



Effect of Solvent on the Luminescence Quenching of Ruthenium(II)-Polypyridyl Complexes with Polyphenols

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ABSTRACT

The quenching of ruthenium(II)-polypyridyl complexes {[Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine), [Ru(dmbpy)₃]²⁺ (dmbpy = 4,4'-dimethyl-2,2'-bipyridine) and [Ru(dtbpy)₃]²⁺ (dtbpy = 4,4'-di-ter-butyl-2,2'-bipyridine)} with polyphenols (gallic acid, quercetin,) have been studied in 50 % aqueous acetonitrile and aqueous medium at pH 11 by means of luminescence quenching technique. The absorption and emission maximum of these complexes in 50 % aqueous acetonitrile and aqueous medium are in the range of 450-458 nm and 612-626 nm respectively. The excited state lifetime of [Ru(bpy)₃]²⁺, [Ru(dmbpy)₃]²⁺ and [Ru(dtbpy)₃]²⁺ complexes in 50 % aqueous acetonitrile are 740, 580 and 697 ns, whereas in aqueous medium are 614, 380 and 510 ns respectively. The excited state lifetime of these complexes in 50 % aqueous acetonitrile is longer than that of aqueous medium. The quenching rate constant (*k_q*) of these complexes with gallic acid and quercetin in both media are determined from the Stern-Volmer equation. The observed quenching rate constant values are highly sensitive to the nature of the reaction medium, ligands associated to the complexes and the substituent present in the polyphenols. The reductive quenching of these complexes with polyphenolate ions has been confirmed from the transient absorption spectrum. The formation of phenoxyl radical and [Ru(bpy)₃]⁺ as transient species is confirmed by its characteristic absorption at 400 and 510 nm. Solvent effect seems to play a vital role on the quenching of gallic acid and quercetin with Ru(II) complexes in 50 % aqueous acetonitrile and aqueous medium at pH 11.

Keywords: Ruthenium(II)-polypyridyl complexes; Polyphenols; Stern-Volmer equation; Quenching rate constant; Solvent effect

INTRODUCTION

Phenolic acids (gallic acid) and flavonoids (quercetin) constitute one of the most common and widespread groups of substances in flowering plants, occurring in all vegetative organs, as well as in flowers and fruits. They are considered as secondary metabolites involved in the chemical defense of plants against predators and in plant-plant interferences. Polyphenols have considerable interest in the field of food chemistry, pharmacy and medicine due to a wide range of favorable biological effects including antioxidant properties. The antioxidant property of polyphenols is mainly due to their redox properties. They act as reducing agents (free radical terminators), hydrogen donors, singlet oxygen quenchers and metal chelators [1]. In addition to antioxidant and free-radical scavenger properties, polyphenols have numerous other biological activities, such as antihistamine activity, as well as anti-inflammatory, vasodilatory, and protecting against cardiovascular diseases [2]. Gallic acid is found in almost all plants, plants known for their high gallic acid content include gallnuts, grapes, tea, hops and oak bark. Gallic acid seems to have anti-fungal and anti-viral properties. Gallic acid acts as an antioxidant and helps to protect the cells against oxidative damage and it shows cytotoxicity against cancer cells, without harming healthy cells. Quercetin is a plant-derived flavonoid, specifically a flavonol, used as a nutritional supplement. Quercetin consists of 3 rings and 5 hydroxyl

groups and it may have anti-inflammatory and antioxidant properties. It has been investigated for a wide range of potential health benefits and it reduces the risk of certain cancers. Luminescence quenching is an important technique used to obtain adequate information about the 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 [3]. The conversion of phenol to phenoxyl radical is of interest to chemists because of its involvement in biologically important processes [4]. The one electron oxidation of phenolates to the resulting phenoxyl radical is a key step in the oxidation of phenols. The study of the kinetic and thermodynamic aspects of electron transfer to generate phenoxyl radicals bearing bulky groups in the *ortho*- and *para*- positions may help to understand the different biological roles of phenols. The photochemistry and photophysics of transition metal complexes containing d^6 electronic configuration, particularly Ru(II)-polypyridyl complexes $[\text{Ru}(\text{NN})_3]^{2+}$, have attracted the chemists in the field of solar energy conversion [5], artificial photosynthesis [6], optical sensing [7] and luminescent probes for characterizing microheterogeneous environments, owing to their favorable photophysical properties, excited state reactivity and chemical stability [8]. The excited state properties of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes are largely affected by the introduction of electron-donating and electron-withdrawing groups in the 4,4'-position of 2,2'-bipyridine [9]. Numerous works have been reported on the importance of the substituent, pH, steric and electronic effects on the photoinduced electron transfer (PET) reactions of *ortho*-, *meta*- and *para*-substituted phenolate ions to the excited state Ru(II)-polypyridine complexes in various solvents [10-12]. The present study concentrates on the effect of solvent on the quenching of the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with gallic acid and quercetin in 50 % aqueous acetonitrile and aqueous medium at pH 11. The quenching reactions of polyphenols with the $[\text{Ru}(\text{NN})_3]^{2+}$ complex proceeds through PET reaction in both media and has been studied by luminescent quenching technique. The excited state properties like emission maxima and lifetime of these complexes vary with the solvent. The transient absorption spectra confirm the electron transfer nature of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with polyphenols, where quenching process proceeds through the formation of phenolate ions.

