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(24) Microanalysis showed high carbon to metal ratios and it was found that the sample lost weight on standing indicating a loss of solvent of crystallization and/or replacement of solvent by atmospheric water. To provide a sample of suitable stability for the measurement of its magnetic susceptibility by the Faraday method, the solid was allowed to equilibrate to constant weight in a stream of filtered air for 24 h; analyses of this sample are best fit by the formula $[Co(dmg)_3\{Ni(H_2O)_2\}_2]PF_6 \cdot 4H_2O$. A similar procedure was used in the preparations to follow.

Quenching and Quenching Reversal of Tris(2,2′-bipyridine)ruthenium(II) Emission in Polyelectrolyte Solutions[1]

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Abstract: The emission from the lowest charge transfer excited state of $Ru(bpy)_3^{2+}$ is very efficiently quenched by low concentrations of Cu^{2+} ions when polyvinylsulfate (PVS) is present in the solution. Stern–Volmer constants 2×10^3 higher than in the absence of PVS can be easily obtained. This efficient quenching completely vanishes and the emission is nearly totally restored when higher concentrations of the same quencher, or of inert cations, are added. The efficient quenching results from Cu^{2+} and $Ru(bpy)_3^{2+}$ residing in the potential field of the same polymer. However, as soon as the quencher (or the inert cation) displaces $Ru(bpy)_3^{2+}$ from the polyelectrolyte, quenching reversal is observed. Quantitative results regarding the number of available sites and the relative binding constants of Cu^{2+} and $Ru(bpy)_3^{2+}$ can be deduced from the minima and the quenching reversal portions of the quenching curves. Possible utilization of this or similar systems in solar energy conversion and storage is indicated.

The physical properties of polyelectrolytes have long attracted the attention of various interdisciplinary interests. The resemblance of polyelectrolyte solutions to many biological fluids as well as their obvious practical and theoretical importance has yielded a large volume of studies. Although in many of these studies the emphasis is on the thermodynamics of such systems,[2,3] their inevitable influence on reaction kinetics has been recognized.[4] The work of Morawetz and coworkers and of Ise and co-workers has shown, for example, that the rate of the Hg^{2+} sensitized aquation of Co(III) pentaamine halide complexes, as well as the rate of reduction of these complexes by various cations, is accelerated by several orders of magnitude when small amounts of polyelectrolytes are added to these solutions.[5,6]

The photoredox properties of tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) have drawn much attention recently.[7-10] The ability of the lowest charge transfer excited state (CT)-$Ru(bpy)_3^{2+*}$ to participate as an electron donor in redox reactions as well as the ability of the oxidized $Ru(bpy)_3^{3+}$ to oxidize water or hydroxide ions[11] has been utilized in several proposed solar energy conversion systems.[12,13] In a recent communication from this laboratory it was shown that the $Ru(bpy)_3^{2+}$ complex can be solubilized in negative micellar solutions, thereby greatly affecting the specific reaction rates of this complex, both in the ground and excited states, with charged entities such as e_{aq}^-, Zn^+, Co^+, Cd^+, Cu^{2+}, or $Fe(CN)_6^{3-}$.[14] These results and the current interest in both $Ru(bpy)_3^{2+}$ and polyelectrolytes led us to study the effect of polyelectrolytes on the rate of quenching of emission from (CT)$Ru(bpy)_3^{2+*}$. Effects essentially similar to those described here were observed for the quenching of uranyl fluorescence by Fe^{2+} ions in polyelectrolyte solutions.[15]

Experimental Section

All nonpolymeric chemicals used in this study were of reagent grade and, except where otherwise indicated, were once recrystallized. The potassium salt of polyvinylsulfate (PVS) was purified as described by Breslow and Kutner.[16] The specific viscosity of a 1% solution of the polymer was determined with a Cannon viscometer and from the correlation between this and the intrinsic viscosity in 0.1 M Na_2SO_4, the average molecular weight[16] was determined to be ~250 000. Solutions for irradiation were prepared from the stock 1% polymer solution in water and were irradiated a few hours after preparation. Emission spectra were recorded on a Hitachi fluorescence spectrometer (Model MPF-2A). Excitation was carried out at 450 nm and emission was usually recorded at 605 nm (emission slit ±5 nm). $Ru(bpy)_3Cl_2$ was twice recrystallized and its concentration in solution was determined spectrophotometrically assuming an ϵ_{453} of 14 000. Triply distilled water was used in this study. For measurement of the oxygen effect on the emission intensity, solutions were saturated with the desired gas (prepurified argon, dry air, or prepurified oxygen) by bubbling for 15 min in the rubber capped irradiation cells. For all other experiments air saturated solutions were used. Several comparison experiments were run with excitation at 480 nm where the extinction is 50% that at 450 nm. Since in these experiments the only noticeable effect was to cut the intensity of emission by about 50%, we conclude that no complications due to the amount of absorbed light affect our results.

