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# Photoluminescence electron transfer quenching of ruthenium(II)-polypyridyl complexes with biologically important phenolate ions in aqueous acetonitrile solution

Sheeba Daniel · Allen Gnana Raj George

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**Abstract** The photoinduced electron transfer reactions of three Ru(II) complexes with phenolate ions of polyphenols (gallic acid, quercetin, *p*-coumaric acid, and ferulic acid) and thymol have been measured in 50 % aqueous acetonitrile at pH 11 and the observed quenching constant ( $k_q$ ) values are sensitive to the nature of the ligand and the structure of the phenolate ion. The change of  $k_q$  values with  $\Delta G^0$  is in accordance with the Marcus semiclassical theory of electron transfer. The static as well as dynamic nature of quenching is confirmed from the ground-state absorption studies. The reductive quenching of the Ru(II) complexes by the phenolate ions has been confirmed from the transient absorption spectra. The formation of phenoxyl radical as a transient is confirmed by its characteristic absorption at 400 nm.

**Keywords** Ruthenium(II)-polypyridyl complex · Photoinduced electron transfer · Quenching · Stern–Volmer equation · Marcus semiclassical theory

## Introduction

Polyphenols are ubiquitous in nature and their biological properties include antioxidants, anticancer and anti-inflammatory effects [1–3]. The antioxidant activity of phenolic compounds is due to their ability to scavenge free radicals, donate hydrogen atoms or electron, or chelate metal cations [4–7]. Phenoxyl radicals are formed in thermochemical, photochemical and biochemical processes which

involve the oxidation of phenols. Phenoxyl-type radicals are involved in biological redox processes and in the biosynthesis of natural products. The conversion of phenol to phenoxyl radical is of interest to chemists because of its involvement in important biological and industrial processes and in the degradation of chemical waste [8–11]. The one electron oxidation of phenolate to the resulting phenoxyl radical is a key step in the oxidation of phenols. The generation of phenoxyl radical involves either H-atom or electron abstraction from phenol and phenolate ion, respectively. The study of the kinetic and thermodynamic aspects of electron transfer (ET) to generate phenoxyl radicals bearing bulky groups in the *ortho*- and *para*-positions may help to understand the different biological roles of phenols [12–15].

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 [16, 17]. The oxidation potential decreases with an increase in the number of phenolic –OH groups [18].

Ruthenium polypyridyl complexes, such as  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy = 2,2'-bipyridine), are among the most investigated in fields that include solar energy conversion [19, 20], artificial photosynthesis [21], optical sensing [22, 23], and luminescent probes for characterizing microheterogeneous environments, owing to their favorable photophysical properties, excited state reactivity, and chemical stability [24, 25]. The excited state properties like emission lifetime, quantum yield, wavelength of emission maximum and redox potential of  $[\text{Ru}(\text{bpy})_3]^{2+}$  are largely affected by the introduction of electron-donating and electron-withdrawing groups in the 4,4'-position of 2,2'-bipyridine [26].

S. Daniel · A. G. R. George (✉)  
Department of Chemistry and Research Centre, Scott Christian  
College (Autonomous), Nagercoil 629003, Tamil Nadu, India  
e-mail: gallengraj@gmail.com

The excited state properties of ruthenium(II)-polypyridyl complexes ( $[\text{Ru}(\text{NN})_3]^{2+}$ ) can also be finely tuned by changing the nature of the solvent or medium. Many efforts have been made in recent years to design and synthesize molecules to mimic the important light-driven process, photosystem II [27–29]. Realizing the importance of Ru(II)-polypyridyl complexes as model photosensitizers and phenols as electron donors in photosystem II, several researchers have investigated the photoinduced electron transfer (PET) reactions of ruthenium(II)-polypyridyl complexes with several phenols in homogeneous medium and the formation of phenoxyl radical as the transient has been established using time-resolved techniques [12–15, 30–34]. The PET 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 an increase in the electron transfer distance [12–15]. The rate of ET 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 ( $\Delta G^0$ ) of the reaction, the reorganization energy ( $\lambda$ ) and the electron transfer distance ( $d$ ) between the donor and acceptor [12–15, 34].

Phenols are known to quench the luminescence of  $*[\text{Ru}(\text{NN})_3]^{2+}$  by the mechanism involving ET from phenols to photoexcited Ru(II) complexes [12, 13, 30–34]. The quenching studies are performed in the presence of NaOH, since most of the phenols do not quench  $*[\text{Ru}(\text{NN})_3]^{2+}$  in neutral medium [14, 15]. As far as phenols are concerned they are in the undissociated form at low pH, i.e.,  $\text{pH} < \text{p}K_a$ , but they are in the form of phenolate ions at high pH, i.e.,  $\text{pH} > \text{p}K_a$ . Further in more acidic condition, the reducing capacity of the phenols may be suppressed due to protonation, whereas in more basic condition, the reducing capacity of the phenols enhances due to the formation of phenolate ions [16, 17]. When the phenols are in the undissociated form, the formation of phenoxyl radical involves the removal of hydrogen atom. It may take place in a single step or in a sequence of steps, i.e., the ET followed by proton transfer (PT) or PT followed by ET. Because of its importance in different situations, the study of the mechanism of the conversion of phenol to phenoxyl radical has received much importance in recent years, particularly with the excited state  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes [35–37].

Based on the reviews, the present study concentrates on the quenching behavior of tris (4,4'-dialkyl-2,2'-bipyridine) ruthenium(II) complexes with polyphenols and thymol in 50 % aqueous acetonitrile at pH 11. The transient absorption spectra confirm the formation of phenoxyl radical and  $[\text{Ru}(\text{NN})_3]^+$  complex and thus foretell the electron transfer

nature of the reaction of the excited state  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with quenchers in 50 % aqueous acetonitrile at pH 11. Further, the electronic absorption spectra validate the nature of quenching (static or dynamic) that takes place in these PET reactions. Marcus Semiclassical theory of electron transfer is applied successfully for the photoluminescence quenching of ruthenium(II)-polypyridyl complexes with these phenols.