EXPERIMENTAL SECTION

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 (gallic acid, quercetin) were procured from Sigma-Aldrich. 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 [13,14].

Equipment

Absorption spectra were measured using SYSTRONICS 2203 double beam spectrophotometer. Emission spectra were recorded using JASCO FP-6300 spectrofluorometer. 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. 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. All the sample solutions used for 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 298 K.

Luminescent Quenching Studies

The $[\text{Ru}(\text{NN})_3]^{2+}$ complexes as well as the quenchers gallic acid and quercetin in 50 % aqueous acetonitrile and aqueous medium were freshly prepared for each measurement. 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 photochemical reduction of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes to $[\text{Ru}(\text{NN})_3]^+$ with these phenolate ions has been studied by the luminescence quenching technique. The luminescence measurements were performed at different quencher concentration (2×10^{-5} - 1.4×10^{-4} M) and the quenching rate constant (k_q) were determined from Stern-Volmer plots using the equation given below.

$$I_0/I = 1 + k_q \tau_0 [\text{Q}] \quad (1)$$

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.

RESULTS AND DISCUSSION

The structure of the ligands and the quenchers used in the present study is shown in Figure 1. The absorption and emission spectral data, the excited state lifetime (τ) of the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in 50 % aqueous acetonitrile and in aqueous medium, at pH 11 is measured and are collected in Table 1. The absorption maximum of metal to ligand charge transfer (MLCT) transition undergoes bathochromic shift by 8 nm by the introduction of 4,4'-dimethyl and 4,4'-di-*tertiary* butyl group in to the 2,2'-bipyridine ligand in 50 % aqueous acetonitrile, whereas in aqueous medium it shows a shift of 6 nm. The substitution of 4,4'-dimethyl and 4,4'-di-*tertiary* butyl group into the 2,2'-bipyridine lowers π^* level of the ligand and thus shifts the MLCT transition to the longer wavelength region. The emission maxima of the $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes occur in the region 614 - 622 nm and 612 - 626 nm in 50 % aqueous acetonitrile and aqueous medium at pH 11. The emission maximum of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{dmbpy})_3]^{2+}$ show a slight shift of 2-3 nm whereas, $[\text{Ru}(\text{dtbpy})_3]^{2+}$ shows 8 nm shift by changing the solvent from 50 % aqueous acetonitrile to aqueous medium. The change in the polarity of the solvent shifts the emission maximum of the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes to some extent [15]. Here, solvent plays an important role in the emission properties of the complexes. The lifetime of the three complexes in 50 % aqueous acetonitrile and aqueous medium at pH 11 has been measured using laser flash photolysis technique. The substituents present in the 4,4'-position of the 2,2'-bipyridine ligand greatly affect the lifetime of the complexes in both media at pH 11. The excited state lifetime of these complexes in 50 % aqueous acetonitrile is longer than that in aqueous medium. Addition of water to the organic solvents substantially decrease the lifetime of $*[\text{Ru}(\text{NN})_3]^{2+}$ and it has been recognized that non-radiative deactivation of $*[\text{Ru}(\text{NN})_3]^{2+}$ is favourable in protic solvents and this lead to a decrease in the lifetime of the complexes taken in the present study in aqueous medium.

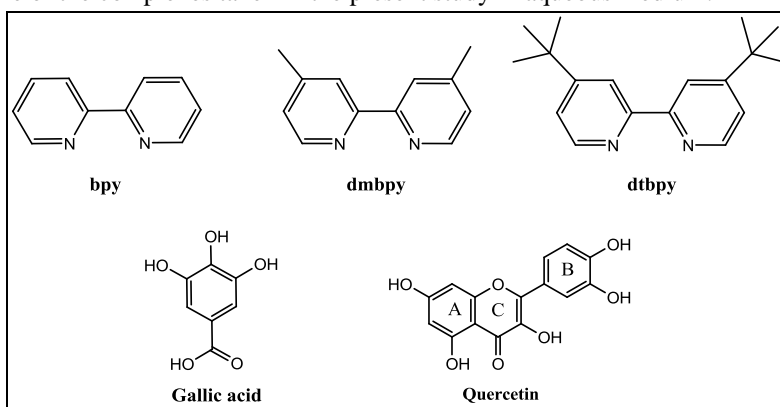


Figure 1: Structure of ligands and the quenchers

Table 1: Absorption, emission spectral data and excited state lifetime (τ) of $[\text{Ru}(\text{NN})_3]^{2+}$ in 50 % aqueous acetonitrile and aqueous medium, at pH 11