Results and Discussion

The Effect of PVS on Absorption and Emission Spectra. Up to 0.9% PVS was found to be without any noticeable effect on the absorption spectrum of 2×10^{-5} M $Ru(bpy)_3^{2+}$ in the visible region where $Ru(bpy)_3^{2+}$ has its CTTL band (λ_{max} 453 nm). In the UV region the spectrum matched exactly the sum of the $Ru(bpy)_3^{2+}$ absorption and the residual absorption of the polymer (or impurities therein). Similarly, the effect of

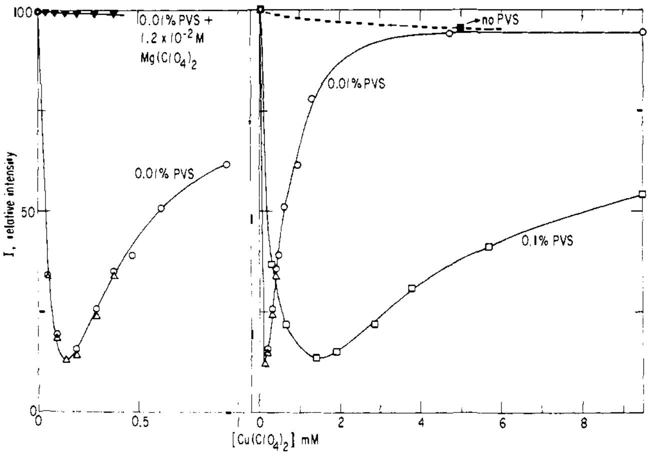

Figure 1. The effect of [Cu^{2+}] on emission intensity from (CT)Ru(bpy)$_3^{2+}$* in the presence of PVS. Concentrations of PVS are indicated near the appropriate curves: (□; ○) [$Ru(bpy)_3^{2+}$] = 2.78×10^{-5} M; (△) [$Ru(bpy)_3^{2+}$] = 1.39×10^{-5} M; (▼) [$Ru(bpy)_3^{2+}$] = 2.78×10^{-5} M and 1.2×10^{-2} M $Mg(ClO_4)_2$ added; (■) [$Ru(bpy)_3^{2+}$] = 2.78×10^{-5} M, no PVS.

PVS on the emission spectrum of (CT)Ru(bpy)$_3^{2+}$* is relatively small. The emission maximum is at 605 nm (uncorrected for photomultiplier wavelength dependence) regardless of the amount of PVS in this range of concentrations. A small increase in the half-width (5 nm in 0.9% PVS), but definitely beyond the experimental error, could be observed. The complete resemblance in both emission and absorption spectra with or without PVS clearly indicates that the Ru(II) ion fully retains its ligands in the polyelectrolyte solution and that the polyelectrolyte hardly affects the energy levels of the complex ion. Furthermore, since in Ar saturated solutions of Ru(bpy)$_3^{2+}$ the same intensity of emission is obtained with or without the polymer, we can safely conclude that no quenching of the (3CT)Ru(bpy)$_3^{2+}$ by PVS occurs. However, the lack of an effect of PVS on the emission spectrum should be compared with the pronounced red shift recently observed in the emission spectrum of (CT)Ru(bpy)$_3^{2+}$ in dodecyl sulfate micellar solutions.[14] It is hard to imagine how Ru(bpy)$_3^{2+}$ can escape the large electrostatic potential field of the polyelectrolyte (see below), and it seems, therefore, that the micellar effect on the emission spectrum is caused by the hydrocarbon chains and not by the charged sulfate groups. This is in accord with the fact[14] that the red shift of emission of (CT)Ru(bpy)$_3^{2+}$* in alcohols increases with alcohol chain length.

