

Luminescence quenching of $\text{Ru}(\text{phen})_3^{2+}$ by some polymer–cobalt(III) complexes – Effect of micelles and DNA

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Abstract. Studies on the luminescence quenching of $\text{Ru}(\text{phen})_3^{2+}$ (phen = 1,10-phenanthroline) by the polymer–cobalt(III) complex ions, $\text{cis-}[\text{Co}(\text{phen})_2(\text{BPEI})\text{Cl}]^{2+}$ and $\text{cis-}[\text{Co}(\text{bpy})_2(\text{BPEI})\text{Cl}]^{2+}$ (bpy = 2,2'-bipyridine, BPEI = branched polyethyleneimine) in DNA as well as in various micellar media by steady-state emission spectroscopic technique have been reported. The quenching rate constants were arrived through Stern–Volmer equation. The results have been analysed based on hydrophobic as well as electrostatic binding between polymer–cobalt(III) complexes and DNA/micelles.

Keywords. Luminescence quenching; $\text{Ru}(\text{phen})_3\text{Cl}_2$; polymer–cobalt(III) complexes; DNA; micelles.

1. Introduction

The photochemistry and photophysics of molecules bound to micelles is an area of steadily increasing importance.^{1–3} This interest arises in part from the utilization of these systems in solar energy conversion schemes. Recently there are many reports on the photochemical electron transfer between such bound molecules.^{4–6} These systems could provide one route to produce long-lived charge separation and, ultimately, artificial photosynthesis.

Luminescent transition-metal complexes such as $\text{Ru}^{\text{II}}(\text{L})_3^{2+}$ (L = 1,10-phenanthroline or its substituted derivatives) have been utilized as photosensitizers in such areas as solar energy conversion,⁷ electron-transfer studies,^{8,9} chemi- and electroluminescent systems,^{10,11} binding dynamics of heterogeneous media¹² and probes of macromolecular structure.¹³ These complexes are the most frequently used probes in the above applications due to strong visible absorption, high photochemical stability, efficient luminescence, and relatively long-lived metal to ligand charge (MLCT) excited states.¹⁴

Experiments in many laboratories have focused on measurements of electron transfer rates between metal centres over long distances in proteins or protein pairs as a function of distance, driving force, and the intervening medium.¹⁵ In these studies the notion of

charge transfer in nucleic acids has been postulated¹⁶ and DNA has been examined as a medium for electron transfer reactions.¹⁷

Barton and co-workers have reported some accelerated electron-transfer between metal complexes mediated by DNA.¹⁸ This report concerns with the DNA-mediated long range electron transfer from photoexcited 1,10-phenanthroline complexes of ruthenium to isostructural complexes of cobalt(III), rhodium(III), and chromium(III) bound along the helical strand of DNA (The main thrust behind these studies was to understand the electron transfer processes in the excited state and as a probe of fundamental aspects of electron transfer process).

Here we report the photosensitization reactions of $\text{Ru}(\text{phen})_3^{2+}$ with two polymer–cobalt(III) complexes (figure 1) in DNA as well as in various microheterogeneous environments such as anionic sodium dodecyl sulphate (SDS), cationic cetyltrimethylammonium bromide (CTAB) and nonionic Triton X-100 (TX-100) micelles.

2. Experimental

2.1 Materials and methods

The polymer–cobalt(III) complexes, $\text{cis-}[\text{Co}(\text{phen})_2(\text{BPEI})\text{Cl}]^{2+}$ and $\text{cis-}[\text{Co}(\text{bpy})_2(\text{BPEI})\text{Cl}]^{2+}$ (phen = 1,10-phenanthroline, bpy = 2,2'-bipyridine, BPEI = branched polyethyleneimine) were prepared as