## Experimental

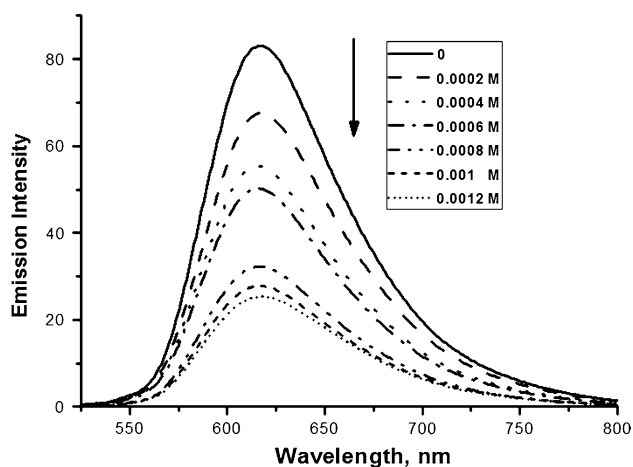
### Materials

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , 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, thymol, 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  $\text{NN} = 2,2'$ -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 [33, 38, 39]. The chloride salt of  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex was treated with sodium tetrafluoroborate to get the  $\text{BF}_4^-$  salt  $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ .

### Equipments

Samples of the  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes as well as the quenchers in 50 % aqueous acetonitrile 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 [40]. 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)



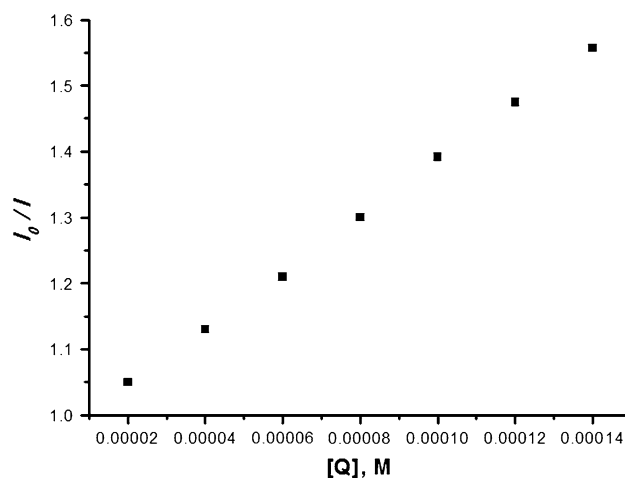
**Fig. 1** The change in emission intensity of  $[\text{Ru}(\text{dtbpv})_3]^{2+}$  with different concentrations of *p*-coumaric acid ( $2 \times 10^{-4}$ – $1.2 \times 10^{-3}$  M) in 50 % aqueous acetonitrile at pH 11

the absorbance change. Transient spectra were obtained by a point-to-point technique, monitoring the absorbance changes ( $\Delta A$ ) 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 complexes,  $[\text{Ru}(\text{NN})_3]^{2+}$  and the oxidation potentials of the polyphenols and thymol in 50 % aqueous acetonitrile at pH 11 were determined by cyclic voltammetric technique using CH1604C electrochemical analyzer. A glassy carbon (working electrode), Pt (counter electrode) and (Ag/Ag<sup>+</sup>) electrode (reference electrode) were used for the electrochemical measurements and tetrabutylammonium perchlorate was the supporting electrolyte. Cyclic voltammograms were recorded after purging the solution with dry nitrogen gas for 30 min.

#### Luminescent quenching studies

The photochemical reduction of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with these phenolate ions has been studied by the luminescence quenching technique. A mixed solvent system is used in the present study due to solubility problems with some substituted phenolate ions in aqueous medium. The  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes taken in the present study are stable in 50 % aqueous acetonitrile at pH 11 and their stability was checked by absorption spectral studies. 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 sample solutions were purged carefully with dry nitrogen for 30 min. The concentrations of the complexes were maintained at  $1.5 \times 10^{-5}$  M in all the samples and the quencher concentrations were between  $2 \times 10^{-5}$  and  $1.4 \times 10^{-3}$  M. The luminescence



**Fig. 2** Stern–Volmer plot for the reductive quenching of  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  with quercetin in 50 % aqueous acetonitrile at pH 11

measurements (Fig. 1) 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 (Fig. 2) using the equations given below [41, 42]:

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

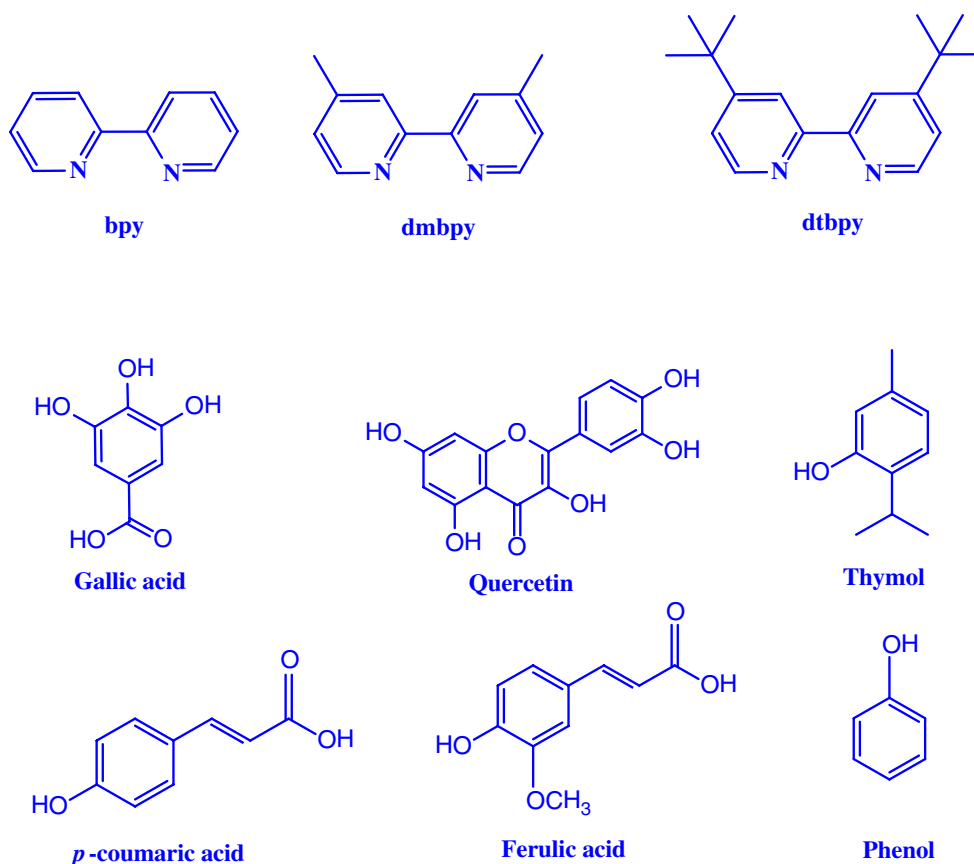
$$K_{\text{SV}} = k_q\tau \quad (2)$$

where  $I_0$  and  $I$  are the luminescence intensities of Ru(II) complexes in the absence and presence of quencher and  $\tau$  is the excited state lifetimes of Ru(II) complexes in the absence of quencher, respectively,  $K_{\text{SV}}$  is the Stern–Volmer constant and  $k_q$  is the quenching rate constant.

#### Results and discussion

The structure of the ligands and the quenchers used in the present study are shown in Fig. 3. The absorption and emission spectral data, the excited state lifetime ( $\tau$ ) and redox potential of the  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes vs. Ag/Ag<sup>+</sup> in 50 % aqueous solution at pH 11 are measured and the data collected in Table 1.

The lifetime of the Ru(II)-polypyridyl complexes is highly sensitive to the change of medium. Lifetime of the Ru(II)-polypyridyl complexes in 50 % aqueous acetonitrile at pH 11 has been measured in the present study and collected in Table 1. However, the  $\tau$  values of these complexes in mixed solvents are available in the literature, the experimental conditions used in this study are different, i.e., at pH 11. Hence, the measurements have been done in 50 %



**Fig. 3** Structure of the ligands and the quenchers

**Table 1** Absorption and emission spectral data, excited state lifetime and redox potentials of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes in 50 % aqueous acetonitrile at pH 11 at 293 K

Complex	Absorption maximum, nm	Emission maximum, nm	Excited state lifetime ( $\tau$ ), ns	Redox potential	
				$E^0_{(\text{Ru}^{2+}/+)} \text{, V}$	$E^0_{(\text{Ru}^{2+*}/+)} \text{, V}$
$[\text{Ru}(\text{bpy})_3]^{2+}$	450	614	740 (740) <sup>a</sup>	-1.36	0.74
$[\text{Ru}(\text{dmbpy})_3]^{2+}$	458	622	580 (540) <sup>a</sup>	-1.45	0.65
$[\text{Ru}(\text{dtbpy})_3]^{2+}$	458	618	697 (728) <sup>b</sup>	-1.39	0.71

<sup>a</sup> The value in the parenthesis represents the reported lifetime of Ru(II) complexes in 50 % aqueous acetonitrile at pH 13, Ref. [12]

<sup>b</sup> The value in the parenthesis represents lifetime in 80 %  $\text{CH}_3\text{CN}$ -20 %  $\text{H}_2\text{O}$  at pH 13, Ref. [13]

aqueous acetonitrile at pH 11 and the measured values vary slightly from the reported values [12, 13].

Luminescence quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  in 50 % aqueous acetonitrile at pH 11

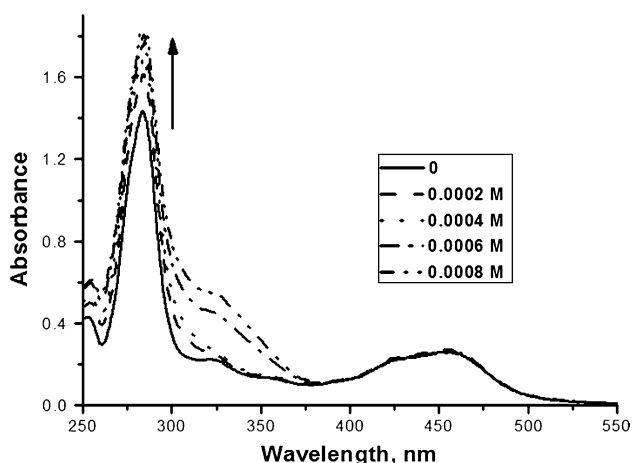
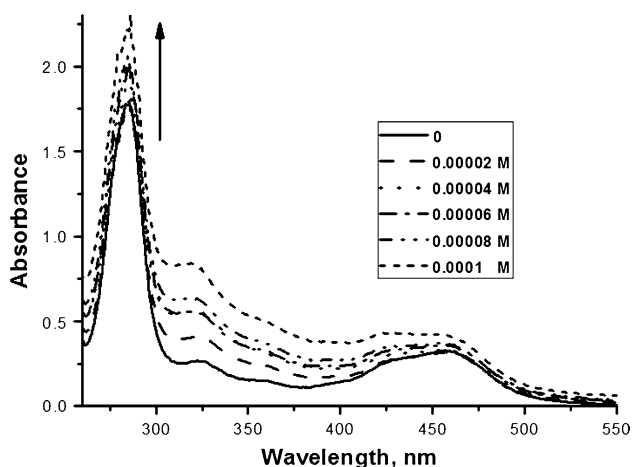
The bimolecular quenching rate constant ( $k_q$ ) values for the reductive quenching of three Ru(II)-polypyridyl complexes  $*[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $*[\text{Ru}(\text{dmbpy})_3]^{2+}$  and  $*[\text{Ru}(\text{dtbpy})_3]^{2+}$  with phenolate ions of polyphenols and thymol measured from the Stern–Volmer plots are given in Table 2. Further, the

