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The Synthesis and Luminescence Quenching of the Water-soluble Polymer-supported Tris(2,2′-bipyridine)ruthenium(II) Analogue

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The *p*-aminostyrene-*N*-vinylpyrrolidone copolymer-supported tris(2,2′-bipyridine)ruthenium(II) analogue, $[Ru(bpy)_2(pbyCOOH)]^{2+}$ (bpy=2,2′-bipyridine and pbyCOOH=polymeric bipyridine ligand), has been prepared, and the luminescence behavior of the polymer complex has been investigated in an aqueous solution. The efficiency of the quenching of the excited state of the polymer complex with $[Fe(CN)_6]^{4-}$, $[Co(phen)_3]^{2+}$, and Cu^{2+} is compared with that of $[Ru(bpy)_3]^{2+}$. The quenching of the excited state of the polymer complex by Cu^{2+} is strongly enhanced by the effect of the polymer chains. In the polymer complex/Cu^{2+} system, the quenching by Cu^{2+} in the presence of poly(*p*-styrenesulfonate) is much more effective than in the absence of the polyion. The characteristics of the polymer complex in terms of the luminescence behavior are discussed.

Recently much attention has been paid to the photochemical property of tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, and the utilization of the excited state of $[Ru(bpy)_3]^{2+}$, $*[Ru(bpy)_3]^{2+}$, in solar-energy-conversion systems has been proposed by many workers.[1-6] The photochemistry of $[Ru(bpy)_3]^{2+}$ in micellar-core and polyelectrolyte solutions,[4] and those of $[Ru(bpy)_3]^{2+}$ derivatives in aqueous solutions[3,7,8] and the exterior aqueous phase of phospholipid vesicle[9] have been studied.

For the photosensitized reactions of $[Ru(bpy)_3]^{2+}$ and the related complexes, it would be desirable to immobilize them in polymer chains in order to prevent non-productive back reactions and in order to promote efficient energy capture by the reactive species.[10] The polymer-supported bis(2,2′-bipyridine)ruthenium(II) complexes, $[Ru(bpy)_2(pvp)]^{2+}$ and $[Ru(bpy)_2(pvp)Cl]^{+}$ (pvp=poly(4-vinylpyridine)), have been synthesized.[10] However, these complexes were easily decomposed by thermal and photo-substitution reactions. Polymer-supported metal complexes with bipyridine ligands were prepared by the reaction of a polystyrene-supported bipyridine ligand with a variety of transition-metal salts by Card and Neckers.[11]

In this connection, we marked a water-soluble $[Ru(bpy)_3]^{2+}$ analogue with a polymeric ligand as a polymer-bound photosensitizer.