Quenching by O_2 in PVS Solutions. The effect of O_2 on the emission intensity was checked in water and in 0.11% PVS solution. The Stern–Volmer constant was calculated using

$$K_{SV} = [(I_0/I) - 1]/[Q] \tag{I}$$

where [Q] is the concentration of the quencher, and I_0 and I are the emission intensity in the absence and presence of the quencher, respectively. From air and O_2 saturated solutions we derive $K_{SV} = 2200$ and 1650 in the absence and presence of PVS, respectively. Assuming that the natural lifetime of (CT)Ru(bpy)$_3^{2+}$* is $\tau = 0.6 \times 10^{-6}$ s[8] independent of the presence of PVS, one obtains the second-order rate constant for quenching by O_2, $k_q = K_{SV}/\tau = 3.7 \times 10^9$ and 2.7×10^9 M^{-1} s^{-1}. This relatively small decrease in k_q in the presence of PVS is easily accounted for by the decrease in the diffusion coefficient of Ru(bpy)$_3^{2+}$ when the complex is bound to the polymer. However, this also means that O_2 molecules can move almost uninhibited in the various domains of the polyelectrolyte chain and its potential field. This small change does not affect our interpretation of the rest of the results which were obtained with air saturated solutions.

The Phenomenon of Quenching and Its Reversal. The effects of Cu^{2+} ions under various conditions on the intensity of emission from (CT)Ru(bpy)$_3^{2+}$* are shown in Figure 1. At low concentrations Cu^{2+} seems to quench the emission very efficiently. However, as [Cu^{2+}] is increased, the emission intensity passes through a minimum and from there on increases with [Cu^{2+}]. It can be seen in Figure 1 that, under favorable conditions, practically all of the emission is restored. Similar peculiar quenching and its reversal, though not as sharp as in this case, was observed in PVS solutions of uranyl ions in the presence of Fe^{2+} and a similar rationalization will be adopted here.[15] The efficient quenching at the lower [Cu^{2+}] clearly results from a scavenging reaction between Cu^{2+} and (CT)Ru(bpy)$_3^{2+}$* residing close to one another in the domain of the same polymer chain. At higher [Cu^{2+}] the quenching ions start to displace Ru(bpy)$_3^{2+}$ out of the polymer. Since the quenching of free (CT)Ru(bpy)$_3^{2+}$ by free or bound Cu^{2+} is relatively inefficient, almost complete restoration of the emission is possible.

Several results, in addition to the quenching reversal phenomenon, confirm this interpretation. The quenching curve should be independent of [$Ru(bpy)_3^{2+}$] as long as [$Ru(bpy)_3^{2+}$] is much lower than [P]/2 or [Cu^{2+}], where [P] represents the molar concentration of available sites (sulfate groups) in the solution and [P]/2 corrects for the fact that each divalent cation occupies two sites. In Figure 1, results are shown for two [$Ru(bpy)_3^{2+}$] at 0.01% PVS. The quenching portion, the position of the minimum, and the reversal portion are indistinguishable (within the small experimental error) for both concentrations. On the other hand, when the number of available sites is increased, the whole quenching and reversal curve should be shifted and by the same amount as is the increase in [PVS]. Inspection of the position of the minima in the two curves shown in Figure 1, taken with 0.01 and 0.1% PVS, reveals that the ratio between them is 10, as is the ratio between the concentration of available sites in the two experiments. Furthermore, suppose that we block all the available sites on the polymer by an excess of inert salt. Under such conditions the whole system should totally ignore the presence of the polyelectrolyte and behave exactly as in plain water. Results in the presence of 0.01% PVS and 1.2×10^{-2} M Mg^{2+} (Figure 1, upper curve) substantiate this expectation.

