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Research Article

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Photoinduced electron-transfer reactions of tris(4,4'-dinonyl-2,2'-bipyridyl) ruthenium(II) cation with phenolate ions in aqueous acetonitrile

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ABSTRACT

The photoredox reactions of biologically important phenols (p-coumaric acid, ferulic acid, thymol, quercetin and gallic acid) with the excited state $^*[Ru(nbpy)_3]^{2+}$ *(nbpy = 4,4'-dinonyl-2,2'- bipyridine) complex proceeds through photoinduced electron transfer reaction in 50 % aqueous acetonitrile at pH 11 and has been studied by luminescent quenching technique. The complex shows absorption and emission maximum at 456 and 618 nm and it shows a life time at 625 ns in 50 % aqueous acetonitrile at pH 11. The dynamic nature of quenching is confirmed from the ground state absorption studies. The reductive quenching of* $[Ru(nbpy)_3]^{2+}$ *by the phenolate ions have been confirmed from the transient absorption spectra. The quenching rate constant,* (k_q) *is highly sensitive to the availability of active phenolate ions, oxidation potentials of the phenols, the free energy change,* (ΔG^0) *of the reaction and the electron transfer distance between the donor and the acceptor.*

Keywords: Luminescence quenching; Stern-Volmer equation; Photooxidation of phenols; photoinduced electron transfer; free energy change

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INTRODUCTION

Relating to artificial photosynthetic systems which are capable to harvest and exploit photons enabled by solar energy, ruthenium(II) complexes coordinated by N-heterocycles, such as 2,2'-bipyridines (bpy), have been widely studied due to their predictable coordination behavior as well as their interesting photophysical and electrochemical properties[1-3]. Ruthenium(II)-polypyridine complexes have particularly drawn significant interest, since they are able to catalyze reduction and oxidation processes under visible light irradiation enclosing a broad range of substrates. These privileges could be utilized for applications including, e.g., the photocatalytic decomposition of water and the implementation in photovoltaic devices [4, 5]. The light sensitizing feature of ruthenium coordination compounds has been further used as luminescent chemosensors as well as for the production of singlet molecular oxygen [6, 7].

Polyphenols 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 secondary metabolites involved in the chemical defence of plants against predators and in plant-plant interferences. Several thousand plant polyphenols are known, encompassing a wide variety of molecules that contain at least one aromatic ring with one or more hydroxyl groups in addition to other substituents. The antioxidant activity of phenolic compounds is due to their ability to scavenge free radicals [8], donate hydrogen atoms or electron, or chelate metal cations [9]. The conversion of phenol to phenoxyl radical is of interest to chemists because of its involvement in biologically important processes [10-12]. The one electron oxidation of phenolates to the resulting phenoxyl radical is a key step in the oxidation of phenols. The photoinduced electron- transfer reactions of ruthenium(II)-polypyridyl complexes with several *ortho-*, *meta-* and *para-* substituted phenolate ions are highly influenced by the change of structure of the ligands of the complex as well as the substrates. The decrease in the quenching rate constant (k_q) value with increase in the bulkiness of the ligand as well as the quencher has been explained in terms of increase in the electron transfer distance [13-16]. Miedlar and Das presented a detailed report on the reductive quenching of $*[Ru(bpy)_3]^{2+}$ by several substituted phenolate ions [17]. The rate of electron transfer from a donor molecule to an acceptor in a solvent is controlled by several factors and the most important of them are the free energy change of the reaction (ΔG^0), the reorganization energy (λ) and the electron transfer distance (d) between the donor and acceptor [18].

Investigations on the quenching efficiency of Ruthenium(II) polypyridyl complexs with phenols have been made so far and the present study concentrates on the quenching behavior of the $[Ru(nbpy)_3]^{2+}$ (nbpy = 4,4'-dinonyl-2,2'-bipyridine) complex with polyphenols in 50 % aqueous acetonitrile at pH 11. The transient absorption spectra confirms the electron transfer nature of $[Ru(nbpy)_3]^{2+}$ with polyphenols in 50 % aqueous acetonitrile at pH11, where quenching process proceeds through the formation of phenolate ions. Further, the nature of quenching (static or dynamic) is recorded by electronic absorption spectra as well as quenching rate constant.

