

QUENCHING OF TRIS(4,4'-DINONYL-2,2'-BIPYRIDYL)RUTHENIUM(II) COMPLEX WITH GALLIC ACID AND QUERCETIN IN DMSO

Sheeba Daniel¹ and G. Allen Gnana Raj²

Abstract-The reaction of excited state $[Ru(nbpy)_3]^{2+}$ ($nbpy = 4,4'$ -dinonyl-2,2'-bipyridine) complex with polyphenols (gallic acid and quercetin) proceeds through photoinduced electron transfer reaction in DMSO and has been studied by luminescence quenching technique. The complex shows absorption and emission maximum at 457 and 628 nm and it shows a lifetime of 804 ns in DMSO. The excited state reduction potential of the complex ($E^0Ru^{2+*/+}$) in DMSO is 0.72 V vs Ag/Ag⁺. The static nature of quenching is confirmed from the ground state absorption studies. The association constant (K_a) for this reaction is determined from the Benesi-Hildebrand plot using absorption intensity data. The quenching rate constant, (k_q) is determined from the Stern-Volmer equation and it is highly sensitive to the substituent present in the polyphenols, oxidation potential of the polyphenols, the free energy change (ΔG^0) of the reaction and the electron transfer distance between the complex and the quenchers. The reductive quenching of $[Ru(nbpy)_3]^{2+}$ by phenolate ions has been confirmed from transient absorption spectrum. The formation of phenoxyl radical as a transient is confirmed by its characteristic absorption at 400 nm. Structural effects seem to play an important role in the photoinduced electron transfer reactions in DMSO.

Keywords: Static quenching; Association constant; Stern-Volmer equation; photoinduced electron transfer; structural effects

Introduction

Phenols have been intensively studied since they are involved in many chemical, electrochemical, photochemical or biochemical electron-transfer reactions and their acid-base equilibrium are widely used as reference data in establishing linear free energy relationships. Beside their antioxidant properties, they act as efficient luminescent quenchers leading to interesting photoredox reactions. Information about the electrochemical potentials of several phenolate-phenoxyl radical couples in water is obtained by pulse radiolysis and by cyclic voltammetry [1]. Time resolved studies of 1O_2 quenching by phenols in aqueous solution at different pH show that the reaction occurs *via* a charge transfer from the phenolate ion, PhO^- , therefore phenols are excellent chain-breaking antioxidants and good 1O_2 quenchers [2].

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 [3]. 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 [4].

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 [5]. The conversion of phenol to phenoxyl radical is of interest to

¹ Department of Chemistry, Holy Cross College (Autonomous), Nagercoil – 4.

² Department of Chemistry and Research Centre, Scott Christian College (Autonomous) Nagercoil – 3

chemists because of its involvement in biologically important processes [6]. 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, have attracted the chemists in the field of solar energy conversion [7], artificial photosynthesis [8], optical sensing [9] and luminescent probes for characterizing microheterogeneous environments, owing to their favorable photophysical properties, excited state reactivity and chemical stability [10]. The excited state properties of Ru(II)-polypyridyl complexes are largely affected by the introduction of electron-donating and electron-withdrawing groups in the 4,4'-position of 2,2'-bipyridine [11].

The synthesis of Ru(II)-polypyridyl complexes with long chain hydrophobic ligands is of great interest in recent years because of their potential applications in thin film devices, sensors, heterogeneous catalysis and for the construction of dye sensitized solar cells [12,13]. The significance of using amphiphilic polypyridyl ruthenium sensitizers has been demonstrated to achieve enhanced stability in dye sensitized solar cells at elevated temperatures and have been successfully used as sensitizers for nanocrystalline dye-sensitized solar cells. Castro and co-workers have successfully designed a sensor for hydrocarbon, based on ruthenium(II)-complex, ($[\text{Ru}(\text{nbpy})_3]^{2+}$ (nbpy = 4,4'-dinonyl-2,2'-bipyridine)) which is able to detect reversibly and to quantify both aromatic and aliphatic hydrocarbons in aqueous samples [14].