The whole curve of emission dependence on [Cu^{2+}] can be described by

$$\frac{I}{I_0} = \frac{[Ru(II)]_b}{[Ru(II)]_{tot}}\left(\frac{1}{1 + K_{SV}[Cu^{2+}]_b}\right) + \frac{[Ru(II)]_f}{[Ru(II)]_{tot}} \tag{II}$$

where the subscripts b and f denote the bound and free ion, respectively, and Ru(II) represents Ru(bpy)$_3^{2+}$. Inherent in eq II are the following assumptions, all substantiated by the experimental results: (a) The efficiency of the natural deexcitation in the excited complex bound to the polymer is the same as in the free state, i.e., same I_0 for both. (b) The extinction coefficient for Ru(bpy)$_3^{2+}$ in and out of the polymer domain is the same. (c) The exchange of bound (CT)Ru(bpy)$_3^{2+}$* with the bulk solution is slow compared to the lifetime of this excited state (≤ 0.6 μs). This assumption, though not strictly verified, cannot be far from reality since fast exchange would not allow the phenomenon of quenching reversal to show up.[15] (d) No quenching occurs in the bulk of the solution. In view of the complete restoration of the emission intensity and of the low efficiency of quenching by Cu^{2+} in plain water, this latter is certainly true for the lower [PVS] and thus lower [Cu^{2+}]. When bulk quenching starts to affect the intensity the last term in eq II should be multiplied by a Stern–Volmer factor containing [Cu^{2+}]$_f$. Equation II can be solved using nonlinear regression techniques, however, the large number of free parameters makes such a solution rather questionable. We therefore prefer to deal with the two portions

Table I. Stern–Volmer Constants and Quenching Rate Constants for the Emission of $Ru(bpy)_3^{2+}$ by Cu^{2+} in PVS Solutions

$[Ru(bpy)_3^{2+}]$, µM	$[Cu(ClO_4)_2]$, mM	F^a	K_{SV}, M^{-1}	k_q,^{b} $M^{-1}\,s^{-1}$	$K_F{}^c$
		0.01% PVS			
27.8	0.047	0.15	4.1×10^4	6.8×10^{10}	12.7
	0.094	0.30	4.4×10^4	7.3×10^{10}	13.8
13.9	0.047	0.15	4.1×10^4	6.8×10^{10}	12.7
	0.094	0.30	4.7×10^4	7.9×10^{10}	14.7
	0.14	0.45	4.7×10^4	7.9×10^{10}	14.6
		0.1% PVS			
27.8	0.38	0.124	4.8×10^3	8.1×10^9	15.2
	0.66	0.214	5.0×10^3	8.4×10^9	15.7
	1.41	0.45	4.6×10^3	7.6×10^9	14.8

[a] Fraction of monomers covered by Cu^{2+}. [b] Calculated from K_{SV} and $\tau = 0.6 \times 10^{-6}$ s[8] using $k_q = K_{SV}/\tau$. [c] Stern–Volmer constant in terms of fractional coverage of the available sites by Cu^{2+}, i.e., $[Cu^{2+}]/([P]/2)$.

of quenching and reversal separately in spite of the approximations involved in such an approach.

Quenching by Cu^{2+} in PVS Solutions. From the quenching portion at low $[Cu^{2+}]$ we can calculate K_{SV} and k_q using eq I as mentioned above. By doing so, we assume that in that range of concentrations both $[Ru(II)]_f$ and $[Cu^{2+}]_f$ are negligible compared to their bound parts. From the independence of Figure 1 on $[Ru(II)]_{tot}$ and from the exact equivalence of the ratio between the minima in this figure and the ratio of [PVS] we can conclude that this assumption is not far from reality.

Results are summarized in Table I. The Stern–Volmer constants are extremely large and should be compared with the values of K_{SV} = 20–100 in water, depending on the ionic strength of the solution.[14] A single experimental point in the right side of Figure 1 demonstrates the inefficiency of quenching in plain water. We have recently found that solubilization of $Ru(bpy)_3^{2+}$ in dodecyl sulfate micelles also enhances K_{SV} up to about 3×10^3 under certain conditions. There can be little doubt that higher measured K_{SV} than those reported in Table I can be obtained by using lower concentrations of PVS, $Ru(bpy)_3^{2+}$, and Cu^{2+}. Nonetheless, the high quenching rate constants k_q obtained at 0.01% PVS are larger by more than an order of magnitude than the diffusion-controlled rate constant for a reaction between similarly doubly charged particles and clearly demonstrate that if we have a dynamic phenomenon here, a reaction between Cu^{2+} and $Ru(bpy)_3^{2+}$ in the potential field domains of the polyelectrolyte occurs. In order to avoid the effect of the concentration of PVS on the quenching efficiency we find it instructive to modify eq I and define K_F, the Stern–Volmer constant in terms of the fraction of coverage of the polymer by Cu^{2+} ions, using