Experimental

Materials. The $[Ru(bpy)_3]Cl_2\cdot 6H_2O$[12] and $[Ru(bpy)_2CO_3]5H_2O$[13] were prepared by the methods previously described. The *p*-aminostyrene was prepared from 1-(*p*-aminophenyl)ethanol.[14] The *p*-aminostyrene(PAS)/*N*-vinylpyrrolidone(VPo) copolymer (**1**) was prepared by the azobisisobuthyronitrile(AIBN)-initiated radical polymerization of PAS with VPo in tetrahydrofuran. Found: C, 67.30; H, 8.19; N, 12.41%. Calcd for $(C_8H_9N)_{0.14}(C_6H_9NO)_{0.86}$: C, 67.19; H, 8.02; N, 12.77%. IR spectra (in cm^{-1}): 3350 3230 (PAS, NH_2), 2930 (VPo ring, CH), 1630 1520 (PAS, ph ring), 1290 (VPo ring, CN). The intrinsic viscosity of the **1** copolymer in an aqueous solution was 0.37 at 25 °C. 2,2′-Bipyridine-4,4′-dicarboxylic acid, $bpy(COOH)_2$, was prepared by the method of Whitten *et al.*[15] The polymeric bipyridine ligand pbpCOOH, **2**, was prepared by the following method under a nitrogen atmosphere. To 50 ml of a *N,N*-dimethylformamide (DMF) solution containing $bpy(COOH)_2$ (2.0 g, 0.0082 mol) and triethylamine (0.83 g, 0.0082 mol), we added ethyl chloroformate (0.89 g, 0.0082 mol). The reaction mixturewas then stirred at 0—5 °C for 1 h. To the reaction mixture we then added 20 ml of a DMF solution of the **1** copolymer (0.32 g, 4.0×10^{-4} mol units of aminostyrene). The solution was stirred at 0—5 °C for 1 h and then kept overnight at room temperature. The volume of the reaction mixture was reduced to *ca.* 20 ml and the resulting precipitate was filtered. Pale yellow powder was dissolved in small amounts of ethanol. The powder of pbyCOOH was reprecipitated twice from ethanol into ether and dried in vacuo (yield, *ca.* 1.6 g). Found: C, 66.25; H, 7.08; N, 12.72%. Calcd for $(C_{20}H_{15}N_3O_3)_{0.14}(C_6H_9NO)_{0.86}$: C, 66.43; H, 6.89; N, 12.45%. IR spectra (in cm^{-1}): 2940 (VPo ring, CH), 1660 (VPo ring, CO), 1630, 1520 sh (PAS, ph ring), 1290 (VPo ring, CN), 1200 (pendant bpy ring). The results of elemental analysis and IR measurements indicate that no appreciable amounts of free amino groups remained on the polymeric ligand; the IR peak at 3350 cm^{-1} (νNH_2) of the PAS/VPo copolymer completely disappeared in the polymeric bipyridine ligand, **2**.

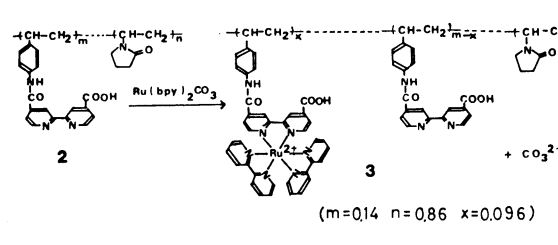
The polymer-supported Ru(II) complex (**3**), which is represented by $[Ru(bpy)_2(pbyCOOH)]^{2+}$, was obtained by the reaction of **2** with $[Ru(bpy)_2CO_3]$. An ethanolic solution (50 ml) of **2** (2.0 g, 0.0020 mol) and $[Ru(bpy)_2CO_3]5H_2O$ (1.13 g, 0.0020 mol) was allowed to reflux for 10 h. After the addition of several drops of 1 M HCl (1 M=1 mol dm^{-3}), the reaction mixture was dialized in cold water for 40 h under dark. The chloride salt of the polymer complex was obtained by the evaporation of the dialyzed solution under reduced pressure and dried in vacuo. The molar fraction of the Ru (II) complex unit (x) of **3** was determined to be 0.096 ± 0.005 by means of the atomic-absorption spectrum, using $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ as the standard material. The dialized solution of the polymer complex was usually kept frozen.

Luminescence and Quencihing Experiments. Deoxygenated samples were used for the experiments. The pH values of the solution were adjusted by the addition of dil HCl or dil NaOH solutions. The ionic strength of the solutions was not adjusted to be constant by the addition of simple salt, since, if a large amount of the salt is added, the potential fields of the polymer domains are shielded with the counter ions. This causes a shrinking of the polymer chains and, thus, a reduction of the polymer effect. The excitation wavelength was 465 nm. Comparison measurements were taken on the same day.

Instruments. The absorption spectra were recorded with a Hitachi 320 spectrophotometer. The infrared spectra (KBr disks) were measured using a Hitachi Model 200-10 infrared spectrophotometer. A Hitachi Model 170-40 atomic absorption spectrometer was used for the determination of ruthenium. The emission spectra were made in 1 cm × 1 cm quartz cell on a Shimadzu RF-500 spectrofluorometer at 25±0.1 °C by means of a thermostated cell holder. A PRA Model 3000 nanosecond fluorometer (Photochemical Research Associates, Inc.) was used for the determination of the excited lifetimes of the polymer complex.