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 [15-17]. The present study concentrates on the quenching behavior of the $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex with quenchers gallic acid and quercetin. The static nature of quenching is studied from the ground state absorption intensity data. The association constant (K_a) for this reaction is determined from the Benesi-Hildebrand plot using absorption intensity data. The quenching rate constant, (k_q) is obtained from the Stern-Volmer plot. The transient absorption spectrum confirms the electron transfer nature of the reaction of the excited state $[\text{Ru}(\text{nbpy})_3]^{2+}$ with polyphenols in DMSO, where the quenching process proceeds through the formation of phenolate ions.

2. Experimental Section

2.1 Materials

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, ligand (4,4'-dinonyl-2,2'-bipyridine) and the quenchers (gallic acid and quercetin) were purchased from Sigma- Aldrich. HPLC grade solvents were used throughout the study for the synthesis of complex as well as for quenching studies. The complex, $[\text{Ru}(\text{nbpy})_3]\text{Cl}_2$ was synthesized according to the procedure previously described [14].

2.2 Equipments

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.

The redox potential of the complex, $[\text{Ru}(\text{nbpy})_3]^{2+}$ and the oxidation potentials of the polyphenols in DMSO medium were determined by cyclic voltammetric technique using CH1604C electrochemical analyzer. A glassy carbon (working electrode), Pt (counter electrode) and (Ag/Ag^+) electrode (reference electrode) were used for the electrochemical measurements and tetrabutylammonium perchlorate was the supporting electrolyte.

2.3 Luminescent quenching studies

The complex, $[\text{Ru}(\text{nbpy})_3]^{2+}$ as well as the quenchers in DMSO were freshly prepared for each measurement. The structure of the ligand and the quenchers used in the present study are shown in **Fig. 1**. The complex and the quenchers taken in the present study are soluble in DMSO and the excited state lifetime of the $[\text{Ru}(\text{nbpy})_3]^{2+}$ is longer in aprotic solvents than that of the protic solvent [14]. The photochemical reduction of $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex to $[\text{Ru}(\text{nbpy})_3]^+$ with these phenolate ions has been studied by the luminescence quenching technique. The luminescence measurements (**Fig. 2**) were performed at different quencher concentration (2×10^{-5} - 1.4×10^{-4} M) and the quenching rate constants (k_q) were determined from Stern-Volmer plots (**Fig. 3**) using the equation given below.

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 $[\text{Ru}(\text{nbp}y)_3]^{2+}$ in the absence of quencher.

The association of $[\text{Ru}(\text{nbp}y)_3]^{2+}$ complex with various concentrations (2×10^{-5} - 1.4×10^{-4} M) of gallic acid and quercetin in DMSO has been studied by absorption spectral technique. The association constant (K_a) of the $[\text{Ru}(\text{nbp}y)_3]^{2+}$ complex with gallic acid and quercetin were determined from the Benesi-Hildebrand equation using absorption intensity data.

where ΔA is the change in absorption of the complex with different concentrations of gallic acid and quercetin ($[G]$) in DMSO. The plots of $1/\Delta A$ versus $1/[G]$ give a straight line, K_a can be obtained from the ratio of Y-intercept to the slope of the straight line.