EXPERIMENTAL SECTION

MATERIALS

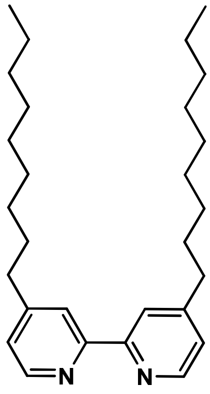
$RuCl_3.3H_2O$, ligand (4,4'-dinonyl-2,2'- bipyridine) and the quenchers (*p*-Coumaric acid, ferulic acid, thymol, gallic acid, quercetin) were purchased from Sigma – Aldrich. HPLC grade solvents were used throughout the study for the synthesis of complex as well as for quenching studies. Deionized water was used in all quenching experiments. The complex, $[Ru(nbpy)_3]\ Cl_2$ was synthesized following the procedure of Castro *et al* [19]. Then the complex was treated with sodium tetrafluoroborate to get the BF_4^- salt $[Ru(nbpy)_3](BF_4)_2$.

2.2 Equipments

Sample solutions of the $[Ru(nbpy)_3]^{2+}$ complex and the quenchers were freshly prepared for each measurement. The absorption spectral measurements were carried out using SYSTRONICS 2203 double beam spectrophotometer. Emission intensity measurements were carried out and the emission spectra were recorded using ELICO SL 174 spectrofluorimeter. All the sample solutions used for emission and excited state lifetime measurements were deaerated for about 25 min by dry nitrogen gas purging by 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 room temperature. 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 [20]. The time dependence of the luminescence decay is 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. The redox potential of the complex, $[Ru(nbpy)_3]^{2+}$ and the oxidation potentials of the polyphenols in 50 % aqueous acetonitrile medium at pH 11 were determined by cyclic voltammetric technique using CH1604C electrochemical analyzer.

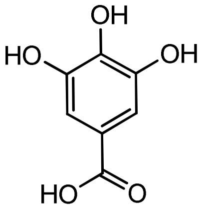
2.3 Quenching studies

The structures of the ligand and the quenchers used in the present study are shown in **Fig. 1**. The photochemical reduction of $[Ru(nbpy)_3]^{2+}$ complex with various concentrations ($2 \times 10^{-4} - 1.4 \times 10^{-3}$) of quenchers in 50 % aqueous acetonitrile at pH 11 has been studied by luminescent quenching techniques. Phenolate ions of the quenchers for the quenching studies were prepared by mixing the corresponding polyphenols with NaOH and the pH of the solution was maintained at 11 to confirm that the quencher was present as phenolate ions.

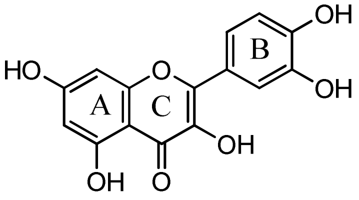


4,4'-dinonyl-2,2'-bipyridine

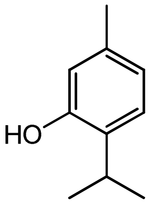
Quenchers



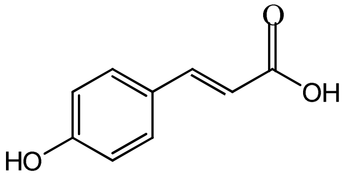
Gallic acid



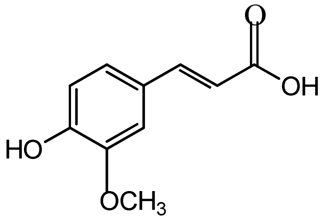
Quercetin



Thymol



p-coumaric acid



Ferulic acid

Fig 1 Structure of ligand and quenchers

The change of emission intensity of *$[Ru(nbpy)_3]^{2+}$ with change of [Q] measured at 298 K is shown in **Fig.2**. The quenching rate constant, k_q, for the reaction was determined by the luminescence-quenching technique from the Stern–Volmer equation using emission intensity data [21].