oxidation potential ( $E^0_{\text{oxd}}$ ) of the phenolate ions and the free energy change ( $\Delta G^0$ ) values, calculated from the reduction potentials of  $[\text{Ru}(\text{NN})_3]^{2+}$  and oxidation potentials of phenolate ions, are also given in Table 2. The Stern–Volmer plots from the emission intensity data (Fig. 2) are linear for all photoredox systems in the present experimental condition.

To check the ground-state complex formation, phenols are added in increments to the  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes and the spectra are recorded at different concentrations. There is no significant change in the absorption spectra of  $[\text{Ru}(\text{NN})_3]^{2+}$  in the presence of phenol, *p*-coumaric

**Table 2** Bimolecular quenching rate constants ( $k_q$ ), oxidation potential of quenchers vs.  $\text{Ag}/\text{Ag}^+$  ( $E_{\text{oxd}}^0$ ) and free energy change ( $\Delta G^0$ ) for the reductive quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  with the phenols in 50 % aqueous acetonitrile at pH 11 at 293 K

Quencher	$E_{\text{oxd}}^0$ , vs. $\text{Ag}/\text{Ag}^+$ (V)	$[\text{Ru}(\text{bpy})_3]^{2+}$		$[\text{Ru}(\text{dmbpy})_3]^{2+}$		$[\text{Ru}(\text{dtbpy})_3]^{2+}$	
		$k_q$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$\Delta G^0$ (eV)	$k_q$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$\Delta G^0$ (eV)	$k_q$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$\Delta G^0$ (eV)
Phenol	0.86	$7.0 \times 10^8$	0.075	$5.3 \times 10^8$	0.16	$3.0 \times 10^8$	0.10
<i>p</i> -coumaric acid	0.63	$8.1 \times 10^8$	-0.15	$6.4 \times 10^8$	-0.07	$5.5 \times 10^8$	-0.12
Ferulic acid	0.57	$2.4 \times 10^9$	-0.21	$1.7 \times 10^9$	-0.13	$1.2 \times 10^9$	-0.19
Thymol	0.44	$4.1 \times 10^9$	-0.34	$3.4 \times 10^9$	-0.26	$2.1 \times 10^9$	-0.31
Quercetin	0.25	$8.5 \times 10^9$	-0.53	$6.8 \times 10^9$	-0.45	$5.7 \times 10^9$	-0.50
Gallic acid	0.37	$1.2 \times 10^{10}$	-0.41	$1.1 \times 10^{10}$	-0.33	$8.2 \times 10^9$	-0.39

**Fig. 4** Absorption spectra of  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  with incremental addition of ferulic acid ( $2 \times 10^{-4}$ – $8 \times 10^{-4}$  M) in 50 % aqueous acetonitrile at pH 11**Fig. 5** Absorption spectra of  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  with incremental addition of quercetin ( $2 \times 10^{-5}$ – $1 \times 10^{-4}$  M) in 50 % aqueous acetonitrile at pH 11

acid, ferulic acid, and thymol ( $2 \times 10^{-4}$ – $1.4 \times 10^{-3}$  M) under the present experimental conditions which helps us to conclude that the contribution from the static quenching

is negligible for phenol, *p*-coumaric acid, ferulic acid, and thymol (Fig. 4). Similar results have been reported for Ru(II)-polypyridyl complexes with *p*-methoxy phenol in acetonitrile and aqueous mediums [13, 15].

Gallic acid and quercetin ( $2 \times 10^{-5}$ – $1.4 \times 10^{-4}$  M) form ground-state complexes with  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes in 50 % aqueous acetonitrile at pH 11, since gallic acid and quercetin have weak absorption close to the region where Ru(II) complexes have strong MLCT absorption. Gallic acid and quercetin have weak absorptions at 454 and 426 nm [16]; hence, gallic acid and quercetin bind with the  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes in the present experimental condition. The absorption spectra of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with the quenchers (Fig. 5), gallic acid and quercetin show a hypsochromic shift of 2–3 nm, which may be 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 equations [43–45] for the absorption and emission spectral data in 50 % aqueous acetonitrile and aqueous medium at pH 11 is given in Table 3. The  $K_a$  obtained for gallic acid and quercetin with  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes is in the order of  $10^3$ – $10^4$   $\text{M}^{-1}$ .

The Stern–Volmer plots for the reductive quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with gallic acid and quercetin in the present experimental condition are indicative of dynamic quenching; it appears reasonable to follow that the formation of adducts is responsible for competition between static and dynamic quenching pathway. Linear Stern–Volmer plots are not a conclusive evidence for dynamic quenching [46, 47]. Though the Stern–Volmer plots are linear for the reductive quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with gallic acid and quercetin, absorption spectral studies and the corresponding association constant values confirm the static nature of quenching. This type of reports has been previously reported for  $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$ /1,4-dihydroquinone couple in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  [47, 48] and  $[\text{Ru}(\text{bpz})_3]^{2+}$ /phenol couple in  $\text{CH}_3\text{CN}$

**Table 3** Association constant,  $K_a$  ( $M^{-1}$ ) obtained from absorption and emission spectral data for gallic acid and quercetin with  $[Ru(NN)_3]^{2+}$  complexes in 50 % aqueous acetonitrile at pH 11 at 293 K

Complex	Association constant, $K_a$ ( $M^{-1}$ )			
	Absorption data		Emission data	
	Gallic acid	Quercetin	Gallic acid	Quercetin
$[Ru(bpy)_3]^{2+}$	$1.8 \times 10^3$	$2.5 \times 10^4$	$2.4 \times 10^3$	$2.1 \times 10^4$
$[Ru(dmbpy)_3]^{2+}$	$6.1 \times 10^3$	$4.2 \times 10^4$	$5.5 \times 10^3$	$3.0 \times 10^4$
$[Ru(dtbp)_3]^{2+}$	$7.9 \times 10^3$	$5.7 \times 10^4$	$7.0 \times 10^3$	$4.8 \times 10^4$

[46]. Thus, the absorption and emission spectral studies on this photoredox systems report static as well as dynamic quenching.