Fig. 1 Structure of the ligand and the quenchers

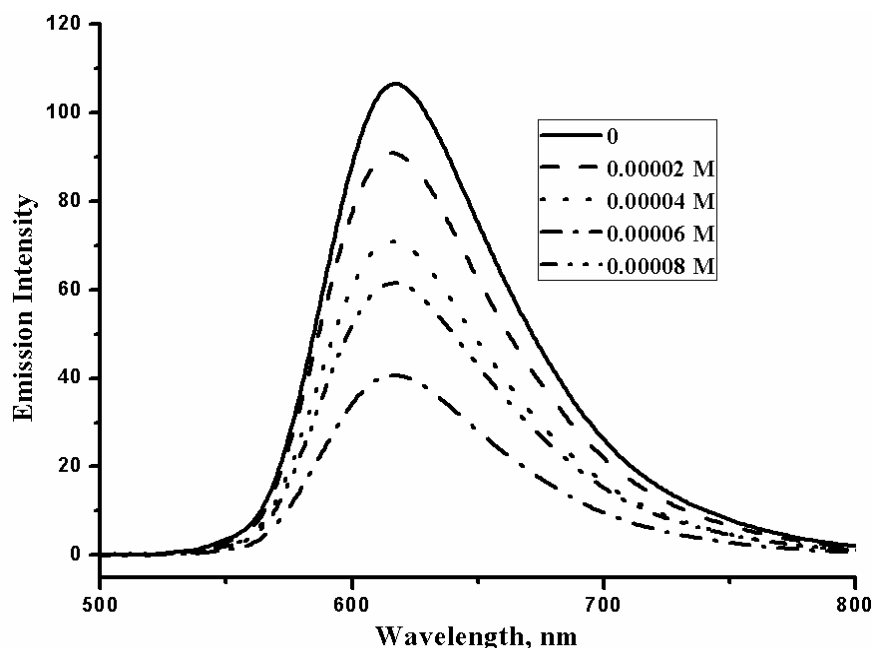


Fig. 2 The change in emission intensity of $[\text{Ru}(\text{nbp}y)_3]^{2+}$ with different concentrations of quercetin (2×10^{-5} - 8×10^{-5} M) in DMSO

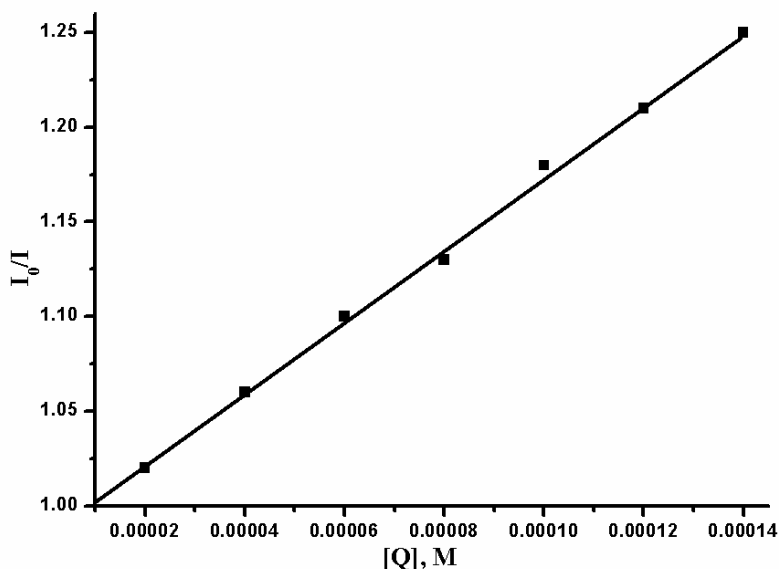


Fig. 3 Stern-Volmer plot for the reductive quenching of $^*[\text{Ru}(\text{nbpy})_3]^{2+}$ with gallic acid in DMSO

3 Results and Discussion

The absorption spectrum of $[\text{Ru}(\text{nbpy})_3]^{2+}$ shows a high energy absorption at 286 nm corresponding to the ligand centered $\pi - \pi^*$ transition and a low energy absorption at 457 nm assigned to the $d\pi - \pi^*$ metal to ligand charge transfer (MLCT) transition. The MLCT involves electronic excitation from the metal orbital $[d\pi(\text{Ru})]$ to the ligand centered acceptor π^* orbitals (ligand). The $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex shows an emission maximum at 628 nm and has an excited state lifetime at 804 ns in DMSO.