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

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 Ru (II) complexes in the absence of quencher. A sample Stern–Volmer plot for the luminescence quenching of *$[Ru(nbpy)_3]^{2+}$ with polyphenol is shown in **Fig.3**.

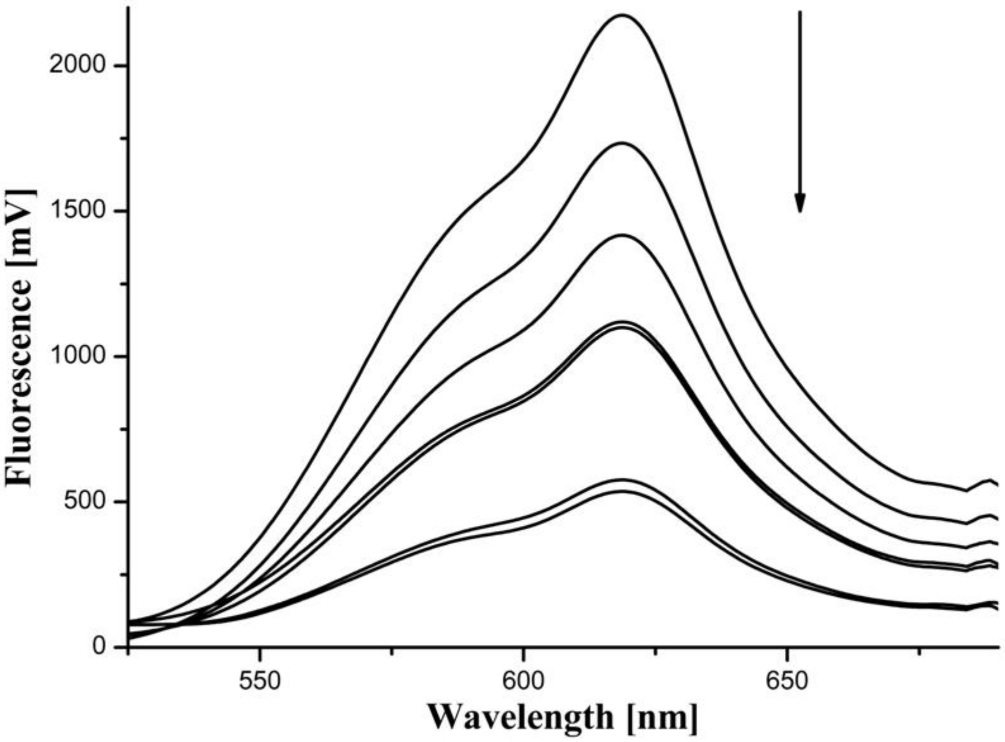


Fig 2 The change in emission intensity of *$[Ru(nbpy)_3]^{2+}$ with different concentrations of gallic acid in 50 % aqueous acetonitrile at pH 11