The  $k_q$  data in Table 2 show that gallic acid acts as the most efficient quencher in this PET reaction. Gallic acid consists of four potential acidic protons having  $pK_a$  values of 4.0 (carboxylic acid), 8.7, 11.4, and >13 (phenolic OHs). The known  $pK_a$  values of the gallate radical are ~4 for the carboxyl group and 5.0 for phenolic hydrogen. In alkaline medium especially above pH 9, the carboxylic acid as well as the three phenolic–OH groups gets ionized [49, 50]. 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 [51, 52]. The  $pK_a$  values of quercetin are 5.87 and 8.48 [16, 53]. The  $pK_a$  values for the phenolic–OH group in phenol, *p*-coumaric acid, ferulic acid and thymol are 10, 9.5, 9.4, and 10.6, respectively [51, 53, 54]. The quenching process is highly sensitive to the pH of the medium. PET reactions are carried out at  $pH > pK_a$  [15]; here, in this quenching study, the pH is maintained at 11. Based on the  $pK_a$  values of the quenchers taken in the present study,  $[Ru(NN)_3]^{2+}$  complexes with quenchers in 50 % aqueous acetonitrile at pH 11 undergo PET reactions.

The bond dissociation energy (BDE) of the phenolic–OH group in gallic acid (75.5 kcal/mol) [53, 55] is less than that of quercetin (77 kcal/mol for 3'–OH and 74.8 kcal/mol for 4'–OH groups of ring B), *p*-coumaric acid, ferulic acid, thymol, and phenol [52, 53]. Based on the BDE, the phenolic–OH group of gallic acid undergoes ionization more easily than quercetin, *p*-coumaric acid, ferulic acid, thymol, and phenol. Interestingly, the quenching rate constant increases, when the number of phenolic–OH groups present in the quencher increases. Here, gallic acid and quercetin consist 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 [51, 52]. 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 [56, 57]. The quenching efficiency of thymol is somewhat lower than quercetin, due to the presence of one phenolic –OH and the isopropyl group at the *ortho*-position of phenol exerting a slight steric hindrance there by reducing the quenching rate constant. The hydroxyl derivatives of cinnamic acid (*p*-coumaric acid and ferulic acid) show the least  $k_q$  values compared to gallic acid, quercetin, and thymol. 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. 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. Here, the nature of the substituent present in the *ortho*- and *para*-positions of phenols affects the  $k_q$  values.

Further, the absorption spectral studies of  $[Ru(NN)_3]^{2+}$  complexes with gallic acid and quercetin in 50 % aqueous acetonitrile at pH 11 show ground-state complex formation, which confirm the static nature of quenching. The ground-state interactions between phenol and the bipyridyl rings of  $[Ru(NN)_3]^{2+}$  complexes are hydrophobic or  $\pi$ -stacking in nature [58, 59]. To the extent that  $\pi$ – $\pi$  stacking interactions exist between the ligands of Ru(II)-polypyridyl complexes and the quenchers, the binding becomes stronger, thus playing a vital role in mediating PET reactions [58, 59]. The association constant calculated for gallic acid and quercetin from the absorption and emission spectral data shows that quercetin undergoes strong binding with the  $[Ru(NN)_3]^{2+}$  complexes than that of gallic acid. Due to this ground-state interaction of gallic acid and quercetin with  $[Ru(NN)_3]^{2+}$  complexes, they act as efficient quenchers compared to *p*-coumaric acid, ferulic acid, thymol, and phenol in the present experimental condition.

The oxidation potential of these quenchers depends on the nature of the substituent present in *ortho*- and *para*-positions of phenols. Phenols with lower oxidation potential exhibit higher quenching rate constant and act as efficient quencher in the PET reactions, a trend that is indicative of ET quenching. The  $k_q$  data given in Table 2 show that the  $k_q$  is sensitive to the oxidation potential of polyphenols and thymol (except quercetin). The compounds with two or more electron-donating groups have lower oxidation potential than mono-substituted phenols, although –OH groups have stronger effect than –OCH<sub>3</sub> ones due to the strong electron-donating ability of the hydroxyl group [7, 60]. The introduction of additional –OH group makes the quencher better electron donor and thus lowers the oxidation potential. The oxidation potential of gallic acid, quercetin,



thymol, ferulic acid, *p*-coumaric acid, and phenol in 50 % aqueous acetonitrile at pH 11 is 0.37, 0.25, 0.44, 0.57, 0.63, and 0.86 V, respectively. Here, the oxidation potential of the phenols containing electron-releasing groups in the *ortho*- and *para*-positions is very low, i.e.,  $\Delta G^0$  becomes more negative. The  $\Delta G^0$  values (Table 2) indicate that all reactions are exergonic except the reaction involving the parent substrate, phenol. The lowest  $k_q$  value observed for the luminescence quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with phenol is in accordance with the highest  $\Delta G^0$  value. This is in good agreement with the reported  $k_q$  value for luminescent quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$  by phenol in aqueous medium at pH 12.5 [14].