Complex	Absorption maximum (nm)		Emission maximum (nm)		Excited state lifetime (ns)	
	50 % aqueous acetonitrile	Aqueous medium	50 % aqueous acetonitrile	Aqueous medium	50 % aqueous acetonitrile	Aqueous medium
$[\text{Ru}(\text{bpy})_3]^{2+}$	450	451	614	612	740	614
$[\text{Ru}(\text{dmbpy})_3]^{2+}$	458	457	622	625	580	380
$[\text{Ru}(\text{dtbpy})_3]^{2+}$	458	457	618	626	697	510

The emission intensities of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes are efficiently quenched in the presence of polyphenols in both the media (Figure 2). The Stern-Volmer plot (Figure 3) from the emission intensity data is linear for all photoredox systems in both media at pH 11.

The experimental bimolecular quenching rate constant (k_q) of $*[\text{Ru}(\text{bpy})_3]^{2+}$, $*[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $*[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes with gallic acid and quercetin in 50 % aqueous acetonitrile and aqueous medium, at pH 11 are shown in Table 2. Gallic acid consists of three phenolic-OH groups and a carboxyl group. Quercetin has two different pharmacophores, the catechol group (ring B) and the benzo- γ -pyrone derivative (ring A and C), of which the catechol moiety is the most reactive one where deprotonation occurs easily [16]. For the sake of comparison of the

quenching efficiencies of the polyphenols with $[\text{Ru}(\text{NN})_3]^{2+}$ complexes, luminescent quenching study of phenol with this complexes is also performed and the results are discussed here. Phenol shows least k_q with $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in both media. Miedlar and Das reported this type of least k_q value for phenol in the photoredox reactions of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex [17]. The k_q data in Table 2 shows that gallic acid acts as the most efficient quencher in this PET reaction. Steric hindrance exerted by the benzo- γ -pyrone derivative at *para*- position of the catechol reduces the quenching efficiency of quercetin when compared to gallic acid. The availability of phenolate ions is more in gallic acid [18], due to the presence of three phenolic-OH groups, acts as the most efficient quencher compared to that of quercetin.

Table 2: The experimental bimolecular quenching rate constant (k_q) of $[\text{Ru}(\text{NN})_3]^{2+}$, complexes with quenchers in 50 % aqueous acetonitrile and aqueous medium, at pH 11

Quencher	Quenching rate constant, k_q ($\text{M}^{-1}\text{s}^{-1}$)					
	$[\text{Ru}(\text{bpy})_3]^{2+}$		$[\text{Ru}(\text{dmbpy})_3]^{2+}$		$[\text{Ru}(\text{dtbpy})_3]^{2+}$	
	50 % aqueous acetonitrile	Aqueous medium	50 % aqueous acetonitrile	Aqueous medium	50 % aqueous acetonitrile	Aqueous medium
Phenol	7.0×10^8	4.6×10^8	5.3×10^8	3.1×10^8	3.0×10^8	2.3×10^8
Quercetin	8.5×10^9	6.3×10^9	6.8×10^9	4.6×10^9	5.7×10^9	3.5×10^9
Gallic acid	1.2×10^{10}	8.8×10^9	1.1×10^{10}	7.1×10^9	8.2×10^9	6.0×10^9

The PET reaction of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with polyphenols proceeds through the same mechanism in 50 % aqueous acetonitrile and aqueous medium. The k_q values of $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{dmbpy})_3]^{2+}$ and $[\text{Ru}(\text{dtbpy})_3]^{2+}$ complexes with polyphenols are more in 50 % aqueous acetonitrile than in the aqueous medium in the same pH. The photoredox reaction is highly sensitive to the change of polarity of the medium, i.e., the reaction is favoured by less polar solvents like CH_3CN , $\text{C}_2\text{H}_5\text{OH}$ and CH_3OH compared to the aqueous medium [13]. The dielectric constant of H_2O is 80 whereas, the value for 50 % aqueous acetonitrile is 55.63 [19]. In the present study 50 % aqueous acetonitrile is less polar than aqueous medium and it shows higher quenching rate constant, thus k_q values varies with the polarity of the solvent. Thus, solvent plays an important role on the PET reactions of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes. Previtali have studied the solvent effect on the excited state quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex by aromatic amines and nitrobenzenes in methanol and acetonitrile and reported higher k_q for methanol than acetonitrile [20]. This results are in accordance with the k_q of $[\text{Ru}(\text{NN})_3]^{2+}$ with polyphenols in both media. The reductive quenching of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes by the phenolate ions have been confirmed from the transient absorption spectrum (Figure 4) The band at 400 and 510 nm in the transient absorption spectrum of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with gallic acid confirms the formation of gallate radical and $[\text{Ru}(\text{bpy})_3]^+$ as transient species.

