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Original Research

Importance of Hydrophobic Interactions on the Luminescence Quenching of Ru(II)-Polypyridyl Complexes with Phenolic Acids and Quercetin in Triton X-100

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Abstract

Photoinduced electron transfer reactions between the excited state Ru(II)-polypyridyl complexes {[Ru(bpy)₃]²⁺ (bpy=2,2'-bipyridine), [Ru(dmbpy)₃]²⁺ (dmbpy = 4,4'-dimethyl-2,2'-bipyridine) and [Ru(dtbp)₃]²⁺ (dtbp = 4,4'-di-ter-butyl-2,2'-bipyridine)} and phenolate ions of polyphenols (gallic acid, quercetin, p-coumaric acid and ferulic acid) has been investigated in Triton X-100 at pH 11 using luminescent quenching technique. The absorption and emission maximum of these complexes are in the range of 449–457 nm and 612–639 nm respectively. The static nature of quenching of these complexes with gallic acid and quercetin are confirmed from the ground state absorption studies. The association constant (K_a) for [Ru(bpy)₃]²⁺, [Ru(dmbpy)₃]²⁺ and [Ru(dtbp)₃]²⁺ complexes with gallic acid and quercetin in Triton X-100 is calculated from the Benesi-Hildebrand plots obtained from absorption spectral data. The observed quenching rate constant (k_q) values are sensitive to the nature of the ligand, medium, the structure of the quenchers and the electron transfer distance between the complex and the quencher. Triton X-100 slightly accelerates the k_q of [Ru(dmbpy)₃]²⁺ and [Ru(dtbp)₃]²⁺ complexes than [Ru(bpy)₃]²⁺ complex to some extent, confirming the predominance of hydrophobic interactions of these complexes in neutral micelle. The reductive quenching of Ru(II)-polypyridyl complexes by phenolate ions has been confirmed from transient absorption spectra. The formation of phenoxy radical as transient is confirmed by its characteristic absorption at 400 nm.

Keywords: Luminescence quenching; Association constant; Stern-Volmer equation; Structural effects; Hydrophobic interaction.

1. Introduction

Polyphenols are a class of phytochemicals found in high concentrations in wine, tea, grapes and a wide variety of other plants and have been associated with prevention of heart disease and cancer. The two main groups of polyphenols are flavonoids (quercetin) and phenolic acids (gallic acid). Phenolic acids are aromatic secondary plant metabolites, widely spread through the plant kingdom. The antioxidant effect of polyphenols can be due to both their radical-scavenging activity and to their metal-chelating properties, of which

the former may dominate. In addition to antioxidant and free-radical scavenger properties, flavonoids also exhibit an inhibitory effect on a number of enzymes and potent anticancer effects [1]. The oxidation potential of a polyphenol provides an estimate of the energy required to donate an electron; the lower the oxidation potential, lesser the energy required to donate an electron, hence it undergoes oxidation easily. The mechanism of oxidation of polyphenols and their stability in solution depend on pH [2]. The oxidation potential decreases with an increase in the number of phenolic –OH groups present in the polyphenols [3].

Luminescence quenching is an important technique used to obtain adequate information about structure and dynamics of luminescent molecules. It is a process, in which the luminescence intensity of the solute decreases by a variety of molecular interactions such as excited state reactions, molecular rearrangements, energy transfer, ground-state complex formation and collision-quenching [4]. The understanding of electron transfer

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has been a long-standing goal in the active research area due to its important role in many industrial, chemical and biological processes. Recent emphasis in this area has been centered on the dynamical aspect of solvent influences as well as on influences of microenvironment on this process. The photoinduced electron transfer (PET) has been found to be a well-known process in various physical, chemical and biological systems [5]. This electron transfer reactions in surfactant solutions are important for effective energy conversion and storage because surfactant micelles help to achieve the separation of the photoproducts by hydrophilic-hydrophobic interactions of the products with the micellar interface [6].

The ruthenium (II) –polypyridyl complexes ($[\text{Ru}(\text{NN})_3]^{2+}$) have been extensively used as probes in micellar media and the photophysical properties vary enormously with the nature of the surfactant and concentration [7]. Many researchers [8–13] have attempted a systematic investigation of binding, partitioning and photosensitization of these $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in homogeneous and micro-heterogeneous media. The electron transfer reactions in micellar solutions, can be either enhanced or slowed down compared to than that of the reactions in aqueous solutions without added co-solutes [14]. The presence of hydrophobic groups like alkyl and aryl in the ligands of Ru(II) lead to strong binding of $[\text{Ru}(\text{NN})_3]^{2+}$ with micelles through hydrophobic interaction. The strength of binding depends on the combination of electrostatic attractions or repulsions and hydrophobic effects. Bowers et al. [15,16] studied the surface and aggregation behavior of aqueous solutions containing Ru(II) metallosurfactants.