Results and Discussion

The reaction of pbyCOOH with $[Ru(bpy)]_2CO_3$ (Eq. 1) was completed in about 10 h at 50 °C: the initial absorption maximum at *ca.* 500 nm due to $[Ru(bpy)_2CO_3]$ shifted at *ca.* 460 nm due to the ligand-substitution reaction. The absorption and emission spectra of an aqueous solution of **3** and $[Ru(bpy)_3]^{2+}$ are shown in Fig. 1. In an aqueous solution, the molar extinction coefficients of the polymer complex and $[Ru(bpy)_3]^{2+}$ at their absorption maxima are 1.48±0.05 M^{-1} (459 nm) and 1.40±0.02 M^{-1} (455 nm) respectively. No appreciable change in the absorption spectrum of the polymer complex was observed for at least 3 d at room temperature.



(1)

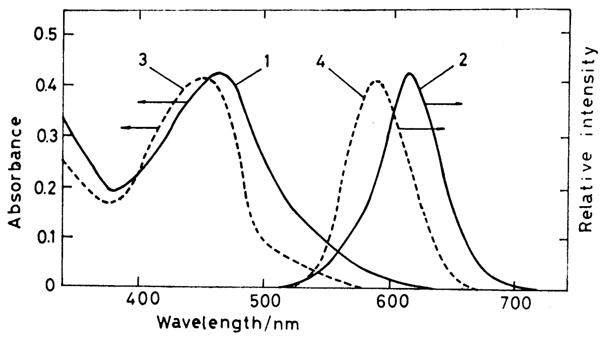


Fig. 1. Absorption and luminescence spectra of $[Ru(bpy)_2(pbyCOOH)]^{2+}$ (1 and 2) and $[Ru(bpy)_3]^{2+}$ (3 and 4) in aqueous solution at 25 °C. [Ru(II)]= 3.0×10^{-5} M.

The absorption maximum of the CTTL band of the polymer complex was dependent on the pH of the solution, whereas the molar extinction coefficient of the absorption maximum was relatively insensitive to the pH. The relative emission intensity was, however, greatly dependent on the pH, and the luminesecence maximum was not so sensitive to the pH. The pH dependence of the absorption maximum (Fig. 2) can be attributed to the acid dissociation of the –COOH on the bipyridine ring. The acid-dissociation constant of the ground state of the polymer complex, pK_a^0, was estimated to be 2.80±0.05 from the titration curve (Fig. 2).

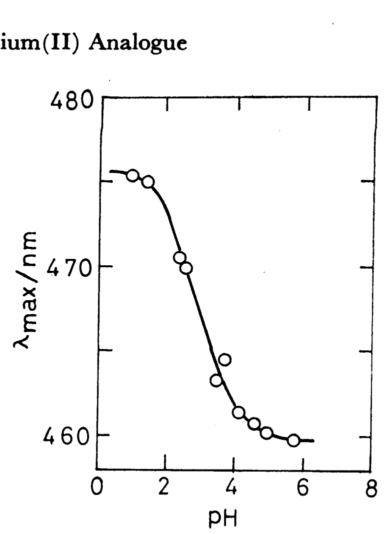


Fig. 2. Dependence of λ_{max} of $[Ru(bpy)_2(pbyCOOH)^{2+}]$ on pH at 25 °C.

The direct measurement of the excited-state equilibrium for $[Ru(bpy)_2(pby(COOH)_2)]^{2+}$, where bpy-$(COOH)_2$ is 2,2′-bipyridine-4,4′-dicarboxylic acid, had been accomplished by Giordano *et al.*[16] by means of luminescence titration. They demonstrated that the two acid groups of the complex behave identically and that the acid-dissociation constant of the ground state and that of the excited state were 5.50±0.05 and 8.50±0.05 respectively at 25 °C. In the present system, the pK_a^* of the polymer complex was also calculated from Eq. 2.[16]