The order of  $\Delta G^0$  values for the ET reaction of  $[\text{Ru}(\text{NN})_3]^{2+}$  with phenolate ions in 50 % aqueous acetonitrile at pH 11 is phenol > *p*-coumaric acid > ferulic acid > thymol > gallic acid > quercetin. The order of  $k_q$  values for luminescent quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  by the phenolate ions in the present experimental conditions is gallic acid > quercetin > thymol > ferulic acid > *p*-coumaric acid > phenol. The  $\Delta G^0$  value for the ET reaction of  $[\text{Ru}(\text{NN})_3]^{2+}$  with quercetin is lower than that of gallic acid, but lower  $k_q$  value of this photoredox system indicates that the  $k_q$  not only depends on the  $\Delta G^0$  value but also on other factors like reorganization energy ( $\lambda$ ) and electron transfer distance ( $d$ ) between the electron donor and the acceptor [34]. The  $k_q$  values of thymol, ferulic acid, *p*-coumaric acid, and phenol depend on the  $\Delta G^0$  values.

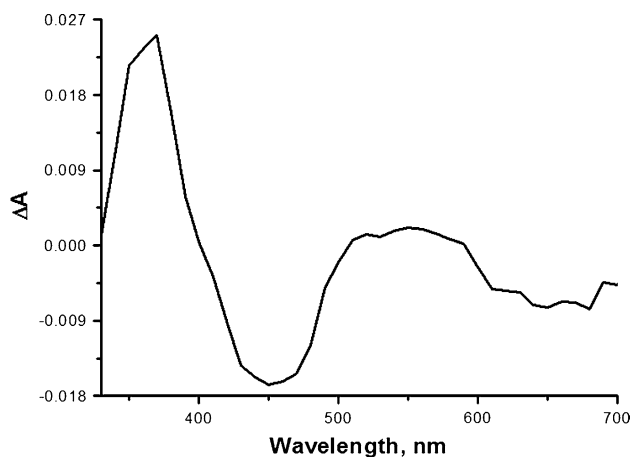
The  $k_q$  also depends on the electron transfer distance between the sensitizer (Ru(II)) and the quencher. The  $k_q$  value for the luminescence quenching of Ru(II) complexes with the phenols in 50 % aqueous acetonitrile at pH 11 changes with the change of the ligand, the value decreases from  $[\text{Ru}(\text{bpy})_3]^{2+}$  to  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  when the ligand is changed from bpy to dtbpy. The introduction of bulky ligand increases the size of the reactant and the distance of ET which affects the rate of ET [14]. The ET distance is calculated by simply adding the radii of  $[\text{Ru}(\text{NN})_3]^{2+}$  and  $\text{ArO}^-$ . 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, respectively [13]. The radius of the quenchers is estimated from MM2 molecular model and the radii of gallic acid, quercetin, thymol, and phenol are 4.1, 5.93, 3.9, 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 ET distance.

The ET distances 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 ET distances of  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  and  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  complexes with thymol and phenol are 11, 11.8 and 13.1 Å; 10.9, 11.7 and 13

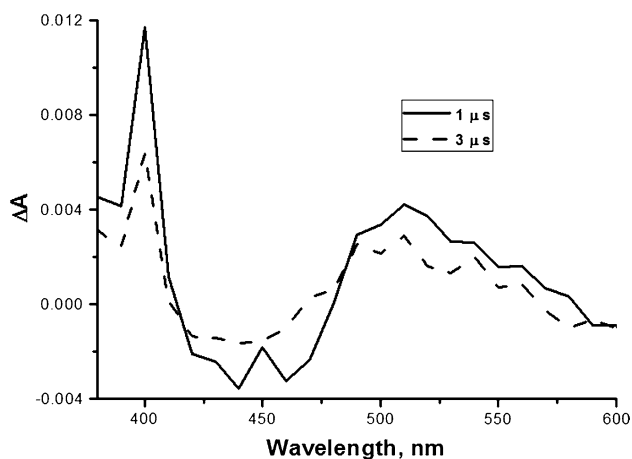
Å. The ET distances of  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  and  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  complexes with *p*-coumaric acid and ferulic acid are same and the values are 11.9, 12.7 and 14 Å, respectively. Thus, the ET between the phenolate ion and the  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes obtained in the present study is in the range 10.9–15.13 Å. Phenol shows less ET distance than thymol, gallic acid, *p*-coumaric acid, ferulic acid, and quercetin. Based on the ET distance, phenol shows higher quenching rate constant than other quenchers taken in the present study, but this is not true in this case due to its uppermost  $\Delta G^0$  value. Quercetin exerts greater ET distance than other quenchers, but due to the lowest  $\Delta G^0$  value, they act a more efficient quencher than thymol, ferulic acid, *p*-coumaric acid, and phenol. Though quercetin shows lowest  $\Delta G^0$  value than gallic acid, it reduces the quenching efficiency when compared to gallic acid due to its greater ET distance. These findings indicate that the  $k_q$  value depends not only on the ET distance but also on  $\Delta G^0$  value

The ET distance is more in  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  than  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$  hence, the  $k_q$  value of  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  with the quenchers is lower than that of the other complexes in the present study. The  $k_q$  of the three complexes with the polyphenols and thymol is in the order  $[\text{Ru}(\text{bpy})_3]^{2+} > [\text{Ru}(\text{dmbpy})_3]^{2+} > [\text{Ru}(\text{dtbpy})_3]^{2+}$ . The  $k_q$  of  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  and  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  with gallic acid is  $1.2 \times 10^{10}$ ,  $1.1 \times 10^{10}$  and  $8.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, which indicates a decrease in the quenching efficiency by changing the ligands from bpy to dtbpy. These results are in good agreement with the  $k_q$  obtained for the quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  and  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  with 2,6-di-*tert*-butyl phenolate ion in 80 %  $\text{CH}_3\text{CN}$ –20 %  $\text{H}_2\text{O}$ ; the  $k_q$  for  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  is 30 times less than that for  $[\text{Ru}(\text{bpy})_3]^{2+}$  [13].