$$K_F = [(I_0/I) - 1]/F \qquad \text{(III)}$$

where $F = [Cu^{2+}]/([P]/2)$. As is discussed below the number of available sites on the polymer poses some difficulty and is less than the stoichiometric concentration of sulfate groups; nevertheless, for this calculation [P] was taken as the stoichiometric concentration. K_F is given in the last column of Table I and it can be seen that over the range of concentration studied K_F remains fairly constant. This means that under these conditions the efficiency of quenching by Cu^{2+} is independent of $[Cu^{2+}]$ and might indicate free movement of Cu^{2+} ions inside the polyelectrolyte domain. However, the question of whether the quenching reaction is a dynamic phenomenon or a static effect, as well as the determination of the exact mode of this reaction, is expected to be answered by fast laser photolysis experiments in which we are currently involved.

At the low coverage conditions of Table I the polymer is in the extended rodlike conformation and, following Oosawa,[17] we can calculate the effective cylindrical volume in which the Cu^{2+} and $Ru(bpy)_3^{2+}$ ions are moving. For 0.01% PVS concentration the cylindrical radius[17] is 10 Å, and with 2.5 Å length per monomer unit the effective volume is 2.9×10^{-4} L. From Table I, $K_{SV} = 4.4 \times 10^4$ L/mol (based on total volume of 1 L), so that if all the reaction is in 2.9×10^{-4} L, $K_{SV} \simeq 2.9 \times 10^{-4} \times 4.4 \times 10^4 = 13\ M^{-1}$. This crude estimate is close to the value of 20 M^{-1} in plain water, suggesting that the actual quenching reactions in water and in the polyelectrolyte solution are similar in efficiency and the changes in rate are mainly due to the increase in effective local concentration of the reacting species. Ionic strength effects in this microenvironment are probably of minor importance.

Some attention should be drawn to the position of the minima in the curves of Figure 1. Since the rate of quenching of the emission of $(CT)Ru(bpy)_3^{2+*}$ by Cu^{2+} outside the polymer is extremely low compared to its rate in the polymer domains and since the condensation effect[2] should allow complete coverage of the effective number of sites even at relatively small excess of the Cu^{2+} counterions, the minima are expected to occur very close to the point where $[Cu^{2+}] + [Ru(bpy)_3^{2+}] = [P]_{eff}/2$. Close examination reveals that the minima occur at about ½ of the equivalent stochiometric number of available sites. As noted previously, the polymer tends to retain its water of hydration even after drying in vacuo at 80 °C for long periods of time.[16] This effect might distort by a few percent the calculated concentrations but we believe that it would not account for most of the calculated unoccupied sites. The presence of the original univalent counterion of the polyelectrolyte is not expected to, and, as shown later, does not effectively replace Cu^{2+} or other divalent ions on the polymer at such low concentrations. It seems, therefore, that above 50% coverage of the polymer by Cu^{2+}, the charge density along the polymer reaches the critical point below which additional binding no longer occurs.[2]

Quenching Reversal by M^{n+}. The quenching reversal part can be analyzed in terms of the relative association constants of $Ru(bpy)_3^{2+}$ (denoted Ru(II)) and Cu^{2+} to the polyelectrolyte as follows:

$$Ru(II)_f + (2P) \overset{K_1}{\rightleftharpoons} Ru(II)_b \qquad (1)$$

$$Cu^{2+}{}_f + (2P) \overset{K_2}{\rightleftharpoons} Cu^{2+}{}_b \qquad (2)$$

As can be seen in Figure 2, other metal ions can displace the $Ru(II)_b$ from the polymer and, as expected, divalent ions are much more efficient than monovalent ions in this respect. In order to calculate K_1/K_2 we assume the simple equilibria 1 and 2 to yield

$$\frac{K_1}{K_2} = \frac{[Ru(II)]_b}{[Ru(II)]_f}\frac{[Cu^{2+}]_f}{[Cu^{2+}]_b} \qquad \text{(IV)}$$

Table II. Relative Association Constants for $Ru(bpy)_3^{2+}$ and Cu^{2+}, K_1/K_2, Under Various Experimental Conditions