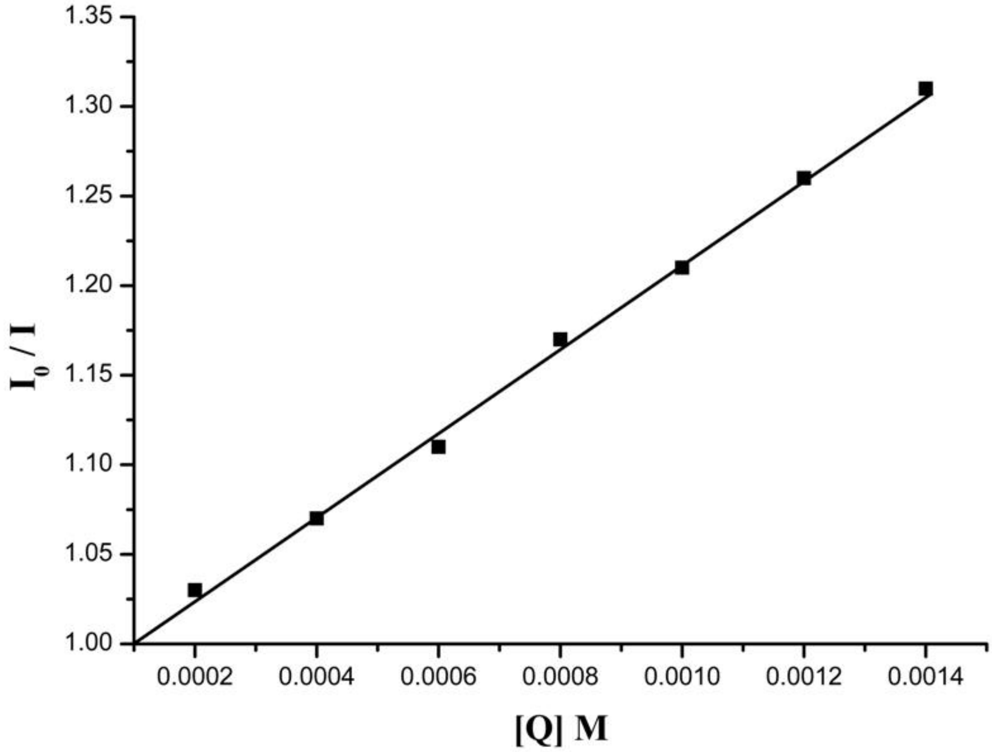


Fig 3 Stern – Volmer plot for the reductive quenching of *$[Ru(nbpy)_3]^{2+}$ with ferulic acid in50 % aqueous acetonitrile at pH 11

RESULTS AND DISCUSSION

The absorption spectrum of $[Ru(nbpy)_3]^{2+}$ complex shows a high energy absorption at 286 nm corresponding to the ligand centered $\pi - \pi^*$ transition and the low energy absorption at 456 nm assigned to the d $\pi - \pi^*$ metal to ligand charge transfer (MLCT) transition. The MLCT involves electronic excitation from the metal orbital [dπ (Ru)] to the ligand centred acceptor π^* orbitals (ligand). The $[Ru(nbpy)_3]^{2+}$ complex shows an emission maximum at 618 nm and excited state life time at 625 ns in 50 % aqueous acetonitrile at pH 11. The ground state and excited state redox potentials vs Ag/Ag^+ of the $[Ru(nbpy)_3]^{2+}$ complex in this medium are −1.28 V and 0.82 V respectively. The free energy change (ΔG^0) values are calculated from the excited state redox potential of $[Ru(nbpy)_3]^{2+}$ and oxidation potentials of phenolate ions. The experimental bimolecular quenching rate constant (k_q) of $^*[Ru(nbpy)_3]^{2+}$, oxidation potentials of phenolate ions and ΔG^0 in 50 % aqueous acetonitrile at pH 11 are shown in **Table 1.**

Table 1 Rate constants, oxidation potential of quenchers and free energy changes for the reductive quenching of $[Ru(nbpy)_3]^{2+}$ with phenols in 50 % aqueous acetonitrile at pH 11

Quencher	k_q	E^0_{oxd} vs Ag/Ag^+ (V)	ΔG^0 (eV)
p-coumaric acid	2.4×10^8	0.63	- 0.19
Ferulic acid	5.6×10^8	0.57	- 0.25
Thymol	7.1×10^8	0.44	- 0.38
Quercetin	1.4×10^9	0.25	- 0.57
Gallic acid	4.6×10^9	0.37	- 0.45