The ground state reduction potential of the $[\text{Ru}(\text{nbpy})_3]^{2+}$ in DMSO is $-1.37 \text{ V vs Ag/Ag}^+$ electrode. The redox potentials of excited state couples are calculated from the potential of the ground state couples and the zero-zero energy, E_{0-0} (found to be 2.1 eV) [11]. The excited state redox potential of the complex ($E_{\text{Ru}}^{0, 2+*/+}$) is 0.72 V vs Ag/Ag^+ . The free energy change (ΔG^0) values are calculated from the excited state redox potential of $[\text{Ru}(\text{nbpy})_3]^{2+}$ and oxidation potentials of polyphenols.

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

The absorption spectral studies of $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex with the incremental addition of gallic acid and quercetin show a steady increase in the MLCT absorption maximum, indicates the formation of ground state complex (Fig. 4). Gallic acid and quercetin has a weak absorption near the MLCT absorption of the complex, hence gallic acid and quercetin binds with the MLCT absorption peaks of $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex in the ground state [18]. The absorption spectra of $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex with gallic acid and quercetin show a hypsochromic shift of 5 to 10 nm, which may be due to the formation of ground state complex. The K_a of $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex with gallic acid and quercetin in DMSO is calculated from Benesi-Hildebrand plot (Fig. 5) and the result is tabulated in Table 1. Thus the ground state complex formation of $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex with gallic acid and quercetin in DMSO validate the presence of static quenching.

Table 1 Association constant, K_a (M^{-1}) for gallic acid and quercetin with $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex in DMSO

Quencher	Association constant, K_a (M^{-1})
Gallic acid	5.7×10^3
Quercetin	9.6×10^4

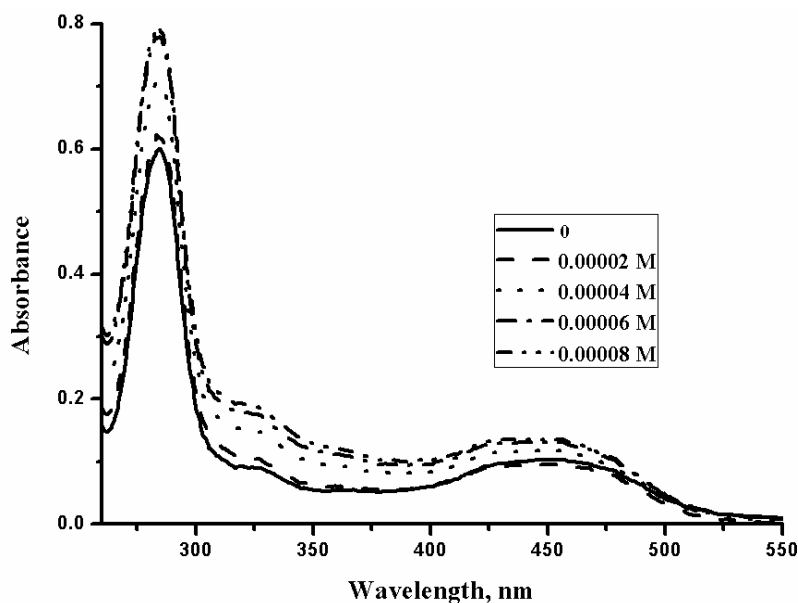


Fig. 4 Absorption spectra of $[Ru(nbpy)_3]^{2+}$ with incremental addition of gallic acid in DMSO

