl viologens.

Interestingly, the quenching rates in pH 8 are much retarded by the presence of SDS micelle. Since the reduction potential of RBPY^+ in SDS micellar solutions does not differ significantly from the corresponding values in SDS-free solutions, we cannot ascribe this to the change in reducibility of the quenchers upon binding to SDS micelle. This is confirmed by the large enhancement of the quenching rate of 1-methyl-4-cyanopyridinium ion (C_1CNP^+) by SDS micelle (see Table 1).

The observation of retardation of reactions between ions of the same charge by micelles of opposite charge is unusual. However, the similar retarding effect of SDS was found in the quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ luminescence by lipophilic quenchers such as nitrobenzene and oxygen.⁹ It was also shown that the luminescence quenching of $\text{Ru}(\text{bpy})_3^{2+}$ by dimethyl viologen (MV^{2+}) is retarded in the presence of poly(methacrylic acid) near pH 5.²⁵ The retardation was explained in terms of different solubilization or binding sites of the reactants in the anionic microparticles.²⁵

A few studies address the location of $\text{Ru}(\text{bpy})_3^{2+}$ in SDS micelle. Meisel *et al.* first inferred that the cation is em-

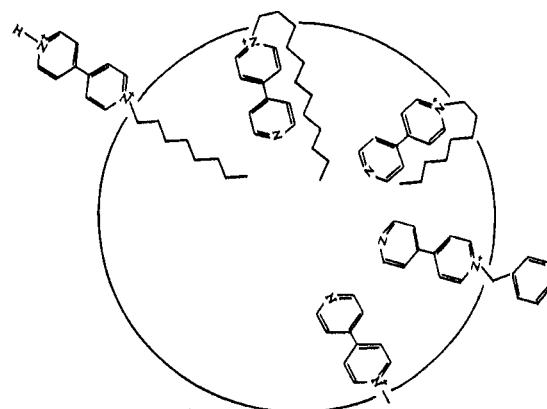


Figure 5. Schematic sketch for solubilization structures of RBPY^+ cations and their protonated forms in SDS micelle.

bedded in a highly negatively-charged microenvironment of the micelle.³ This is generally believed by many investigators and could successfully explain the results of quenching experiments involving $\text{Ru}(\text{bpy})_3^{2+}$ in SDS micelle.^{4,6,7,9} Kunjappu *et al.* suggested that $\text{Ru}(\text{bpy})_3^{2+}$ is bound to a more nonpolar hydrophobic region of SDS hemimicelle and micelle, from the quenching study of $\text{Ru}(\text{bpy})_3^{2+}$ luminescence by doxylstearic acids.²⁶ The bulky nitroxide radical moiety of the doxylstearic acids may result in more open structure of the hydrophobic region of the micelle and allow the probe molecules for deeper penetration into the micelle. The present study supports that $\text{Ru}(\text{bpy})_3^{2+}$ is located at interfacial Stern region of the micelle (see below).

The opposite effect of SDS micelle on the quenching of $\text{Ru}(\text{bpy})_3^{2+}$ luminescence by RBPY^+ depending on pH can be taken as an evidence for the fact that the acidic (HRBPY^{2+}) and basic (RBPY^+) forms of the quenchers are localized in different regions of the micelle: the large enhancement of the rate of the quenching reaction in acidic solution clearly indicates that HRBPY^{2+} and $\text{Ru}(\text{bpy})_3^{2+}$ are in close proximity, while retardation in basic media indicates that RBPY^+ and $\text{Ru}(\text{bpy})_3^{2+}$ are further apart. The possible locations are the negatively charged interfacial Stern region and hydrophobic interior of the micelle. Because of the double positive charge of HRBPY^{2+} , the binding site of the HRBPY^{2+} should be Stern layer. Thus it can be concluded that $\text{Ru}(\text{bpy})_3^{2+}$ and HRBPY^{2+} are located in the Stern layer, while RBPY^+ is in the hydrophobic interior. An nmr study by Zoltewicz and Bloom suggested that 1-methyl-4,4'-bipyridinium ion (C_1BPY^+) occupies time-dependent positions, either in the hydrocarbon region by intercalation or on the surface in the Stern layer of SDS micelle.²¹ If so, the apparent quenching rate would be average of the contribution from both locations. The decrease in the quenching rate by SDS strongly suggests that RBPY^+ is predominantly embedded into the hydrophobic region of the micelle. The lipophilic character of RBPY^+ can successfully explain the observation of transmembrane permeability of C_1BPY^+ across dihexadecylphosphate membrane, while dimethyl viologen (MV^{2+}) is impermeable across the membrane.¹⁹

In conclusion, the quenching behavior of 1-alkyl-4,4'-bipyridinium cation for $\text{Ru}(\text{bpy})_3^{2+}$ luminescence is similar to that of the corresponding 1-methyl-1'-alkyl-4,4'-bipyridinium

(methylalkyl viologen) in acidic homogeneous aqueous and SDS micellar solutions. The quenching rate in basic solutions is much slower than that in acidic media as the reduction potential of the deprotonated form of the quencher is more negative than that of the protonated form. The presence of SDS micelle further retards the quenching rate in basic solutions. The opposite effect of SDS micelle on the quenching rate depending on pH was explained by different binding sites for HRBPY²⁺ and RBPY⁺: and the protonated quencher (HRBPY²⁺) are located in the Stern layer of SDS micelle where Ru(bpy)₃²⁺ binds, while the deprotonated quenchers (RBPY⁺) are in the hydrophobic hydrocarbon region due to lipophilicity of the cations.

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- Complexation of a quencher with a luminescer is expected to show positive deviation in I_0/I vs [Q] plot. However, the deviation is not usually observed at low concentration of quenchers having weak binding tendency with the luminescer.⁸ This seems the reason why we failed to observe upward curvature in Figure 1.
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