*For correspondence

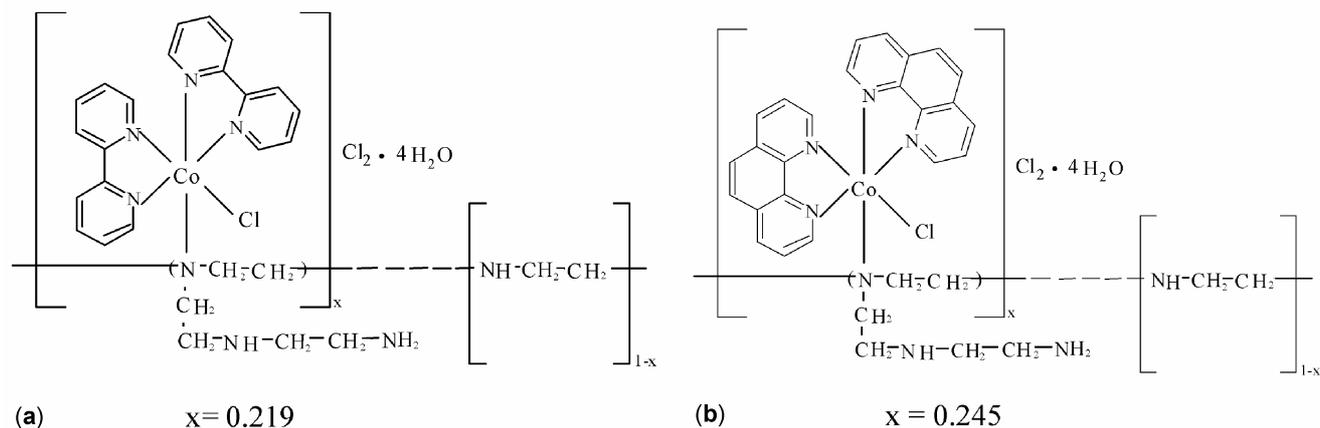


Figure 1. Structure of *cis*-[Co(bpy)₂(BPEI)Cl]Cl₂·4H₂O (a), *cis*-[Co(phen)₂(BPEI)Cl]Cl₂·4H₂O (b).

described.^{19,20} Ru(phen)₃Cl₂ and Triton X-100 were purchased from Sigma-Aldrich, Germany. SDS and CTAB were obtained from Merck and used as received. Calf thymus DNA was obtained from Sigma, Germany. The DNA concentration per nucleotide was determined by electronic absorption spectroscopy using the known molar extinction coefficient value of 6600 M⁻¹ cm⁻¹ at 260 nm.²¹

Emission intensity measurements were made on a JASCO FP 770 spectrofluorimeter. Lifetime measurements were carried out on a nitrogen laser system described elsewhere.²² Deoxygenation was accomplished by bubbling with solvent-saturated N₂,²³ and all measurements were made at room temperature (~30°C). Ruthenium complex solutions employed were 2 μM in concentration and calf thymus DNA was added (in the ratio of 40 : 1 of nucleotide to ruthenium) and the solutions were allowed to incubate 15 min before enhanced spectra were recorded. Fluorescence quenching studies of DNA bound Ru(phen)₃²⁺ were carried out in buffer solutions (50 mM NaCl–5 mM Tris-HCl, pH 7.5) and all other titrations were carried out in 0.1 M of various micellar solutions (SDS, CTAB, TX-100) in 0.1 M H₂SO₄ and the concentration of Ru(phen)₃²⁺ and polymer-cobalt(III) complexes used were 0.2 × 10⁻⁴ M and 0–0.5 × 10⁻³ M respectively. Excitation was carried out in the visible band of the Ru(phen)₃²⁺ complex at wavelengths where absorption by the quencher was minimized. Emission was monitored at wavelengths where the polymer-cobalt(III) complexes do not show appreciable absorption.

For titrations with sonicated calf thymus DNA, concentrated stock solutions of metal complexes

were added to DNA solution, followed by extensive shaking. When micelles were used, samples were prepared by adding concentrated solutions of surfactant to dilute metal complexes to avoid precipitation. The surfactants were used at sufficiently higher concentrations than their respective cmc (critical micelle concentration) values as reported.²⁴

Stern–Volmer plots were used to extract quenching rate constants (k_q) according to the equation,

$$I_0/I = 1 + K_{SV} [Q],$$

$$k_q = K_{SV}/\tau,$$

where I_0 = emission intensity in the absence of quencher (Q), I = emission intensity at quencher concentration $[Q]$, K_{SV} = Stern–Volmer constant which is equal to the product of k_q , and τ , the emission life time of the sensitizer in the absence of quencher.