Based on the reviews, the present study concentrates on the PET reactions of tris(4,4'-dialkyl-2,2'-bipyridine) ruthenium (II) –complexes with phenolate ions of the polyphenols in Triton X-100 (non-ionic micelles) at pH 11. The ground state absorption spectral data confirms the static as well as dynamic quenching of these complexes in microheterogeneous media. The association constant (K_a) of the tris(4,4'-dialkyl-2,2'-bipyridine)ruthenium(II)-complexes with gallic acid and quercetin in Triton X-100 is calculated from the Benesi-Hildebrand plots obtained from absorption spectral data. The quenching rate constant, (k_q) is obtained from the Stern-Volmer plot. In order to know the role of Triton X-100 in this PET reaction, the observed results are compared with the results obtained from aqueous medium at pH 11 [12,13]. The transient absorption spectra confirm the electron transfer nature of the excited state $[\text{Ru}(\text{NN})_3]^{2+}$ with polyphenols in Triton X-100 at pH 11, where the quenching process proceeds through the formation of phenolate ions.

2. Experimental Section

2.1. Materials

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, ligands (2,2'-bipyridine (bpy), 4,4'-dimethyl-

2,2'-bipyridine (dmbpy), 4,4'-di-tert-butyl-2,2'-bipyridine (dtbpy)) and the quenchers (phenol, p-coumaric acid, ferulic acid, gallic acid, quercetin) were procured from Sigma-Aldrich. Triton X-100 was purchased from Merck. HPLC grade solvents were used throughout the study for the synthesis of complex as well as for quenching studies. The double-distilled deionized water was used for the quenching studies.

The three $[\text{Ru}(\text{NN})_3]^{2+}$ complexes {where NN = 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), 4,4'-di-t-butyl-2,2'-bipyridine (dtbpy)} were synthesized by reacting $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with the corresponding ligands according to the procedure previously described [17,18]. The chloride salt of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex was treated with sodium tetrafluoroborate to get the BF_4^- salt $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$.

2.2. Equipments

Samples of the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes as well as the polyphenol quenchers in Triton X-100 (0.001 M) at pH 11 were freshly prepared for each measurement. Absorption spectra were measured using SYSTRONICS 2203 double beam spectrophotometer. The emission spectra were recorded using JASCO FP-6300 spectrofluorometer. All the sample solutions used for the emission and excited state lifetime measurements were deaerated for about 30 min by dry nitrogen gas purging keeping the solutions in cold water to ensure that there is no change in volume of the solution. All the spectral measurements were carried out at 293 K. Excited state lifetime and transient absorption measurements were made with laser flash photolysis technique using an Applied Photophysics SP-Quanta Ray GCR- 2(10) Nd:YAG laser as the excitation source. The time dependence of the luminescence decay was observed using a Czerny-Turner monochromator with a stepper motor control and a Hamamatsu R-928 photomultiplier tube. The production of the excited state on exposure to 355 nm was measured by monitoring (pulsed Xenon lamp of 250 W) the absorbance change. Transient spectra were obtained by a point-to-point technique, monitoring the absorbance changes (ΔA) after the flash at intervals of 10 nm over the spectral range 300–700 nm, averaging at least 30 decays at each wavelength.

2.3. Luminescent quenching studies

The photochemical reduction of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with various concentrations of polyphenols has been studied by the luminescence quenching technique. The quenching studies are performed in the presence of NaOH, since most of the phenols do not quench $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in neutral medium [19]. Phenolate ions for the quenching studies were prepared by mixing the corresponding phenol with NaOH and the pH of the solution was maintained at 11 to confirm the existence of quenchers as phenolate ion. The $[\text{Ru}(\text{NN})_3]^{2+}$

complexes taken in the present study are stable at pH 11 and their stability was checked by absorption spectral studies. The sample solutions were purged carefully with dry nitrogen for 30 min. The concentrations of the complexes were maintained at 1.5×10^{-5} M in all the samples and the quencher concentrations were between 2×10^{-5} and 1.4×10^{-3} M. The luminescence measurements were performed at different quencher concentrations at 293 K. Luminescent intensities were recorded for at least six different concentrations for each quencher and the quenching rate constant values were determined from the Stern–Volmer plot using the equation given below:

$$I_0/I = 1 + k_q \tau_0 [Q]$$

where I_0 and I are the emission intensities in the absence and presence of quencher respectively and τ_0 is the emission lifetime of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in the absence of quencher.

3. Results and Discussion

The structure of the ligands and the quenchers used in the present study are shown in Fig. 1. The photophysical properties like absorption and emission spectral data and the excited state lifetime of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in aqueous and Triton X-100 at pH 11 are given in Table 1. The values in the aqueous medium at pH 11 are closely related to the reported values of the complexes in aqueous solution [20]. The photophysical properties of the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes change from homogeneous to microheterogeneous medium.