The reductive quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  by the phenolate ions has been confirmed from the transient absorption spectra (Figs. 6, 7). The band at 400 and 510 nm in the transient absorption spectra of  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  with gallic acid (Fig. 7) confirms the formation gallate radical and  $[\text{Ru}(\text{dmbpy})_3]^+$  as transient species. Thus, the present study confirms the reductive quenching of tris(4,4'-dialkyl-2,2'-bipyridine)ruthenium(II) complexes with phenolate ions. These results corroborate with the previous reports on the reductive quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Ru}(\text{H}_2\text{dcbpy})_3]^{2+}$  with 4-methoxy phenolate ions [12, 15]. 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 ET occurs in this association complex  $[\text{Ru}(\text{NN})_3]^{2+} \dots \text{ArO}^-$  resulting in 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 ET leading to the formation of the original reactants.



**Fig. 6** Transient absorption spectrum of  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  in 50 % aqueous acetonitrile recorded after 1  $\mu\text{s}$  of 355 nm laser flash photolysis

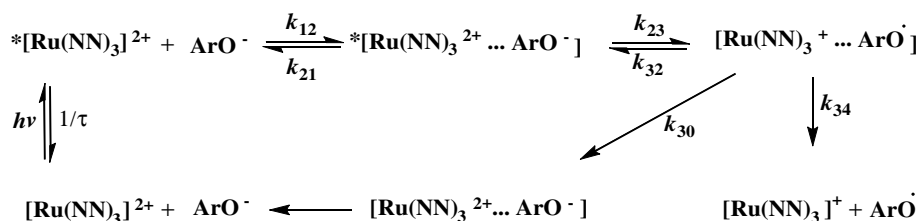


**Fig. 7** Transient absorption spectra of  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  in the presence of  $1 \times 10^{-4}$  M gallic acid in 50 % aqueous acetonitrile recorded after 1 and 3  $\mu\text{s}$  of 355 nm laser flash photolysis

**Kinetics of electron transfer reactions of Ru(II) complexes with phenols**

The rate constants of the ET reaction ( $k_{\text{et}}$ ) using Marcus semiclassical theory of ET have been calculated after finding the ET nature of these photoredox systems

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



[61–64]. According to the semiclassical formulation of Marcus theory, the rate constant for the PET from  $\text{ArO}^\cdot$  to  $[\text{Ru}(\text{NN})_3]^{2+}$  is given by Eq. 3.

$$k_{\text{et}} = 4\pi^2/h|H_{\text{DA}}|^2[4\pi\lambda_0k_{\text{B}}T]^{-1/2} \sum_{m=0}^{\infty} e^{-S} S^m/m! \times \exp[-(\lambda_0 + \Delta G^0 + mh\nu)^2/4\lambda_0k_{\text{B}}T] \quad (3)$$

where  $H_{\text{DA}}$  is the electronic coupling coefficient between the redox centers, the reorganization energy  $\lambda$  is composed of solvational  $\lambda_0$  and vibrational  $\lambda_i$  contributions with  $S = \lambda_i/h\nu$ ,  $\nu$  is the high-energy vibrational frequency associated with the acceptor and  $m$  is the density of product vibrational levels. The terms  $h$  and  $k_{\text{B}}$  are the Planck's and Boltzmann constants, respectively.

According to Rehm and Weller, the free energy change of ET reaction ( $\Delta G^0$ ) is calculated from Eq. 4 [65].

$$\Delta G^0 = E_{(\text{D}^+/\text{D})} - E_{(\text{A}/\text{A}^-)} - E_{0-0} + w_{\text{p}} \quad (4)$$

where  $E_{(\text{D}^+/\text{D})}$  is the oxidation potential of donors,  $E_{(\text{A}/\text{A}^-)}$  is the reduction potential of acceptor,  $E_{0-0}$  the lowest excited state energy of Ru(II) complexes, and  $w_{\text{p}}$  is the Coulombic stabilization energy of the radical ion pair intermediate formed in the course of the PET reaction and its value is  $-0.045$  eV [66]. The  $\Delta G^0$  values calculated for different donor and acceptor pairs in 50 % aqueous acetonitrile at pH 11 from Eq. 4 are shown in Table 2. The value of  $\lambda_0$  can be evaluated classically using dielectric continuum model, Eq. 5.

$$\lambda_0 = \frac{(\Delta e)^2}{4\pi\epsilon_0} \cdot (1/2r_{\text{D}} + 1/2r_{\text{A}} + 1/d) \cdot (1/D_{\text{OP}} - 1/D_{\text{S}}) \quad (5)$$

where  $e$  is the elementary charge,  $\epsilon_0$  is the permittivity of free space,  $D_{\text{op}}$  and  $D_{\text{s}}$  are the optical and static dielectric constants, respectively. The terms  $r_{\text{D}}$  and  $r_{\text{A}}$  are the radii of the electron donor and the acceptor and  $d$  is the separation distance between the donor and the acceptor in the encounter complex. The value of  $\lambda_0$  calculated from Eq. 5 for the PET reactions of  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  and  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  complexes with polyphenols and thymol in 50 % aqueous acetonitrile at pH 11 is in the range 0.55–0.84 eV. The value of  $\lambda_i$  is found to be 0.2 eV and is employed

in the calculation of rate constant for ET. Thus, the values of  $\lambda$  for these photoredox systems are in the range 0.75–1.04 eV. The  $-\Delta G^0$  values (Table 2) for all the photoredox reactions in the present study are less than that of the reorganization energy; thus, the rate constant of these photoredox reactions falls in the normal region. In the normal region ( $-\Delta G^0 < \lambda$ ), the ET rate increases with increasing driving force.