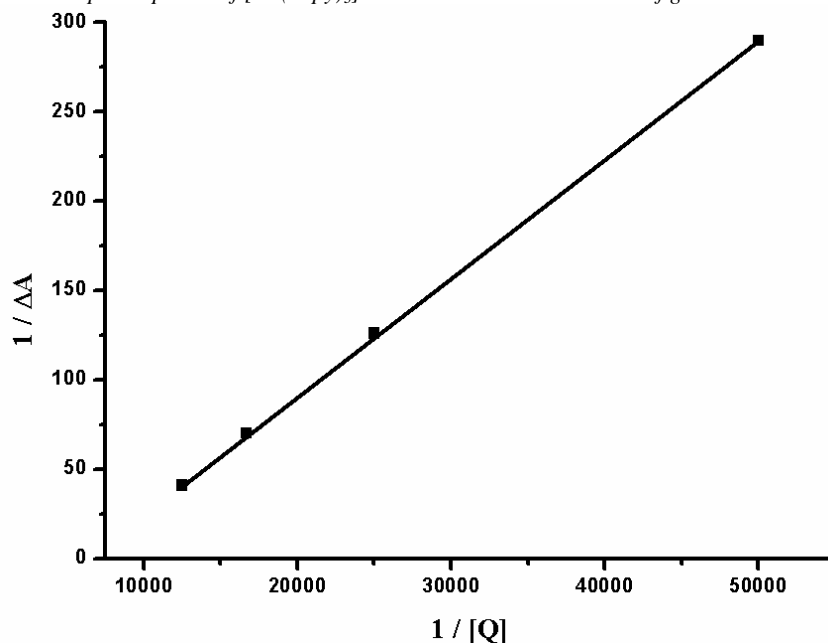


Fig. 5 Benesi-Hildebrand plot on MLCT absorption of $[Ru(nbpy)_3]^{2+}$ complex with incremental addition of quercetin in DMSO

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

The experimental bimolecular quenching rate constant (k_q) of $^*[Ru(nbpy)_3]^{2+}$, oxidation potentials of quenchers vs Ag/Ag^+ , and ΔG^0 in DMSO are shown in **Table 2**. The Stern–Volmer plots from the emission intensity data (**Fig. 3**) are linear for gallic acid and quercetin in the present experimental condition. In DMSO, a hydrogen bonding interaction is established between the phenolic–OH groups of the phenols and the oxygen atom of DMSO ($O-H \cdots O$), which polarize the O–H bond, making the proton transfer easier. This proton transfer yields phenolate ion, which act as quenchers in this PET reactions. 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 [19]. For the sake of comparison of the quenching efficiencies of the polyphenols with $[Ru(nbpy)_3]^{2+}$ complex, luminescent quenching study of phenol with this complex is also performed and the results are discussed here. Phenol shows least k_q with $[Ru(nbpy)_3]^{2+}$ complex in DMSO. Miedlar and Das reported this type of least k_q value for phenol in the photoredox reactions of $[Ru(bpy)_3]^{2+}$ complex [20]. 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 [21], due to the presence of three phenolic–OH groups, acts as the most efficient quencher compared to that of quercetin.

Table 2 Quenching rate constants (k_q), oxidation potential of quenchers vs Ag/Ag^+ (E_{oxd}^0) and free energy changes (ΔG^0) for the reductive quenching of $[Ru(nbpy)_3]^{2+}$ with the quenchers in DMSO

Quencher	k_q ($M^{-1}s^{-1}$)	E_{oxd}^0 vs Ag/Ag^+ (V)	ΔG^0 (eV)
Phenol	1.4×10^8	0.78	0.06
Quercetin	2.5×10^9	0.30	-0.42
Gallic acid	6.2×10^9	0.08	-0.64

The bond dissociation energy (BDE) for the phenolic-OH group in gallic acid (75.5 Kcal/mol) is less than that of quercetin (77 Kcal/mol) and phenol (90 Kcal/mol) in the present study [19]. The presence of pyrogallol (three adjacent phenolic-OH groups) substitution pattern reduces the BDE in gallic acid [22]. Due to this low BDE, gallic acid undergoes ionization easily and acts as the most efficient quencher. Though quercetin consists of four phenolic-OH groups, the BDE of catechol group (ring B) is less compared to the phenolic-OH groups in ring A; therefore the catechol group undergoes oxidation easily. The quenching rate constant depends on the number of phenolic-OH groups present in the quencher. As the number of phenolic-OH group increases the quenching rate constant also increases. Here in this study the quenching rate constant for gallic acid is higher than that of quercetin, owing to the presence of three phenolic-OH groups.