The $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in the present study show a high energy absorption in the 285 - 295 nm region corresponding to the ligand centered $\pi - \pi^*$ transition and the low energy absorption in the 449 - 457 nm region assigned to the $d\pi - \pi^*$ MLCT transition. The MLCT involves electronic excitation from the metal orbital [$d\pi$ (Ru)] to the ligand centred acceptor

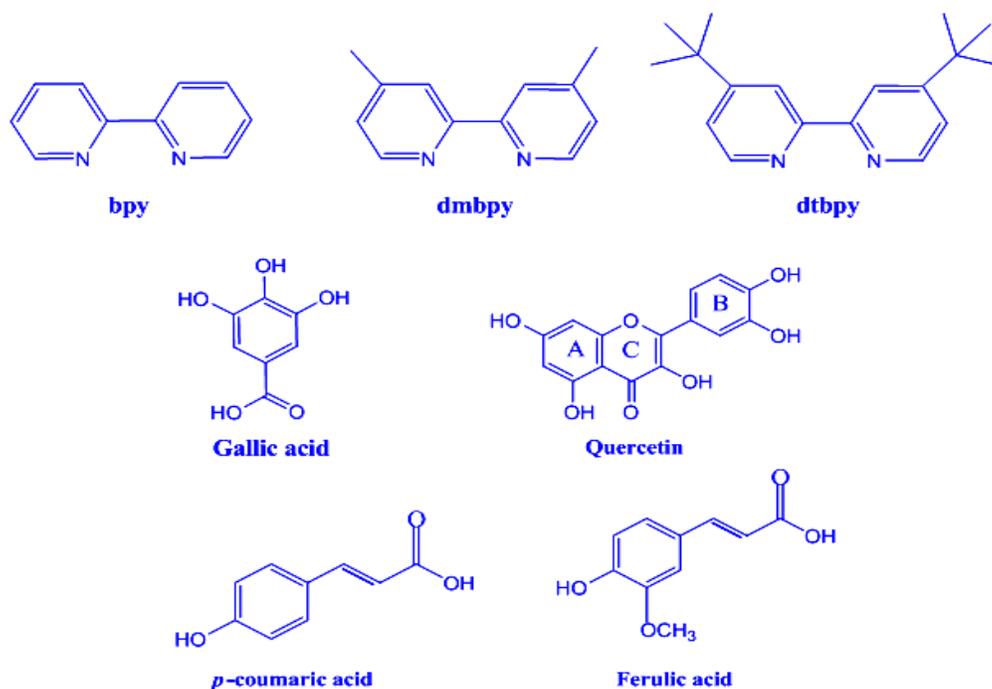


Fig.1. Structure of the ligands and the quenchers

Table 1 Absorption, emission spectral data and excited state lifetime of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in aqueous and Triton X-100, at pH 11.

Complex	Absorption maximum (nm)		Emission maximum (nm)		Excited state lifetime (ns)	
	Aqueous	Triton X-100	Aqueous	Triton X-100	Aqueous	Triton X-100
$[\text{Ru}(\text{bpy})_3]^{2+}$	451 (452)	449	612 (613)	613	614 (620)	600
$[\text{Ru}(\text{dmbpy})_3]^{2+}$	457 (460)	456	625 (630)	625	380 (330)	360
$[\text{Ru}(\text{dtbpy})_3]^{2+}$	457 (456)	456	626	639	510	654

The values in the parenthesis represent the reported absorption maximum, emission maximum and excited state life time of Ru (II) complexes in aqueous medium at pH > 7, ref. [30].

π^* orbitals. $[\text{Ru}(\text{bpy})_3]^{2+}$ shows an MLCT absorption maximum at 451 nm in aqueous medium at pH 11. The absorption maximum of MLCT undergoes bathochromic shift by 6 nm due to the introduction of dmbpy and dtbpy as ligands instead of bpy in aqueous medium. Triton X-100 shows a slight shift in the absorption maxima of the complexes.

All the complexes taken in the present study are highly luminescent and show emission maxima in the range of 612 - 639 nm in aqueous and Triton X-100 at pH 11. The emission maximum of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ in aqueous medium at pH 11 are 612, 625 and 626 nm whereas in Triton X-100, under the present condition are 613, 625 and 639 nm respectively. The emission spectral data show a bathochromic shift of 13 and 14 nm by the introduction of dmbpy and dtbpy as ligands instead of bpy in $\text{Ru}(\text{NN})_3]^{2+}$ complexes in aqueous medium. Triton X-100 does not much affect the emission maximum of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{dmbpy})_3]^{2+}$ while, $[\text{Ru}(\text{dtbpy})_3]^{2+}$ shows a bathochromic shift of 13 nm indicating the importance of hydrophobic interactions due to the presence of tertiary-butyl group in the 4,4'-position of 2,2'-bipyridine with the alkyl chain of the Triton X-100. This bathochromic shift on the emission maximum of $[\text{Ru}(\text{NN})_3]^{2+}$ in microheterogeneous medium clearly shows an interaction between these species and suggests a decrease in the ligand $\pi-\pi^*$ energy gap due to the interaction of the ligand π^* orbitals with the hydrophobic regions of the micelles [21].