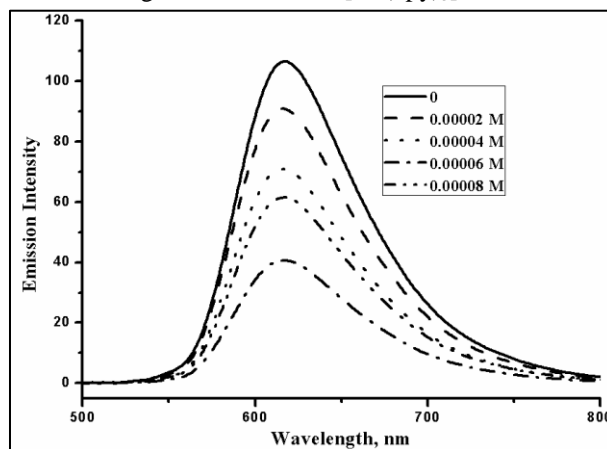


Figure 2: The change in emission intensity of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ with different concentrations of quercetin (2×10^{-5} - 8×10^{-5} M) in aqueous medium at pH 11

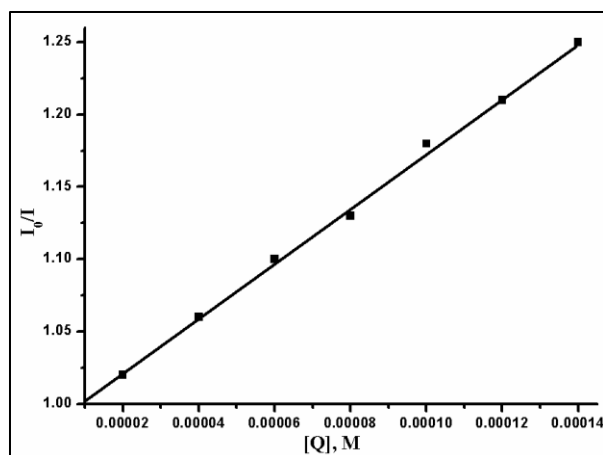


Figure 3: Stern-Volmer plot for the reductive quenching of $^{*}[\text{Ru}(\text{dtbp})_3]^{2+}$ with gallic acid in 50 % aqueous acetonitrile at pH 11

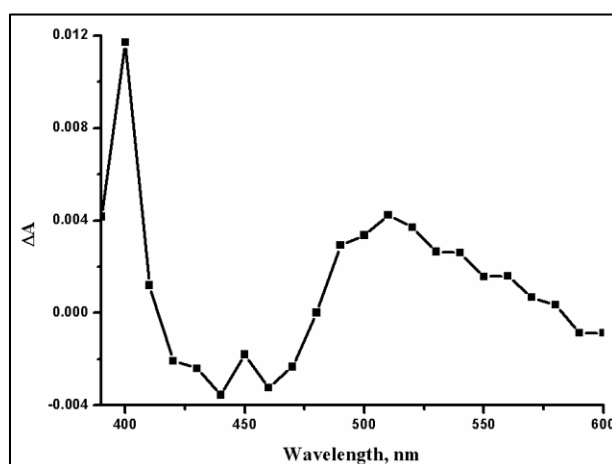


Figure 4: Transient absorption spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the presence of 0.00008 M gallic acid in aqueous medium recorded at 5 μs of 355 nm laser flash photolysis

CONCLUSION

The $[\text{Ru}(\text{NN})_3]^{2+}$ complexes, in the excited state undergoes facile electron transfer reaction with polyphenols in 50 % aqueous acetonitrile and aqueous medium, at pH 11 and the k_q is sensitive to the polarity of the medium. Gallic acid behaves as an efficient quencher in both media. The observed quenching rate constant values are highly sensitive to the nature of the reaction medium, ligands associated to the complexes and the substituent present in the polyphenols. Transient absorption spectra confirm the reductive quenching nature of these complexes with polyphenols. The detection of gallate radical and $[\text{Ru}(\text{bpy})_3]^+$ as transient species in the transient absorption spectrum confirms the electron transfer nature of the reaction. Thus the present study confirms the operation of structural and solvent effect on the electron transfer reactions of biologically important phenolate ions with the excited state $[\text{Ru}(\text{NN})_3]^{2+}$ complexes.

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