The ground state absorption studies of $[Ru(nbpy)_3]^{2+}$ complex with gallic acid and quercetin confirms the static nature of quenching. The association constant for gallic acid and quercetin are in the order of 10^3 - 10^4 M^{-1} . This binding is due to the π - π stacking interactions exist between the ligands of Ru(II)-complex and the quencher. Because of the ground state complex formation in gallic acid and quercetin with $[Ru(nbpy)_3]^{2+}$ complex in DMSO, they act as efficient quenchers compared to that of phenol. The ratio of k_q by K_a gives the first-order rate constant for reduction (k_{red}) in the excited state sensitizer-quencher adducts. The k_{red} for the excited state sensitizer-quencher adducts for gallic acid and quercetin are calculated and are given in Table 3. The k_{red} values for $[Ru(nbpy)_3]^{2+}$ complex with gallic acid and quercetin are in the order of 10^6 - 10^4 s^{-1} . The k_{red} values for the complex with gallic acid is more than that of quercetin, this also confirms that gallic acid acts as an efficient quencher in this PET reaction.

Table 3 First-order rate constants for reduction, k_{red} (s^{-1}) in the excited-state quenching with gallic acid and quercetin - $[Ru(nbpy)_3]^{2+}$ adduct in DMSO

Quencher	First-order rate constants, k_{red} (s^{-1})
Gallic acid	1.08×10^6
Quercetin	2.60×10^4

The k_q is sensitive to the ΔG^0 of the reaction and the oxidation potential of phenols. It is apparent from the data in Table 2 that phenols with lower oxidation potential exhibit higher quenching rate constant, is an indication for electron transfer quenching. The oxidation potential (0.78 V) and ΔG^0 (0.06 eV) of phenol also supports the lowest k_q for $[Ru(nbpy)_3]^{2+}$ in DMSO. This is in good agreement with the reported k_q value for luminescent quenching of $[Ru(bpy)_3]^{2+}$ by phenolate ions in aqueous medium at pH 12.5 [15]. Gallic acid has very low oxidation potential due to the presence of three -OH groups (0.08 V) and the ΔG^0 value is more negative (-0.64 eV) for this photoredox system. This is understandable as the introduction of additional -OH group makes the quencher better electron donor and ΔG^0 becomes more negative. Hence it undergoes oxidation easily and acts as an efficient quencher compared to the other phenols taken in the present study. The oxidation potential and the corresponding ΔG^0 value of quercetin is 0.30 V, and -0.42 eV. Thus the k_q values are highly sensitive to the oxidation potential of the quenchers and the ΔG^0 of the reactions.

The k_q also depends on the electron transfer distance between the complex and the quenchers. From MM2 molecular model, the calculated radii for gallic acid and quercetin are 4.1 and 5.93 Å. The radius of quercetin is more than that of gallic acid, as the radius of the quencher increases the electron transfer distance between the complex and the

quencher also increases. This result also concludes that gallic acid acts as an efficient quencher than quercetin in this photoredox reaction. Thus, the k_q value depends not only on the oxidation potential of the quenchers and the ΔG^0 of the reactions but also on the electron transfer distance between the complex and the quencher.

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 $[\text{Ru}(\text{nbpy})_3]^{2+}$ in DMSO at various time delays is shown in **Fig. 6**. 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. 7**) of the complex with gallic acid (0.00008 M) confirms the formation of gallate radical and $[\text{Ru}(\text{nbpy})_3]^+$ as transient species. The transient absorption spectrum confirms the electron transfer of this complex in gallic acid. Thus, the present study confirms the reductive quenching of $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex with gallic acid and quercetin in DMSO.