The lifetime (Table 1) of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{dmbpy})_3]^{2+}$ are not much affected by Triton X-100 while, $[\text{Ru}(\text{dtbpy})_3]^{2+}$ shows an appreciable lifetime of 654 ns. $[\text{Ru}(\text{bpy})_3]^{2+}$ exhibits negligible spectral shifts and greater solvent exposure due to the non-interacting or weakly interacting $[\text{Ru}(\text{bpy})_3]^{2+}$ with the Triton X-100 monomer or micelles. Also, the +2 charge of the complex favours solvation by water than Triton X-100. These two factors provide a reasonable explanation for the observed lack of interaction between $[\text{Ru}(\text{bpy})_3]^{2+}$ and Triton X-100. Thus the lifetime of $[\text{Ru}(\text{bpy})_3]^{2+}$ is not much affected by the addition of Triton X-100 [22]. These results lead us to conclude that hydrophobic interactions become predominant if hydrophobic alkyl groups are introduced in the 4,4'-position of the ligand 2,2'-bipyridine, thus $[\text{Ru}(\text{dtbpy})_3]^{2+}$ shows a longer lifetime in Triton X-100.

3.1. Absorption spectral studies of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with polyphenols

The absorption spectral studies of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes with the incremental addition of p-coumaric acid and ferulic acid are performed in order to check the formation of ground state complexes in aqueous and Triton X-100 (0.001 M) medium at pH 11. There is no shift in the MLCT absorption maximum of these complexes with the addition of the phenolic derivatives,

thus no detectable ground state complexation or chemical reactions are observed which concludes the dynamic nature of quenching of the complexes in the present experimental conditions (Fig. 2). Similar results have been reported for Ru(II)-polypyridyl complexes with p-methoxy phenol in acetonitrile and aqueous mediums [23].

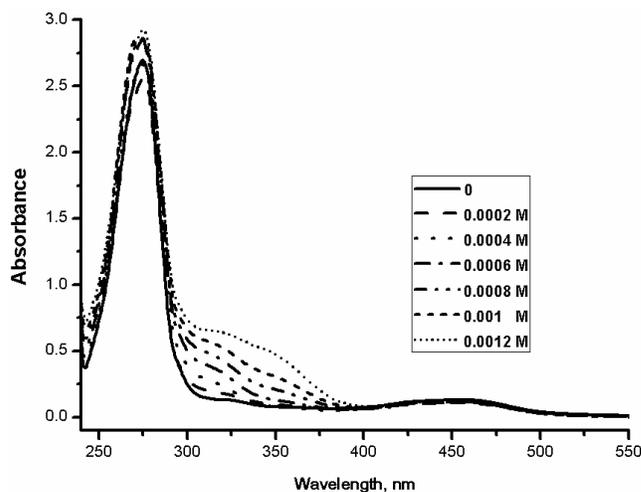


Fig. 2. Absorption spectra of $[\text{Ru}(\text{dtbp}_3)]^{2+}$ complex with incremental addition of ferulic acid (2×10^{-4} – 1.2×10^{-3} M) in Triton X-100 at pH 11

The absorption spectral studies of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with the incremental addition of gallic acid and quercetin shows a slight increase in the MLCT absorption maximum, indicates the formation of ground state complex (Fig. 3). Gallic acid and quercetin have weak absorption at 454 and 426 nm [2]. Gallic acid and quercetin bind with the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in aqueous and Triton X-100 medium, since gallic acid and quercetin have weak absorption close to the region where Ru(II) complex have strong MLCT absorption. The absorption spectra of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with gallic acid and quercetin shows a hypsochromic shift of 2 to 3 nm, due to the formation of ground state complex. The association of gallic acid and quercetin with $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in the ground state may be due to the static nature of quenching. The association constant (K_a) of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with gallic acid and quercetin calculated from the Benesi–Hildebrand plot (Fig.4) using the Benesi–Hildebrand equation [24] for the absorption spectral data in aqueous and Triton X-100 medium at pH 11 is given in Table 2. The K_a obtained for gallic acid and quercetin with $[\text{Ru}(\text{NN})_3]^{2+}$ complexes is in the order of 102–104 M⁻¹.

3.2. Emission studies of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with polyphenols

The change in luminescent intensity for the reductive quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$

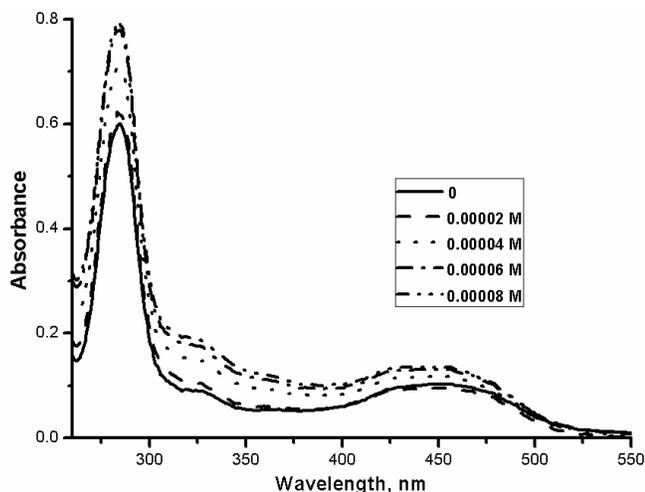


Fig. 3. Absorption spectra of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ complex with incremental addition of gallic acid (2×10^{-5} - 8×10^{-5} M) in Triton X-100 at pH 11