$$pH = pK_a^* - \log \frac{\tau_p^*}{\tau_d^*}, \tag{2}$$

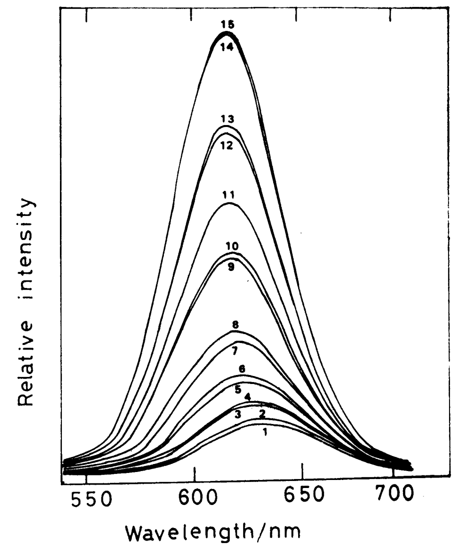


Fig. 3. Variation of the luminescence spectra of $[Ru(bpy)_2(pbyCOOH)]^{2+}$ on pH in aqueous solution at 25 °C. pH: 1, 1.26; 2, 1.64; 3, 2.18; 4, 2.63; 5, 3.27; 6, 3.29; 7, 3.49; 8, 3.54; 9, 3.90; 10, 4.08; 11, 4.18; 12, 4.58; 13, 4.89; 14, 5.83; 15, 6.13.

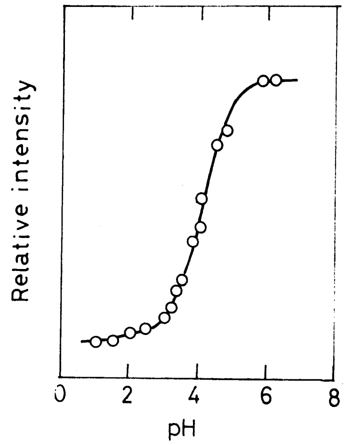


Fig. 4. Luminescence titration of $[Ru(bpy)_2(pbyCOOH)]^{2+}$ in aqueous solution at 25 °C.

where the pH was taken at the inflection point in the relative intensity *vs.* the pH curve (Fig. 4) and where τ_p^* and τ_d^* are the lifetimes of the excited state of the protonated and deprotonated species of the polymer complex respectively. The effect of the pH on the luminescence spectrum and the luminescence titration curve of the polymer complex are shown in Fig. 3 and 4 respectively. For the polymer complex, the values of τ_p^* and τ_d^* were estimated to be 287±0.01 ns (pH 1.4) and 359±0.02 ns (pH 6.0) at 25 °C. From Eq. 4, we obtained $pK_a^*=4.30\pm0.05$. The results show that the protonated complex species is a weaker acid in the lowest excited state than in the ground state. This seems to indicate that the charge transfer from the central Ru(II) ion to the polymer ligand (Process a) is predominant.

$$\begin{tikzcd}
{[\mathrm{Ru^{II}(byp)_2(pbyCOOH)}]^{2+}} \arrow[r, "a"] \arrow[d, "b"'] & {[\mathrm{Ru^{III}(bpy)_2(pb\bar{y}COOH)}]^{2+}} \\
{[\mathrm{Ru^{III}(bpy)(bpy)(bp\bar{y}COOH)}]^{2+},} &
\end{tikzcd}$$

where $bp\bar{y}$ and $pb\bar{y}COOH$ indicate the mononegatively charged species of bpy and that of pbyCOOH respectively. The negatively charged density on the bipyridine rings of pbyCOOH should increase according to the charge transfer from the Ru(II) to the polymer ligand.