The emission intensity quenching rate constants (k_q) were calculated from Stern–Volmer constants (K_{SV}), which were in turn taken from the slopes of the Stern–Volmer plots of (I_0/I) versus $[Q]$. The two types of quenching rate constants k_q^i and k_q^s in DNA media were calculated separately using the corresponding lifetime values of surface bound and intercalative Ru(phen)₃²⁺ available from the literature¹³ and the K_{SV} value of this work, which is corresponding to the total quenching in DNA. The other k_q values in micellar media were calculated using the lifetime values which were found out by the methods described elsewhere in this work (table 1).

Table 1. Electron-transfer quenching rate constants (M⁻¹s⁻¹) for Ru(phen)₃²⁺ polymer–cobalt(III) complexes *cis*-[Co(bpy)₂(BPEI)Cl]Cl₂·4H₂O (A) and *cis*-[Co(phen)₂(BPEI)Cl]Cl₂·4H₂O (B) in the presence of DNA and various micellar media.

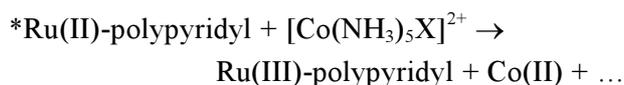
Sensitizer	Quencher	DNA			Neat acid <i>k_q</i>	SDS <i>k_q</i>	CTAB <i>k_q</i>	TX-100 <i>k_q</i>
		<i>k_qⁱ</i>	<i>k_q^s</i>	<i>k_q^f</i>				
Ru(phen) ₃ ²⁺	A	7.57 × 10 ¹⁰	2.09 × 10 ¹⁰	11.12 × 10 ¹⁰	7.28 × 10 ⁸	3.44 × 10 ⁸	5.25 × 10 ⁸	4.79 × 10 ⁸
	B	5.40 × 10 ¹⁰	1.49 × 10 ¹⁰	10.65 × 10 ¹⁰	5.61 × 10 ⁸	2.58 × 10 ⁸	4.38 × 10 ⁸	4.22 × 10 ⁸

The quenching rate constants *k_q^s*, *k_qⁱ* and *k_q^f* are for the surface bound and intercalated Ru(phen)₃²⁺ on DNA, and free Ru(phen)₃²⁺ in buffer solution (5 mM Tris + 50 mM NaCl, pH 7.5), respectively. Lifetimes of DNA bound Ru(phen)₃²⁺ for intercalative, surface bound modes and free Ru(phen)₃²⁺ in buffer are 733, 2645 and 525 ns respectively [13]. Lifetimes of Ru(phen)₃²⁺ in neat acid, SDS, CTAB and TX-100 respectively are 0.905, 1.77, 0.996, 0.984 μs (this work)

3. Results and discussion

3.1 Quenching mechanism

Grafney and Adamson,²⁵ who first reported the quenching of *Ru(II)-polypyridyl complex by some [Co(NH₃)₅X]²⁺ complexes, proposed an electron transfer mechanism as shown below:



Navon and Sutin and other workers have also subsequently shown that the quenching of Ru(II)-polypyridyl complexes by several cobalt(III)-amine complexes occurs by electron transfer^{26,27}. Now it is generally accepted that the electron transfer mechanism is responsible for such quenching involving Ru(phen)₃²⁺ as sensitizer and cobalt(III)-amine complexes as quenchers. So by analogy, it is reasonable to assume that in the present work also CT *Ru(phen)₃²⁺ plays as the electron donor to the polymer–cobalt(III)-amine complexes (i.e. electron transfer quenching).