Since the quenching process occurs via ET, the redox quenching process can be discussed in terms of the mechanism shown in Scheme 1. By applying steady-state action to the short-lived species in Scheme 1, the following expression (Eq. 6) for the observed bimolecular quenching rate constant,  $k_{\text{obs}}$  ( $k_q$ ) can be derived.

$$k_q = k_{12}/1 + (k_{12}/(k_{23}K_{\text{eq}})) \quad (6)$$

$K_{\text{eq}}$  is the equilibrium constant for the formation of the encounter complex and  $k_{12}$  is the rate constant for the diffusion process to form the encounter complex. The  $k_{12}$  is calculated from Eq. 7 [63].

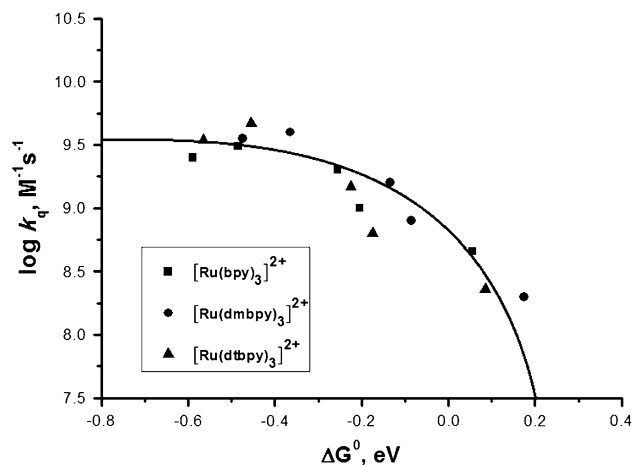
$$k_{12} = 2RT/3000 \eta [2 + r_D/r_A + r_A/r_D] f \quad (7)$$

where  $f^{-1} = \int_0^d \frac{e^{u/kT}}{Z_D Z_A e^2/D_S [e^{Kd}/1 + Kd]} e^{kr/r} dr/r^2$ , with  $u = Z_D Z_A e^2/D_S [e^{Kd}/1 + Kd] e^{kr/r}$ .

where  $K = 8\pi e^2 N \eta / (1,000 D_S k T)^{1/2}$ ,  $r_D$  and  $r_A$  are the radii of the reactants and  $\eta$  is the viscosity of the medium. The diffusion rate constant  $k_{12}$ , calculated according to Smoluchowski [67] for non-charged molecules, has a value of  $1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .  $K_{\text{eq}}$  is estimated using the Fuoss equation Eq. 8 [68].

$$K_{\text{eq}} = (4\pi N d^3 / 3000) \exp(-w^r/RT) \quad (8)$$

where  $w^r$  is the work required to bring the reactants to the separation distance  $d$ . Since neutral quenchers are used throughout this study,  $w^r$  is zero. The values of  $K_{\text{eq}}$  are found to be in the range 3.26–8.7  $\text{M}^{-1}$  for the reductive quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $[\text{Ru}(\text{bmbpy})_3]^{2+}$  and  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  complexes with polyphenols and thymol. Since the values of  $k_{12}$  and  $K_{\text{eq}}$  are known, the value for  $k_{23}$  ( $k_{\text{et}}$ ), the rate constant for the process of ET in the encounter complex can be calculated from the observed  $k_q$  values using Eq. 6. To understand the effect of  $\Delta G^0$  on the  $k_q$  of this photoredox system,  $\log k_q$  (experimental and theoretical values) is plotted against  $\Delta G^0$  (Fig. 8). The solid line curve shows the theoretical value of  $\log k_q$  obtained from Marcus semiclassical theory. The data given in Fig. 8 confirm a close agreement between the experimental and theoretical quenching rate constant values. The rate constant for ET reaction of these redox systems is in accordance with Rhem–Weller model; the ET rate increases with an increase in driving force, reaches a diffusion-limit and remains unchanged no matter how exergonic the ET might become [65]. Thus, the semiclassical theory of ET reproduces the experimental results favorably confirming the success of



**Fig. 8** Plot of experimental and theoretical values of  $\log k_q$  vs.  $\Delta G^0$  (eV) of  $[\text{Ru}(\text{NN})_3]^{2+}$  with quenchers in 50 % aqueous acetonitrile at pH 11, solid line represents the theoretical values of  $\log k_q$

the theory of ET and the operation of ET mechanism of the reaction in 50 % aqueous acetonitrile at pH 11.

## Conclusion

The  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $[\text{Ru}(\text{bmbpy})_3]^{2+}$  and  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  complexes undergo facile ET reaction with phenols in 50 % aqueous acetonitrile at pH 11 in the excited state. Absorption spectral studies and the association constant data obtained from the absorption and emission spectral data confirm the static nature of quenching for  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with gallic acid and quercetin. Also, thymol, ferulic acid, *p*-coumaric acid, and phenol undergo dynamic quenching with  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes. The  $k_q$  values of these PET reactions are highly sensitive to the free energy change of the reaction, ET distance between the  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes and the quencher and the reorganization energy. The study further confirms the hydrophobic or  $\pi$ - $\pi$  stacking interactions and the substituent effect on the electron transfer reactions of biologically important phenolate ions with the excited state  $^*[\text{Ru}(\text{NN})_3]^{2+}$  complexes. The detection of phenoxyl radical and  $[\text{Ru}(\text{NN})_3]^+$  as transient in the transient absorption spectra confirms the ET nature of the reaction. Further, the successful application of semiclassical theory of ET to the photoluminescence quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $[\text{Ru}(\text{bmbpy})_3]^{2+}$  and  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  complexes with phenols in 50 % aqueous acetonitrile at pH 11 also supports the ET nature of the reaction.

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