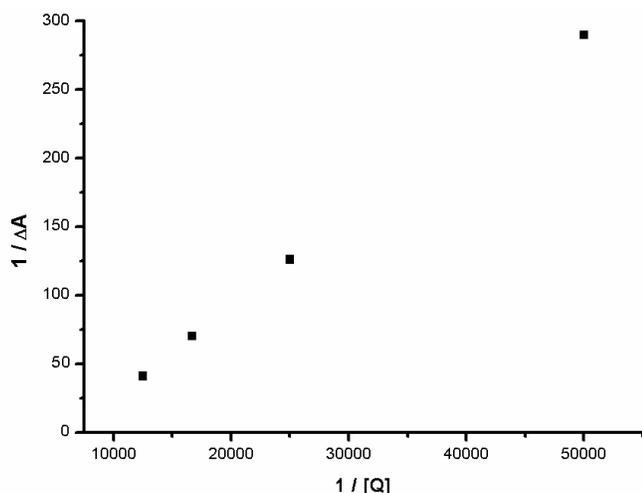


Fig. 4. Benesi-Hildebrand plot on MLCT absorption of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with incremental addition of quercetin in Triton X-100 at pH 11

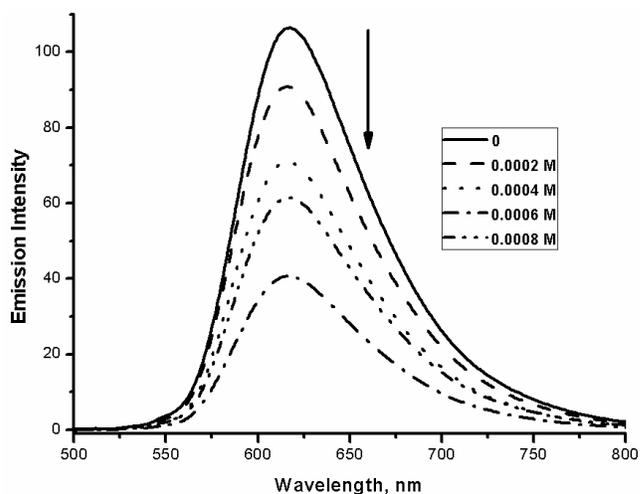


Fig. 5. The change in emission intensity of $*[\text{Ru}(\text{bpy})_3]^{2+}$ complex with different concentrations of *p*-coumaric acid (2×10^{-4} - 8×10^{-4} M) in Triton X-100 at pH 11

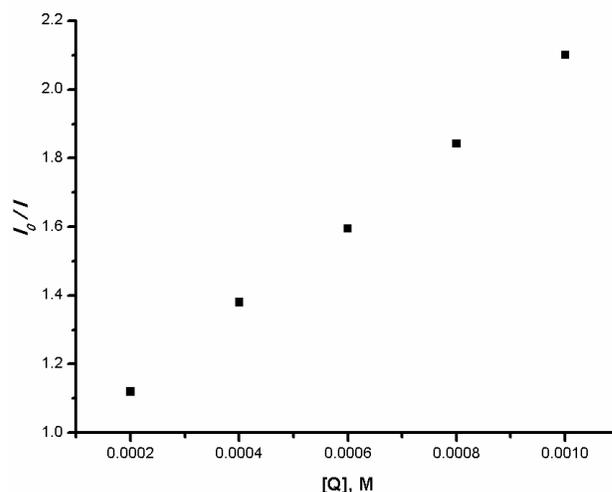


Fig. 6. Stern-Volmer plot for the reductive quenching of $*[\text{Ru}(\text{dtbp})_3]^{2+}$ complex with ferulic acid in Triton X-100 at pH 11

complexes with different concentrations of polyphenols in aqueous and Triton X-100 medium has been studied and is shown in Fig. 5. The Stern-Volmer plots for the emission intensity data (Fig. 6) are linear for these photoredox systems indicating that, dynamic quenching is the predominant process and the contribution from static quenching are negligible in *p*-coumaric acid, ferulic acid and phenol. Linear Stern-Volmer plot is not a conclusive evidence for dynamic quenching [25]. Though the Stern-Volmer plots for the emission intensity data for gallic acid and quercetin are linear, they endure static quenching and this can be confirmed from the absorption spectral studies and the corresponding association constant values. This type of reports has been previously reported for $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}/1,4\text{-dihydroquinone}$ couple in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpz})_3]^{2+}/\text{phenol}$ couple in CH_3CN [26,27]. Thus, the absorption and emission spectral studies on this photoredox systems report static as well as dynamic quenching.

3.3. Luminescence quenching rate constant

The observed k_q in the absence and presence of Triton X-100 are given in Table 2. For all the quenchers used, k_q are not affected appreciably indicating that non-electrostatic interactions between the micelle and the reactants are not important in the case of $[\text{Ru}(\text{bpy})_3]^{2+}$. However, in the case of other two complexes, the k_q increases from $[\text{Ru}(\text{dmbpy})_3]^{2+}$ to $[\text{Ru}(\text{dtbp})_3]^{2+}$ in Triton X-100. Thus in the case of Ru(II) complexes containing alkyl substituted ligands, hydrophobic interactions become important. The binding of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes to neutral micelles such as Triton X-100 involves partitioning of the complex between the hydrophobic areas of the micelle and the aqueous phase. The hydrophobicity is determined by the substituents on the 4,4'-position of the bipyridine ring [28].