3.2 Quenching in the presence of DNA

The DNA double helix, containing a π-stacked array of base pairs in its core, represents a unique and efficient medium for long-range electron transport.²⁸ Changes in the emission properties of the Ru(phen)₃²⁺ bound to DNA have been reported earlier.^{29–31} The increase in emission intensities for Ru(phen)₃²⁺ upon binding to DNA is due largely to the change in the environment of the metal complex. Ru(phen)₃²⁺ appears to bind to double-stranded DNA primarily through two distinct modes: (i) intercalation, and (ii) surface or groove binding. The former type of binding is

sensitive to ligand characteristics such as ligand planarity, the extent of aromaticity for stacking interactions and the depth the ligands penetrate into the double helix. On the other hand, groove binding is more sensitive to the charge of the metal ion, ligand hydrophobicity and size of the complex ion.²⁹

The polymer–cobalt(III) complex, *cis*-[Co(phen)₂(BPEI)Cl]²⁺ (B) can potentially bind to DNA by intercalation and electrostatic and/or by van der Waals interactions.²⁰ But the polymer–cobalt(III) complex, *cis*-[Co(bpy)₂(BPEI)Cl]²⁺ (A) which is expected to be nonplanar due to the interactions between 6 and 6' hydrogens of bpy and possesses a small π-system than phenanthroline, mostly electrostatic and/or van der Waals interactions are possible between this complex and DNA.¹⁹

Figure 2a shows the linear Stern–Volmer plots obtained for the emission quenching of DNA bound Ru(phen)₃²⁺ by polymer–cobalt(III) complexes A and B indicating both these polymer–cobalt(III) complexes can quench the emission. In a report, Purrugganan and co-workers,¹⁸ have observed that the electron transfer rate constant, *k_q^s*, from surface bound Ru(phen)₃²⁺ larger than *k_qⁱ*, the rate constant for electron transfer from the intercalative bound species. In our present study of the quenching of the excited state of Ru(phen)₃²⁺ by both the polymer–cobalt(III) complexes A and B in DNA, we have observed that when Ru(phen)₃²⁺ is intercalatively bound, the electron transfer rate constants, *k_qⁱ*, are higher than the electron transfer rate constants, *k_q^s*, for surface bound complex. Because the polymer–cobalt(III) complexes are tightly bound to DNA due to the presence of multiple binding sites in a single molecule and also the surface bound Ru(II) complex is tightly bound electrostatically. But in the case of intercalative Ru(II) complex has enough mobility to

interact with the polymer-cobalt(III) complexes. Between polymer-cobalt(III) complexes A and B, both the electron transfer rate constants for complex A are always higher than that of the corresponding values for complex B (table 1).

3.3 Quenching in the presence of SDS

SDS forms an anionic micelle with $\text{cmc} = 8.1 \text{ mM}$.²⁴ Many studies of electron transfer reactions in SDS have utilized $\text{Ru}(\text{phen})_3^{2+}$ or $\text{Ru}(\text{bpy})_3^{2+}$ as a photoexcited donor bound to SDS micelles.^{32–36} Several groups have shown that cationic complexes RuL_3^{2+} containing hydrophobic ligands, such as phen or bpy and $\text{Co}(\text{phen})_3^{2+}$ bind to micelles in the Stern layer.³⁷ This mode of interaction is similar to intercalation in DNA that maximizes electrostatic interactions with the charged head groups and nestles the hydrophobic portions of the molecules in the organic portion of the supramolecular structure. Meisel *et al*³⁸ have observed that the maxima in the emission spectrum of $\text{Ru}(\text{phen})_3^{2+}$ in SDS micellar solution was shifted about 20 nm from that in water. In our present study the emission spectrum of $\text{Ru}(\text{phen})_3^{2+}$ in SDS micellar medium is shifted to 18 nm from that in neat acid medium. This may be due to the strong association of Ru(II) complex with SDS.