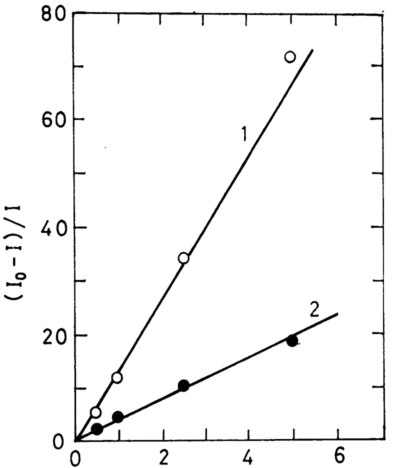


Fig. 5. Stern-Volmer plots for the luminescence quenching of $[Ru(bpy)_3]^{2+}$ (1) and $[Ru(bpy)_2(pbyCOO)]^+$ (2) by $[Fe(CN)_6]^{4-}$ in aqueous solutions at 25 °C. $[Ru(II)]=2.0\times10^{-5}$ M, pH 6.2.

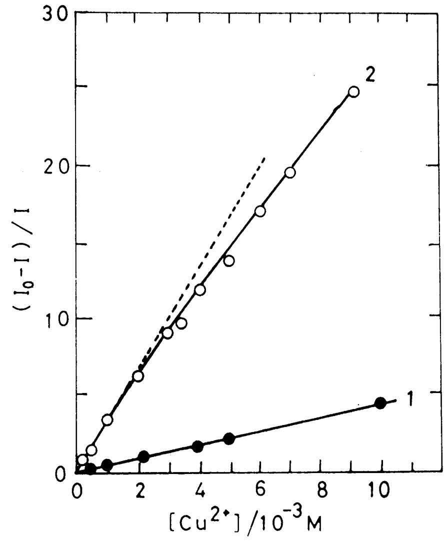


Fig. 6. Stern-Volmer plots for the luminescence quenching of $[Ru(bpy)_3]^{2+}$ (1) and $[Ru(bpy)_2(pbyCOO)]^+$(2) by Cu^{2+} in aqueous solution at 25 °C. $[Ru(II)]=2.0\times10^{-5}$ M, pH 6.2.

The luminescence-quenching studies were carried out in an aqueous solution using such quenchers as $[Fe(CN)_6]^{4-}$, $[Co(phen)_3]^{2+}$, and Cu^{2+}. The quenching experiments for the deprotonated and protonated excited-state polymer complexes were carried out at pH values lower than 1.4 and higher than 5.8 respectively. The Stern-Volmer constants, K_{SV}, and the quenching rate constants, k_q, were obtained from the slopes of the $(I_0-I)/I$ *vs.* [Q] (Q=quencher) plots and K_{SV}/τ^* (τ^*=excited-state lifetime) respectively. From the results shown in Fig. 5, we obtained $K_{SV}=13000$ and $k_q=2.2\times10^{10}$ M^{-1} s^{-1} for the $[Ru(bpy)_3]^{2+}/[Fe(CN)_6]^{4-}$ system. The values of K_{SV} and k_q obtained by Demas and Addington are 44100 and 7.3×10^9 M^{-1} s^{-1} respectively at 21 °C.[17] The extremely large value of k_q for this system was ascribed to the ion-pair formation of $[Ru(bpy)_3]^{2+}$ with $[Fe(CN)_6]^{4-}$; the ion-pairing constant of this systems was estimated to be 3600 at 21 °C.[17] The values of K_{SV} and k_q for the polymer complex and $[Ru(bpy)_3]^{2+}$ are summarized in Table 1. The quenching rate constants for the reactions of the protonated form of the polymer complex with $[Fe(CN)_6]^{4-}$ and Cu^{2+} are not very different from the corresponding rate constants for $[Ru(bpy)_3]^{2+}$. The quenching rate constant could not be determined in the case of $[Ru(bpy)_2(pbyCOOH)]^{2+}/[Co(phen)_3]^{2+}$ since the precipitate was formed in the low-pH region. The smaller rate constant for the reaction of $[Co(phen)_3]^{2+}$ with $^*[Ru(bpy)_2(pbyCOO)]^+$ than that with $^*[Ru(bpy)_3]^{2+}$ seems to reflect the Coulombic repulsion between the polymer-complex domains and $[Co(phen)_3]^{2+}$; a relatively large activation energy would be required to encounter $[Co(phen)_3]^{2+}$ with the

TABLE 1. VALUES OF K_{SV}/M^{-1} AND $(k_q/M^{-1}\ s^{-1})$ IN AN AQUEOUS SOLUTION AT 25 °C[a,c)]