Table 2 Association constant, K_a (M^{-1}) calculated from absorption spectral data for gallic acid and quercetin with $[Ru(NN)_3]^{2+}$ complexes in aqueous and Triton X-100, at pH 11

Complex	Aqueous		Triton X 100	
	Gallic acid	Quercetin	Gallic acid	Quercetin
$[Ru(bpy)_3]^{2+}$	2.9×10^3	4.0×10^4	2.5×10^2	2.4×10^3
$[Ru(dmbpy)_3]^{2+}$	8.2×10^3	5.7×10^4	4.7×10^2	5.2×10^3
$[Ru(dtbp)_3]^{2+}$	8.9×10^3	9.0×10^4	6.4×10^2	6.8×10^3

Table 3 Quenching rate constant, k_q ($M^{-1}s^{-1}$) for $[Ru(NN)_3]^{2+}$ with phenolate ions in the aqueous and Triton X-100, at pH 11

Quencher	$[Ru(bpy)_3]^{2+}$		$[Ru(dmbpy)_3]^{2+}$		$[Ru(dtbp)_3]^{2+}$	
	Aqueous	Triton X-100	Aqueous	Triton X-100	Aqueous	Triton X-100
Phenol	4.6×10^8	4.3×10^8	3.1×10^8	5.1×10^8	2.3×10^8	6.0×10^8
<i>p</i> -coumaric acid	5.7×10^8	5.6×10^8	4.1×10^8	6.2×10^8	3.1×10^8	7.4×10^8
Ferulic acid	1.7×10^9	1.7×10^9	1.2×10^9	2.3×10^9	9.4×10^8	3.5×10^9
Quercetin	6.3×10^9	6.4×10^9	4.6×10^9	7.2×10^9	3.5×10^9	7.9×10^9
Gallic acid	8.8×10^9	8.3×10^9	7.1×10^9	9.1×10^9	6.0×10^9	9.6×10^9

Photoluminescence studies have shown that the binding between $[Ru(NN)_3]^{2+}$ and Triton X-100 micelles is probably vander Waals or hydrophobic in nature. Therefore, binding is by competition between water and the micelles for solvation of the complexes [20]. In Triton X-100, the central micelle core is relatively dry and consists of the phenyl groups and the aliphatic chain. The remainder of the micelle is relatively wet outer sheath of partially hydrated polar ethoxy units. Binding of the sensitizers occurs primarily at the interface of the dry core and the wet ethoxy region of the micelle [28]. The hydrophobic nature of the complex increases from $[Ru(bpy)_3]^{2+}$ to $[Ru(dtbp)_3]^{2+}$ owing to the presence of bulky alkyl group in the 4,4'-position of the bpy ligand. Hence, Triton X-100 (Table 3) slightly accelerates the quenching reaction in the case of $[Ru(dmbpy)_3]^{2+}$ and $[Ru(dtbp)_3]^{2+}$. This acceleration in rate may be mainly by promoting the encounter complex formation and partly by suppressing the reverse electron transfer in the successor complex. Such micellar effects on the encounter complex formation result from the concentration of $[Ru(NN)_3]^{2+}$ and ArO^- through hydrophobic forces and from the lengthened lifetime of $[Ru(NN)_3]^{2+}$ in the micellar-phase [28].

For the sake of comparison of the quenching efficiencies of the polyphenols with these complexes, luminescent quenching study of phenol with these complexes is also performed and the results are discussed here. Phenol shows least k_q for all the three complexes in both media. Miedlar and Das reported this type of least k_q value for phenol in the photoredox reactions of $[Ru(bpy)_3]^{2+}$ complex [29]. The k_q data in Table 3 shows that gallic acid acts as the most efficient quencher in this PET reaction. Gallic acid consist of three phenolic-OH groups, in alkaline medium especially above pH 9 the three phenolic-OH

groups get ionized. The pKa values for the three phenolic-OH groups of gallic acid are 8.7, 11.4 and > 13 [30]. Quercetin has two different pharmacophores, the catechol group in ring B and the three hydroxyl groups in rings A and C, of which the catechol moiety is the most reactive one where deprotonation occurs easily [31]. The pKa values of quercetin are 5.87 and 8.48 [32]. The pKa values for the phenolic-OH group in phenol, *p*-coumaric acid and ferulic acid are 10, 9.5 and 9.4 respectively [32,33]. The quenching process is highly sensitive to the pH of the medium. The pKa values of the quenchers taken in the present study are less than that on the pH of the medium (pH 11), hence they undergoes PET reactions with the $[Ru(NN)_3]^{2+}$ complexes in aqueous and Triton X-100 medium at pH 11.