Figure 2b indicates the linear Stern-Volmer quenching plots of $\text{Ru}(\text{phen})_3^{2+}$ by both the polymer-cobalt(III) complexes A and B in SDS which reveal that both the complexes quench $\text{Ru}(\text{phen})_3^{2+}$. Branched polyethyleneimine is a cationic polymer with the highest positive charge density when fully protonated and it

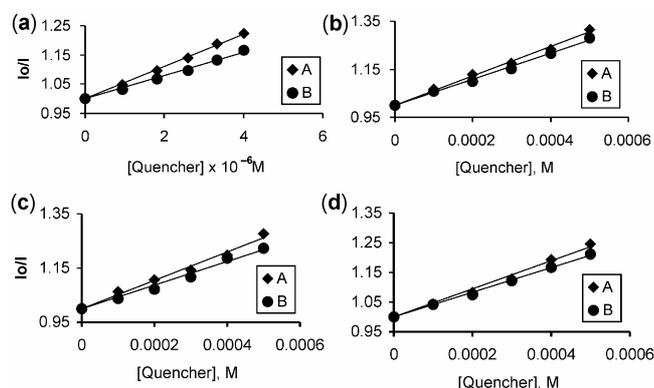


Figure 2. Stern–Volmer plots for the quenching of $\text{Ru}(\text{phen})_3^{2+}$ by polymer-cobalt(III) complexes *cis*- $[\text{Co}(\text{bpy})_2(\text{BPEI})\text{Cl}]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (A) and *cis*- $[\text{Co}(\text{phen})_2(\text{BPEI})\text{Cl}]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (B) (a) in DNA media (b) in SDS media (c) in CTAB media (d) in TX-100 media.

consists of primary, secondary and tertiary amines. Meszaros *et al* have reported that SDS-polycation complexes can form as a result of ionic interactions between cationic groups of the polycation and negatively charged groups of SDS.^{39,40} Li *et al*⁴¹ have also reported that the binding between SDS and BPEI is thought to occur mainly through electrostatic interactions among the participating species. In our polymer-cobalt(III) complexes also, strong electrostatic interactions of protonated amine groups in the polyethyleneimine with SDS are possible. Therefore only less number of complexes could be available in solution for electron transfer reaction. Hence the rate constant for the both the polymer-cobalt(III) complexes in SDS media are expected to be lower than in neat aqueous acid media and this has been observed experimentally (table 1).

3.4 Quenching in the presence of CTAB

CTAB has a cmc of 0.98 mM.²⁴ Previous luminescence studies of Ru(II)-polypyridyl complexes in CTAB have focused on its interactions with non-polar aromatic molecules,⁴² rather than with metal complexes.⁴³ Several Ru(II) probes exhibit binding with CTAB. Unlike the anionic SDS, CTAB micelles have an electrostatic repulsion to cationic Ru(II) probes and also with BPEI of cobalt complexes. Synder *et al*⁴⁰ have shown that there is no evidence for binding of $\text{Ru}(\text{phen})_3^{2+}$ with CTAB. Therefore, interaction of CTAB micelles with these complexes must arise from the hydrophobic effects of the photosensitizer ligands in the alkyl core of the micelle.

Figure 2c indicates the linear Stern-Volmer quenching plots of $\text{Ru}(\text{phen})_3^{2+}$ by the polymer-cobalt(III) complexes A and B in CTAB micelles. As seen from table 1, in comparison with acidic aqueous media, the quenching rate constants for both polymer-cobalt(III) complexes are higher in SDS media but lower in CTAB media. This is because, the effect of electrostatic binding between SDS and $\text{Ru}(\text{phen})_3^{2+}$ is absent in CTAB media and so $\text{Ru}(\text{phen})_3^{2+}$ can move freely in CTAB media compared to SDS media which is responsible for higher quenching efficiency of the $\text{Ru}(\text{phen})_3^{2+}$ complex in CTAB media. Also, the polymer-cobalt(III) complexes contain large number of methyl groups which can show higher hydrophobic interactions with CTAB than with $\text{Ru}(\text{phen})_3^{2+}$. This hydrophobic binding with CTAB micelle can some extent restrict the mobility of $\text{Ru}(\text{phen})_3^{2+}$ in CTAB medium compared to in acidic aqueous medium.