	Quencher		
	$[Fe(CN)_6]^{4-}$	Cu^{2+}	$[Co(phen)_3]^{2+}$
$[Ru(bpy)_2(pbyCOOH)]^{2+}$ d)	1.7×10^3 (5.7×10^9)	26 (8.7×10^7)	—
$[Ru(bpy)_2(pbyCOO)]^{+}$ e)	3.9×10^3 (1.1×10^{10})	360 (1.0×10^9)	42 (1.2×10^8)
$[Ru(bpy)_2(pbyCOO)]^{+}$+PSS f)	—	3.7×10^3 (1.0×10^{10})	—
$[Ru(bpy)_3]^{2+}$	1.3×10^4 (2.2×10^{10})	41 (6.8×10^7)	490 (8.2×10^8)

a) The excited-state lifetimes used for the calculations of the k_q values were 290 ns for $[Ru(pby)_2(pbyCOOH)]^{2+}$, 360 ns for $[Ru(bpy)_2(pbyCOO)]^{+}$, and 600 ns for $[Ru(bpy)_3]^{2+}$ b) at 25 °C. b) Ref. 18. c) The errors of the Stern-Volmer constants and k_q are within ±5%. d) pH 1.4. e) pH 6.2. f) 2.8×10^{-5} M Ru(II) and 1.0×10^{-3} M PSS.

Ru(II) complex moieties on the polymer chains because the polymer domians have a large positive-charge density.

It is noteworthy that the k_q for the reaction of the deprotonated from of the polymer complex with Cu^{2+} is considerably greater than those of $[Ru(bpy)_2(pbyCOOH)]^{2+}$ and $[Ru(bpy)_3]^{2+}$ (Fig. 6 and Table 1). The higher reactivity of $[Ru(bpy)_2(pbyCOO)]^{+}$ with Cu^{2+} can be partly explained in terms of the "effect of the uncoordinated ligand" on the polymer chains. In the case of the polymer complex, uncoordinated bipyridine rings exist with the mole fraction of 0.044 and a part of Cu^{2+} ions probably coordinate to the uncoordinated ligands. Therefore, a hydrid metal complex with Ru(II) and Cu^{2+} is probably formed. The excited state of the Ru(II) complex on the polymer chains probably reacts rapidly with the coordinated Cu^{2+}, which can be represented by $[Cu(pbyCOO)]^{+}$. In the lower pH region. the uncoordinated bipyridine would be protonated; for example, the pK of HL^{+} of 4,4′-bipyridine is 4.44 at 25 °C.[19)] Thus, the hybrid-metal complex should not be formed in the lower pH region. This mainly accounts for the greater k_q value in $[Ru(bpy)_2(pbyCOO])^{+}/Cu^{2+}$ than in $[Ru(bpy)_2(pbyCOOH)]^{2+}/Cu^{2+}$. In the higher-pH region, the interactions between carboxylate ions and amide groups on the polymer ligand and Cu^{2+} ions should also be considered. However, the details of these interactions have not yet been made clear.

On the addition of sodium poly(p-styrenesulfonate), PSS, to $[Ru(bpy)_2(pbyCOO)]^{+}/Cu^{2+}$, a further enhancement of the quenching rate was observed; the value of k_q in the presence of 1.0×10^{-3} M PSS is about ten times greater than that in the absence of PSS and about 150 times greater than k_q for the reaction of $^*[Ru(bpy)_3]^{2+}$ with Cu^{2+}. The acceleration of the quenching rate in this system can be attributed to the formation of the polyion-polyion complex between PSS and $[Ru(bpy)_2(pbyCOOH)]^{+}$. When a large excess of PSS is present, the domains of the polyion-polyion complex should have a large negative charge density. Thus, the Cu^{2+} ions would be accumulated in the negatively charged domains. In such polyion domains, the collision frequencies between the excited state of the Ru(II)-complex moieties and the coordinated Cu^{2+} and uncoordinated Cu^{2+} should be enhanced.

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