The bond dissociation energy (BDE) for the phenolic-OH group in gallic acid is 75.5 Kcal/mol, the presence of pyrogallol (three adjacent phenolic-OH groups) substitution pattern reduces the BDE in gallic acid [34]. The BDE of gallic acid is less than that of quercetin (77 Kcal/mol), *p*-coumaric acid (84.9 Kcal/mol), ferulic acid (83.5 Kcal/mol) and phenol (90 Kcal/mol) [31]. Based on the BDE, the phenolic -OH group of gallic acid undergoes ionization more easily than quercetin, *p*-coumaric acid, ferulic acid and phenol. Interestingly the k_q increases, when the number of phenolic-OH groups present in the quencher increases. Here gallic acid and quercetin consists of more than one phenolic-OH groups. Gallic acid has three phenolic-OH groups, while quercetin has four phenolic-OH groups (2 phenolic-OH groups in ring B and 2 phenolic-OH groups in ring A) out of these the ring B is the most reactive one [31]. Hence gallic acid acts as the most efficient quencher in this photoredox system due to the presence of pyrogallol moiety. The pyrogallol moiety is more

reactive than catechol moiety [35]. The hydroxyl derivatives of cinnamic acid (p-coumaric acid and ferulic acid) show the least k_q values compared to that of gallic acid and quercetin. The p-coumaric acid has a functional –OH group attached to the ring structure in the para- position to the –CH=CH–COOH group. Because of the aryloxy-radical stabilizing effect of the –CH=CH–COOH linked to the phenyl ring by resonance, it can be electrochemically oxidized [36]. Hence, the availability of phenolate ion is much less in p-coumaric acid and ferulic acid thus reducing the quenching rate constant. The k_q value of ferulic acid is somewhat higher than p-coumaric acid due to the presence of electron-releasing methoxy group in the ortho-position of the phenol and this provides additional stabilization of the ferulate radical compared to the phenoxyl radical of p-coumaric acid [37]. Here, the nature of the substituent present in the ortho- and para-positions of phenols affects the k_q values.

The k_q value not only depends on the substituents present in the quenchers but also depends on the electron transfer distance between the complexes and the quencher. The electron transfer distance is calculated by simply adding the radii of $[\text{Ru}(\text{NN})_3]^{2+}$ and ArO^- . The radii of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes are 7.1, 7.9 and 9.2 Å. The radius of the quenchers are estimated from MM2 molecular model and the radii of gallic acid, quercetin and phenol are 4.1, 5.93 and 3.8 Å respectively whereas, p-coumaric acid and ferulic acid show the same radius (4.8 Å). The sum of the radii of electron donor (phenolate ion) and acceptor ($[\text{Ru}(\text{NN})_3]^{2+}$) gives the electron transfer distance. The electron transfer distance of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes with gallic acid are 11.2, 12 and 13.3 Å, whereas for quercetin are 13.03, 13.83 and 15.13 Å respectively. The electron transfer distance of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes with p-coumaric acid and ferulic acid are same and the values are 11.9, 12.7 and 14 Å respectively. The electron transfer distance between the complexes and the gallic acid is higher than that of phenol but the nature of the substituent and the availability of phenolate ions in gallic acid show greater quenching efficiency. Based on these factors, gallic acid shows higher k_q than quercetin, ferulic acid, p-coumaric acid and phenol in aqueous and Triton X-100 at pH 11.

Further the absorption spectral studies of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with gallic acid and quercetin in both medium, at pH 11 shows ground state complex formation, which confirms the static nature of quenching. The ground-state interactions between phenol and the bipyridyl rings of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes are hydrophobic or π -stacking in nature. To the extent that π - π stacking interactions exist between the ligands of Ru(II)- complexes and the quencher, the binding becomes stronger which play a vital role in mediating PET reactions [38]. The K_a calculated for gallic acid and quercetin from the absorption spectral data shows that quercetin undergoes strong

binding with the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes than that of gallic acid. Due to this ground state interaction of gallic acid and quercetin with $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in both media at pH 11, they act as efficient quenchers compared to p-coumaric acid, ferulic acid and phenol.

For all the polyphenols in Triton X-100, there is an increase in the k_q from $[\text{Ru}(\text{bpy})_3]^{2+}$ to $[\text{Ru}(\text{dtbpy})_3]^{2+}$ is reported, this is due to the presence of hydrophobic alkyl groups in the 4,4'-position of the ligand. The k_q value of $[\text{Ru}(\text{bpy})_3]^{2+}$ with gallic acid, quercetin, ferulic acid, p-coumaric acid and phenol in Triton X-100 at pH 11 are 8.3×10^9 , 6.4×10^9 , 1.7×10^9 , 5.6×10^8 and $4.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$; whereas for $[\text{Ru}(\text{dtbpy})_3]^{2+}$ are 9.6×10^9 , 7.9×10^9 , 3.5×10^9 , 7.4×10^8 and $6.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ respectively. The hydrophobic interaction of $[\text{Ru}(\text{dtbpy})_3]^{2+}$ in Triton X-100 is higher than that of $[\text{Ru}(\text{bpy})_3]^{2+}$, hence the k_q of former is slightly higher than that of the latter.