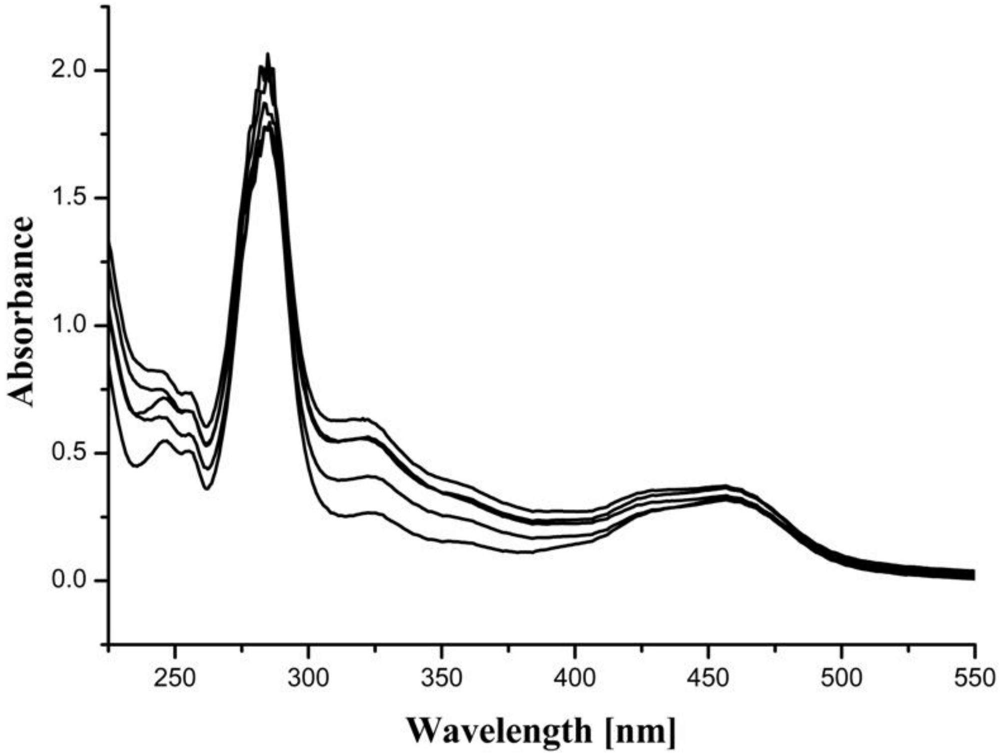


Fig 4 Absorption spectra of $[Ru(nbpy)_3]^{2+}$ in the presence of different concentrations of quercetin in 50 % aqueous acetonitrile at pH 11

3.1 Reductive quenching of $^*[Ru(4,4'\text{-dinonyl-}2,2'\text{-bipyridine})_3]^{2+}$ with phenolate ions

The Stern – Volmer plots for the emission intensity of the photoredox systems (**Fig.3**) are found to be linear which indicates that, dynamic quenching is the predominant process and the contribution from static quenching is negligible. In order to check the ground-state complex formation, quenchers are added in increments to the $[Ru(nbpy)_3]^{2+}$ complex in 50 % aqueous acetonitrile at pH 11 and the absorption spectra are recorded at different concentrations (**Fig. 4**). The absorption spectra of the reactants are equal to the sum of the component spectra. There is no significant change in MLCT absorption maxima of $[Ru(nbpy)_3]^{2+}$ in the presence of the quenchers under the present experimental conditions which helps us to conclude that the contribution from the static quenching is negligible here [13].