$[Cu^{2+}]_{tot}$, mM	$[Ru(II)]_b/[Ru(II)]_f$	$[Cu^{2+}]_f/[Cu^{2+}]_b$	K_1/K_2
$[P]_{eff}/2 = 1.5 \times 10^{-4}$; $[Ru(II)]_{tot} = 2.78 \times 10^{-5}$			
0.28	2.83	1.18	3.34
0.37	1.82	1.85	3.36
0.47	1.57	2.53	3.98
0.61	1.03	3.49	3.59
0.94	0.62	5.76	3.55
$[P]_{eff}/2 = 1.5 \times 10^{-4}$; $[Ru(II)]_{tot} = 1.39 \times 10^{-5}$			
0.28	3.20	1.01	3.24
0.37	2.00	1.66	3.33
$[P]_{eff}/2 = 1.5 \times 10^{-3}$; $[Ru(II)]_{tot} = 2.78 \times 10^{-5}$			
2.82	3.50	0.88	3.08
3.76	2.21	1.51	3.34
5.64	1.22	2.76	3.37
			$K_1/K_2 = 3.42 \pm 0.20$

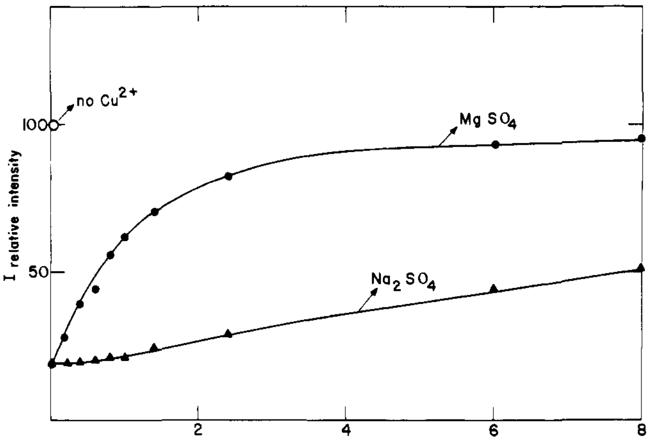

Figure 2. The effect of inert salts in quenching reversal of the emission from $(CT)Ru(bpy)_3^{2+*}$ by Cu^{2+}. 0.01% PVS + 2.05×10^{-5} M $Ru(bpy)_3^{2+}$ + 1.54×10^{-4} M $CuSO_4$ in all solutions: (●) inert salt $MgSO_4$; (▲) inert salt Na_2SO_4; (○) no $CuSO_4$ and no inert salt.

Since under our experimental conditions practically every $(CT)Ru(bpy)_3^{2+*}$ free in the solution is unquenched while every bound one is very efficiently quenched, we assume for these calculations that $[Ru(II)]_f = [Ru(II)]_{tot}(I/I_0)$, i.e., that the first term in eq II is negligible. Although this is not strictly correct, the approximation involved is considered to be small for that portion of the quenching curves which is at $[Cu^{2+}]_{tot}$ above the minima of these curves. From $[Ru(II)]_f$ and from the total concentration of $Ru(bpy)_3^{2+}$ we can calculate $[Ru(II)]_b$. The amount of bound Cu^{2+} ions was calculated from $[Cu^{2+}]_b = [P]_{eff}/2 - [Ru(II)]_b$, where the effective concentration of available sites, $[P]_{eff}/2$, was taken as $[Cu^{2+}]$ at the minimum point in the quenching curves. From $[Cu^{2+}]_b$ and the total $[Cu^{2+}]$, we calculate $[Cu^{2+}]_f$. Again, the approximation involved do not seriously perturb the results, as Table II clearly indicates. The independence of K_1/K_2 over 10-fold increases in $[P]_{eff}$ and 20-fold increases in $[Cu^{2+}]_{tot}$ is considered to substantiate the validity of our approximations. It should be noted that the large $Ru(bpy)_3^{2+}$ ion is more strongly bound than the smaller Cu^{2+} ion.