Triton X-100 slightly enhances the k_q of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes compared to that in aqueous medium due to its predominant hydrophobic interactions. The k_q values of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes with gallic acid, quercetin, ferulic acid, p-coumaric acid and phenol in Triton X-100 at pH 11 are 9.1×10^9 , 7.2×10^9 , 2.3×10^9 , 6.2×10^8 and $5.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, 9.6×10^9 , 7.9×10^9 , 3.5×10^9 , 7.4×10^8 and $6.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. These k_q values are slightly higher than that of the k_q values of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes in aqueous medium at pH 11. This confirms the hydrophobic interactions of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes in Triton X-100. Based on these results it is concluded that the k_q is highly sensitive to the nature of the ligand and medium, nature of the substituents present in the quenchers and the electron transfer distance between the complexes and the quenchers.

3.4. Transient absorption spectral studies

The reductive nature of these photoredox reactions is confirmed from the transient absorption spectra recorded by laser flash photolysis technique. The transient absorption spectrum of $[\text{Ru}(\text{dtbpy})_3]^{2+}$ in Triton X-100 (pH 11) at various time delays is shown in Fig. 7. The spectrum at each time delay consist of bleach around 450 and 600 - 700 nm and a positive absorption with maximum centered at 370 nm. The band at 400 nm and 510 nm in the transient absorption spectrum (Fig. 8) of the complex with ferulic acid (0.0008 M) confirms the formation of ferulate radical and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ as transient species. The transient absorption spectrum confirms the electron transfer of this complex in ferulic acid. Thus, the present study confirms the reductive quenching of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with phenolate ions in Triton X-100 at pH 11.

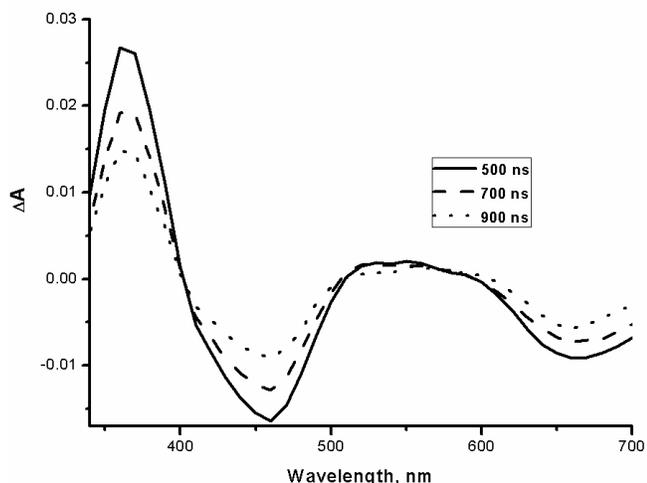


Fig. 7. Transient absorption spectrum recorded after excitation of $[\text{Ru}(\text{dtbpy})_3]^{2+}$ in Triton X-100 (pH 11) at different time intervals

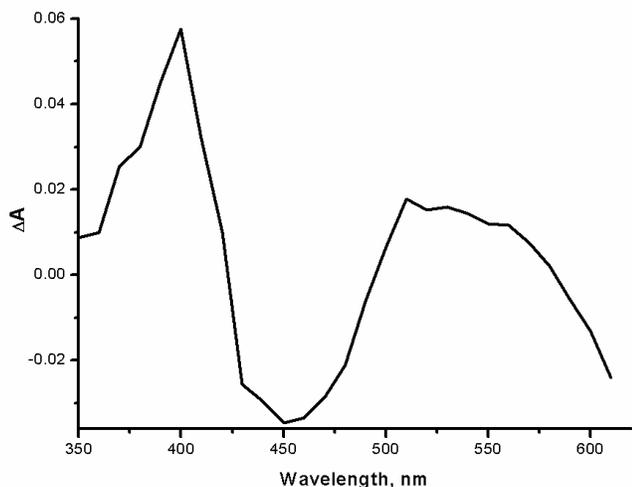


Fig. 8. Transient absorption spectra of $[\text{Ru}(\text{dtbpy})_3]^{2+}$ in the presence of 0.0008 M ferulic acid in Triton X-100 recorded at 5 μs of 355 nm laser flash photolysis

Conclusion

The present study clearly establishes the effect of non-ionic micelle on the quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes with polyphenols at pH 11. Absorption spectral data confirms the dynamic and static nature of quenching of these complexes with polyphenols in Triton X-100. The k_q values are highly sensitive to the nature of the ligand, medium, the structure of the quenchers and the electron transfer distance between the complexes and the quenchers. Here gallic acid behaves as an efficient quencher due to the availability of more phenolate ions, low BDE and less electron transfer distance compared to other polyphenols taken in the present study. The detection of phenoxyl radical and $[\text{Ru}(\text{NN})_3]^+$ as transient in the transient absorption spectra confirms the electron transfer nature of the reaction. The change in medium from homogeneous to microheterogeneous strongly affects the k_q due to the presence of the hydrophobic

interactions of the complexes with neutral micelle. Triton X-100 slightly accelerates the k_q of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ than that of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex to some extent, confirming the predominance of hydrophobic interactions of these complexes in neutral micelle. This study confirms the role of hydrophobic interactions of micelles on the photophysics and photochemistry of Ru(II) complexes in determining the binding of metal complexes with biological molecules and also the substituent effect on the PET reaction of these complexes with polyphenols.

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