The k_q values for gallic acid, quercetin, thymol, ferulic acid and *p*-coumaric acid are 4.6 x 10^9, 1.44 x 10^9, 7.1 x 10^8, 5.6 x 10^8 and 2.4 x 10^8 respectively. In alkaline medium at pH 11 all the phenolic –OH groups in the quenchers taken in the present study are in the phenolate form. Most phenolic compounds with one –OH group do not effectively quench $[Ru(bpy)_3]^{2+}$ photoluminescence [22,23]. Here gallic acid has one –COOH and three phenolic –OH groups and in alkaline medium especially above pH 9 the carboxylic acid as well as the three phenolic –OH get ionized [24]. On the other hand 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 [25]. Steric hindrance exerted by the benzo-γ – pyrone derivative (ring A and C) at *para* – position of the ring B reduces its quenching efficiency. Hence the availability of the phenolate ion for quenching is less in quercetin than gallic acid. Therefore the k_q value of gallic acid is somewhat higher than quercetin. The presence of isopropyl group at the ortho- position of thymol exerts a slight steric effect and reduces the quenching rate constant. The hydroxyl derivaties of cinnamic acid (*p*-coumaric acid and ferulic acid) shows the least k_q values. The –CH=CH–COOH chain at the *para*- position of phenol has electron acceptor properties, and the stabilization of the resulting phenolate ion might be increased by electron delocalization after hydrogen donation by the hydroxyl group. Hence the availability of phenolate ion is much less in *p*-coumaric acid and ferulic acid thus reduces the quenching rate constant, the k_q of latter is somewhat higher than the former due to the presence of electron releasing methoxy group in the *ortho*- position of the phenol. Here the steric and nature of the substituent in the *ortho*- and *para*- positions affects the k_q.

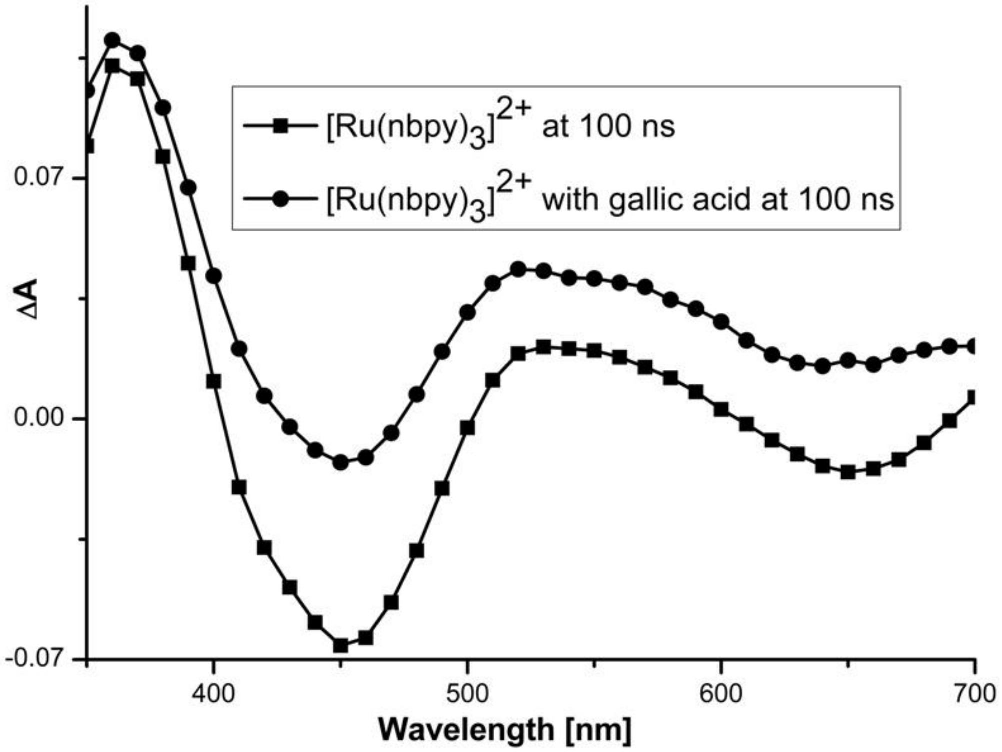
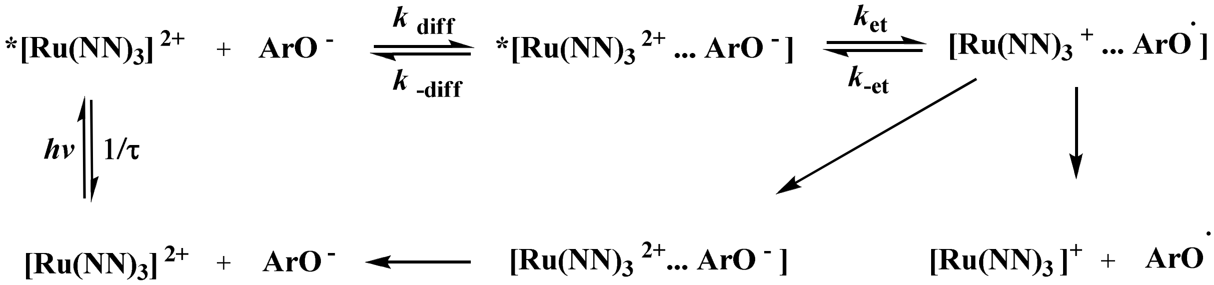