Similar experiments to those described in Figure 2 were performed with inert salts, where $M^{n+} = Mg^{2+}$, Ca^{2+}, and Ba^{2+}. In all these experiments 0.01% of PVS, 1.54×10^{-4} M Cu^{2+}, and 2.05×10^{-5} M $Ru(bpy)_3^{2+}$ were employed. Analysis of these results is somewhat more complicated since the inert ion affects both terms of eq II. Namely, on increasing $[M^{2+}]$ the amount of $Cu^{2+}{}_b$ will decrease:

$$M^{2+}{}_f + Cu^{2+}{}_b \overset{K_3}{\rightleftharpoons} M^{2+}{}_b + Cu^{2+}{}_f \qquad (3)$$

and therefore the rate of quenching of $(CT)Ru(bpy)_3^{2+*}$ on the polymer will decrease. On the other hand, some $Ru(bpy)_3^{2+}$ will also be replaced by the inert ion and thus $[Ru(II)]_f/[Ru(II)]_{tot}$ will also increase. Attempts to fit eq II to the experimental data reveal that, if we assume a nonspecific interaction between the polyelectrolyte and Cu^{2+} or the various M^{2+}, namely, if we assume $K_3 = 1$, calculations consistently yield higher intensities of the emission than actually observed. However, if we assume that $K_3 = 0.75$ for $M^{2+} = Mg^{2+}$ a rather satisfactory fit can be obtained. A comparison between the experimental and calculated emission intensities for that set of experiments is shown in Table III. In these calculations we assume that the number of available sites that are occupied by $Ru(bpy)_3^{2+}$ is negligible compared to those that are occupied by Mg^{2+} or Cu^{2+}, i.e., $[P]_{eff}/2 = [Cu^{2+}]_b + [Mg^{2+}]_b$. Assuming the simple equilibrium reaction 3, $[Cu^{2+}]_b$ can be calculated using various values of K_3. From $[Cu^{2+}]_b/[Cu^{2+}]_f$, thus obtained, and taking $K_1/K_2 = 3.42$ (see Table II) and $K_{SV} = 4.4 \times 10^4$ (Table I) the other terms of eq II can be evaluated to yield the calculated I/I_0. The agreement between the calculated and the experimental values for $K_3 = 0.75$ can be seen by comparing the two last columns of Table III.

Similar, though not identical, results were obtained on replacing $MgSO_4$ by $BaCl_2$ or $CaCl_2$. We, however, hesitate to draw quantitative conclusions from the small differences between these ions. More accurate procedures to evaluate the same information were recently developed using the pulse-radiolysis technique.[18]

Conclusions

Quenching of the emission from $(CT)Ru(bpy)_3^{2+*}$ by Cu^{2+} ions is shown to be greatly enhanced by the presence of small amounts of the polyelectrolyte. This quenching occurs nearly exclusively and very efficiently in the polyelectrolyte potential field domains. All of this quenching can be wiped out at higher concentrations of the quencher, or of inert salts, by the peculiar phenomenon of quenching reversal, where the fluorophor is

Table III. The Effect of Mg^{2+} Ions on Emission Intensity from $(CT)Ru(bpy)_3^{2+*}$ in the Presence of Cu^{2+} [a]

$[Mg^{2+} + Cu^{2+}]_{tot}$	$[Cu^{2+}]_b/[Cu^{2+}]_f$	$(1 + K_{SV}[Cu^{2+}]_b)^{-1}$ [b]	$[Ru(II)]_b/[Ru(II)]_f$ [c]	I/I_0 Calcd	I/I_0 Exptl
2.54×10^{-4}	1.906	0.184	6.52010.29	0.28	
3.54×10^{-4}	0.974	0.230	3.33	0.41	0.39
4.54×10^{-4}	0.654	0.272	2.24	0.50	0.47
5.54×10^{-4}	0.494	0.309	1.70	0.56	0.56
6.54×10^{-4}	0.396	0.342	1.35	0.62	0.61
8.54×10^{-4}	0.263	0.414	0.90	0.72	0.70
1.34×10^{-3}	0.168	0.507	0.57	0.81	0.82

[a] 0.01% PVS, $[P]_{eff}/2 = 1.5 \times 10^{-4}$, 1.54×10^{-4} M $CuSO_4$, 2.05×10^{-5} $Ru(bpy)_3^{2+}$ assuming $K_3 = 0.75$, with varying concentration of $MgSO_4$. [b] $K_{SV} = 4.4 \times 10^4$ from Table I. [c] $K_1/K_2 = 3.42$ from Table II was used to calculate $[Ru(II)]_b/[Ru(II)]_f$ from $[Cu^{2+}]_b/[Cu^{2+}]_f$.

displaced out of the polymer by the other counterion. Both these effects, the enhanced quenching and its reversal, may find important applications in solar energy conversion systems.