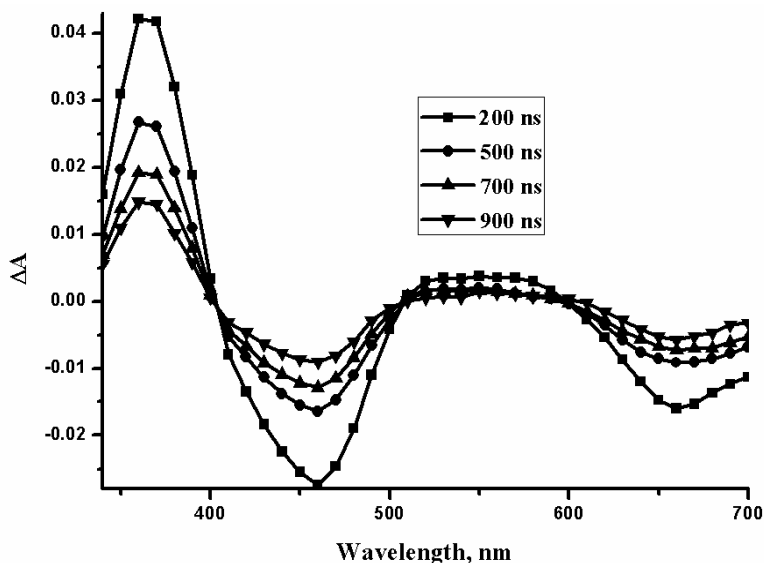


Fig. 6 Transient absorption spectra recorded after excitation of $[\text{Ru}(\text{nbpy})_3]^{2+}$ in DMSO at different time intervals

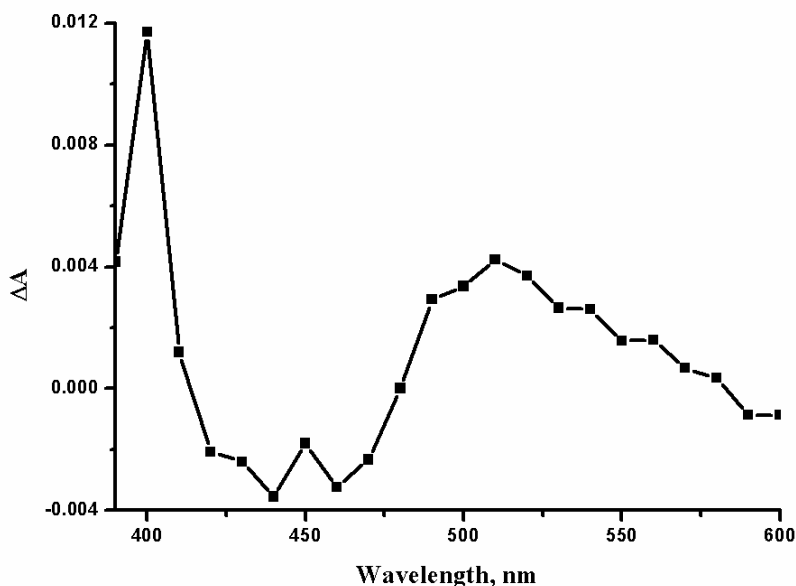


Fig. 7 Transient absorption spectrum of $[\text{Ru}(\text{nbpy})_3]^{2+}$ in the presence of 0.00008 M gallic acid in DMSO recorded at 5 μs of 355 nm laser flash photolysis

Conclusion

The $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex, in the excited state undergoes facile electron transfer reaction with polyphenols in DMSO and the quenching rate constant (k_q) is sensitive to the availability of phenolate ions, oxidation potentials of the polyphenols, ΔG^0 values and the electron transfer distance between the complex and the quencher. Gallic acid behaves as an efficient quencher compared to that of quercetin in DMSO, due to lesser electron transfer distance,

more number of phenolic-OH group, less BDE for the phenolic-OH group, and lower oxidation potential. Absorption spectral studies and the association constant data obtained from the absorption data confirm the static nature of quenching for $[\text{Ru}(\text{nbpy})_3]^{2+}$ complex with gallic acid and quercetin. The transient absorption spectra confirm the reductive quenching nature of this complex with polyphenols in DMSO. The detection of gallate radical and $[\text{Ru}(\text{nbpy})_3]^+$ 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 $\pi - \pi$ stacking interactions on the electron transfer reactions of biologically important phenolate ions with the excited state $^*[\text{Ru}(\text{nbpy})_3]^{2+}$ complex.

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