Fig. 5 Transient absorption spectra of $[Ru(nbpy)_3]^{2+}$ at 100 ns after 355 nm laser flash photolysis in the absence and presence of 0.0008 M gallic acid in 50 % aqueous acetonitrile at pH 11

The ΔG^0 values (**Table 1**) indicate that all reactions are exergonic i.e., ΔG^0 becomes more negative. The oxidation potential and the ΔG^0 values show that quercetin undergoes oxidation easier than gallic acid, but the k_q value indicates gallic acid as efficient quencher than quercetin. The k_q depends not only on the ΔG^0 but also the electron transfer distance between the donor and the acceptor [18]. From MM2 molecular model the radius of gallic acid and quercetin are 3.94 and 5.93 A^0, so the electron transfer distance is more in quercetin and it decrease the k_q. *p*-

coumaric acid shows a high oxidation potential value of 0.63 V and the free energy change is – 0.19 eV, recording a very low quenching rate constant. The oxidation potential of ferulic acid (0.57 V) is less than that of *p*-coumaric acid indicates that the former undergoes oxidation easily, and shows somewhat higher k_q than the latter. The compounds with two or more electron donating groups have lower oxidation potentials and higher antioxidant abilities than monosubstituted phenols, although –OH groups have stronger effects than – OCH_3 ones [26]. Quercetin and gallic acid shows lower oxidation potentials than thymol, ferulic acid and *p*-coumaric acid. Thus, the nature of the substituent present in the phenols also affects the rate of quenching.

The electron transfer nature of the quenching process is confirmed from the transient spectra of $[Ru(nbpy)_3]^{2+}$ (**Fig.5**), recorded in the absence and presence of 0.0008 M gallic acid. The band at 520 nm corresponds to the formation of $[Ru(nbpy)_3]^+$. The behavior of these redox systems can be discussed by a common mechanism depicted in **Scheme 1**. The reactants diffuse together to form the encounter complex at the closest distance of approach. The electron transfer occurs in this association complex $[{}^*Ru(NN)_3{}^{2+} \ldots ArO^-]$ resulting in the the formation of a caged pair of radicals or radical ions. The radical ions either escape from the solvent cage to give the redox products or undergo back electron transfer to the formation of the original reactants.



Scheme 1 Mechanism for the electron transfer quenching of $*[Ru(NN)_3]^{2+}$ with ArO^-

CONCLUSION

The present study clearly establishes the reductive nature of the $*[Ru(nbpy)_3]^{2+}$ complexes with polyphenols in 50 % aqueous acetonitrile at pH 11. The k_q depends on the availability of phenolate ions, oxidation potentials of the phenols and ΔG^0 values and the electron transfer distance between the complex and the quencher. The steric and nature of the substituent in the *ortho*- and *para*- positions also affects the quenching rate constant. Gallic acid behaves as an efficient quencher compared to other phenols due to less electron transfer distance and availability of more number of active phenolate –OH. The study confirms the steric and structural effect on the electron transfer reactions of biologically important phenolate ions with the excited state $*[Ru(nbpy)_3]^{2+}$.

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