Therefore it has been experimentally observed that the quenching rate constants in CTAB media are lower than those of the corresponding values in acidic aqueous media but higher in SDS media.

3.5 Quenching in the presence of triton X-100

Triton X-100 (TX-10) is a polyether nonionic micelle-forming surfactant with $\text{cmc} = 0.32 \text{ mM}$.²⁴ In binding to nonionic (e.g. Triton) micelles, nonelectrostatic interactions are most important. Factors such as increasing the ligand methylation, which increases sensitizers hydrophobicity, will enhance binding. TX-100 binding interactions with Ru(II) probes have been covered previously.⁴⁴ TX-100 micelles consists of two distinct regions. The central micelle core is relatively dry and consists of the phenyl groups and the aliphatic chain. The remainder of the micelle is a relatively wet outer sheath of partially hydrated polar ethoxy units.⁴⁵ Dressick *et al*⁴⁶ have shown that binding of the sensitizer $\text{Ru}(\text{phen})_3^{2+}$ occurs predominantly at the interface of the dry core and the wet ethoxy region of the micelle and shown that $\text{Ru}(\text{phen})_3^{2+}$ does in fact bind weakly to TX-100. Hauenstein *et al*⁴⁷ have also shown that binding of the Ru(II) photosensitizers to TX-102 is similar to that for TX-100. $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$, however, show no change in lifetime even at TX-100 concentration of 100 mM. However, using intensity measurements, they have shown that $\text{Ru}(\text{phen})_3^{2+}$ does in fact bind weakly to TX-100.

Figure 2d shows the Stern-Volmer quenching plots of $\text{Ru}(\text{phen})_3^{2+}$ by the polymer-cobalt(III) complexes in TX-100. The BPEI of polymer-cobalt(III) complexes contain large number of methyl groups which increases the hydrophobicity in the system and therefore the binding between polymer-cobalt(III) complexes and TX-100 may be greater than between $\text{Ru}(\text{phen})_3^{2+}$ and TX-100. As seen from table 1, the corresponding quenching rate constants of polymer-cobalt(III) complexes in TX-100 media are lower than that of in CTAB and neat acid media but higher than that of in SDS medium. This is because, not all the $\text{Ru}(\text{phen})_3^{2+}$ complex molecules can freely move in TX-100 media as these molecules can weakly bind to TX-100 through hydrophobic interaction.

4. Conclusion

We have interpreted the quenching of $\text{Ru}(\text{phen})_3^{2+}$ emission by the polymer-cobalt(III) complexes in

DNA and in various micellar media using the dominance of hydrophobic or electrostatic factors over one another. We have observed that (i) quenching of $\text{Ru}(\text{phen})_3^{2+}$ by the polymer-cobalt(III) complexes occur in all microheterogeneous environments (ii) the quenching rate constants for $\text{cis-}[\text{Co}(\text{phen})_2(\text{BPEI})\text{Cl}]^{2+}$ complex is always lower than that of the corresponding $\text{cis-}[\text{Co}(\text{bpy})_2(\text{BPEI})\text{Cl}]^{2+}$ suggesting that the phenanthroline complex binds strongly with DNA as well as with other micelles due to its higher hydrophobic character. In DNA medium, fluorescence from intercalative $\text{Ru}(\text{phen})_3^{2+}$ is more efficiently quenched by polymer-cobalt(III) complexes than from surface binding $\text{Ru}(\text{phen})_3^{2+}$. The quenching rate constants of polymer-cobalt(III) complexes decreases in the order: Neat acid > CTAB > TX-100 > SDS. In anionic micelles (SDS), the binding of the polymer-cobalt(III) complexes to the micelles to be very tight resulting in low quenching rate constant compared to that in acid, neutral or cationic micelles. In CTAB and TX-100 media the binding between the micelle and the probe molecule is relatively weak, thus a moderate value of quenching rate constants have been observed.

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