Two goals of utmost importance in this context might be achieved by the use of polyelectrolytes:

(a) As is shown in this communication, the rate of quenching of the fluorophor of interest can be greatly enhanced. Although the exact mode of the quenching reaction was not explored in this study, it is conceivable that redox quenching will occur with the appropriate quencher, as it does in the absence of the polyelectrolyte. We are currently involved in fast laser experiments aimed at elucidating the exact quenching mechanism in the presently discussed specific system.

(b) Inhibition of the back reaction between the reduced quencher and oxidized sensitizer might be achieved. As is shown above the monovalent cations are bound much more loosely to the potential field of the polyion than are the divalent cations. It is possible therefore that the reduced quencher (e.g., Cu^+) could be more easily displaced from the potential field than the oxidized sensitizer (say $Ru(bpy)_3{}^{3+}$) and thus their back reaction would be inhibited. Once both these effects are achieved in a single system the efficiency of energy conversion is certain to increase.

The implications of the type of behavior described above as a model for various biological systems are also obvious. In fact, the physical property that exhibits such a behavior does not necessarily have to be light emission. Any physical property that depends exclusively on the mutual presence of the two entities in close proximity is expected to show similar behavior.

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Electrochemical and Spectral Investigations of Ruthenium(II) Complexes of 1,8-Naphthyridine and Its 2-Methyl and 2,7-Dimethyl Derivatives

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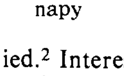
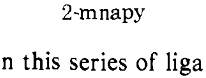
Abstract: Complexes of ruthenium(II) having empirical formulas of $[Ru(napy)_4](PF_6)_2$, $[Ru(2\text{-}mnapy)_4](PF_6)_2$, and $[Ru(2,7\text{-}dmnapy)_3](PF_6)_2$ were prepared and characterized by electrochemical methods, UV-visible, and ^1H NMR spectroscopy. Solutions of the complexes are intensely colored and exhibit visible absorptions near 450 nm characteristic of metal to ligand charge transfer transitions. Ruthenium(II) in the tris 2,7-dmnapy complex is stabilized appreciably by π-back-bonding as evidence by the reversible electrode potential, Ru(III)/Ru(II), of 1.37 V vs. SSCE while in contrast the tetrakis napy and 2-mnapy compounds display less anodic potentials of 1.05 and 1.08 V. The lability of the napy and 2-mnapy complexes to substitution is manifested in the more anodic voltammetric waves which appear with time upon dissolution in acetonitrile. The ^1H NMR spectrum as well as the infrared spectrum of the recovered solvolysis product give strong evidence for the presence of coordinated acetonitrile.

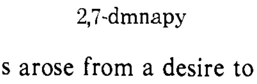
Metal complexes with 1,8-naphthyridine (napy), 2-methyl-1,8-naphthyridine (2-mnapy), and 2,7-dimethyl-1,8-naphthyridine (2,7-dmnapy) have been extensively studied.[2] Interest in this series of ligands arose from a desire to study the unusual manifestations caused by the formation of a four-membered chelate ring when the two nitrogen sites bind to a central metal. The salient result was the characterization of complexes possessing abnormally high coordination numbers,[2a,3] which are favored as a result of the small "bite" of 2.2 Å for the ligands.[4]



napy



2-mnapy



2,7-dmnapy

Although the 1,8-naphthyridines, 2,2′-bipyridine (bipy), and 1,10-phenanthroline (phen) are all heterocyclic amines, the chemistry of the naphthyridine complexes of iron(II)[2a,7,8] differs significantly from $Fe(phen)_3{}^{2+}$ and $Fe(bipy)_3{}^{2+}$. Among the important contrasts are the stoichiometry, magnetic behavior, and the absence of a charge transfer band for the napy complexes. While no rigorous solvolysis study of $Fe(napy)_4{}^{2+}$ has been reported, the Mössbauer and UV-visible spectral data[2a,9] have been suggestive of dissociation of the chelate in acetonitrile to a monodentate form with the vacated site thus occupied by a solvent molecule, e.g., $[Fe(napy)_4(CH_3CN)_4]^{2+}$.[9] In variance to this behavior, the $Fe(bpy)_3{}^{2+}$