

Luminescence quenching of tris (2, 2'-bipyridyl) ruthenium (II) cation with phenolate ions in aqueous medium

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ABSTRACT

The quenching of the excited state $[Ru(bpy)_3]^{2+}$ ($bpy = 2,2'$ - bipyridine) complex with biologically important phenols (p -coumaric acid, ferulic acid, thymol, quercetin and gallic acid) proceeds through photo induced electron transfer reaction in aqueous medium at pH 11 and has been studied by luminescence quenching technique. The complex shows absorption and emission maximum at 450 and 625 nm in aqueous medium. The reductive quenching of $[Ru(bpy)_3]^{2+}$ by phenolate ions has been confirmed from the transient absorption spectrum. The quenching rate constant, (k_q) is highly sensitive to the active phenolate ions present in the quenchers. Structural effects seem to play an important role in the photo induced electron transfer reactions of the complex and the quencher in aqueous medium.

Keywords: Luminescence quenching; Stern-Volmer equation; photo induced electron transfer; structural effects

Introduction

Luminescence quenching is an important technique used to obtain adequate information about structure and dynamics of luminescent molecules. It is a process, in which the luminescence intensity of the solute decreases by a variety of molecular interactions such as excited state reactions, molecular rearrangements, energy transfer, ground-state complex formation and collision-quenching ^[1]. The conversion of phenol to phenoxyl radical is of interest to chemists because of its involvement in biologically important processes ^[2]. The one electron oxidation of phenolate 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 ruthenium polypyridyl complexes ($[Ru(NN)_3]^{2+}$), have attracted the chemists in the design of light-driven water splitting photoanodes ^[3], molecular probes ^[4], construction of solar cells ^[5], artificial photosynthesis, molecular machine devices and organic light emitting diodes ^[6]. This is due to the combination of excellent photophysical and electrochemical properties of the complexes.

Numerous works have been reported on the importance of the substituent, pH, steric and electronic effects on the photoinduced electron transfer reactions of *ortho*-, *meta*- and *para*-substituted phenolate ions to the excited state $Ru(II)$ -polypyridine complexes in various solvents ^[7,8]. The present study concentrates on the quenching behavior of the $[Ru(bpy)_3]^{2+}$ complex with polyphenols and thymol (quenchers) in aqueous medium at pH 11. The Stern-Volmer plot. The transient absorption

spectra confirm the electron transfer nature of the reaction of the excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ with polyphenols in aqueous medium at pH 11, where the quenching process proceeds through the formation of phenolate ions.

Experimental Section

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, ligand (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. The complex, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ was synthesized according to the procedure previously described^[7].

Samples of the complex, $[\text{Ru}(\text{bpy})_3]^{2+}$ as well as the quenchers in aqueous medium were freshly prepared for each measurement. Absorption spectra were measured using SYSTRONICS 2203 double beam spectrophotometer. Emission spectra were recorded using JASCO FP-6300 spectrofluorometer. All the spectral measurements were carried out at 298 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. 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 structure of the ligand and the quenchers used in the present study are shown in Fig. 1. 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 $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with these phenolate ions has been studied by the luminescence quenching technique. The sample solutions were purged carefully with dry nitrogen for 30 min. The luminescence measurements (Fig. 2) were performed at different quencher concentration and the quenching rate constants, k_q , were determined from Stern-Volmer plots (Fig. 3) using the equation given below^[9].

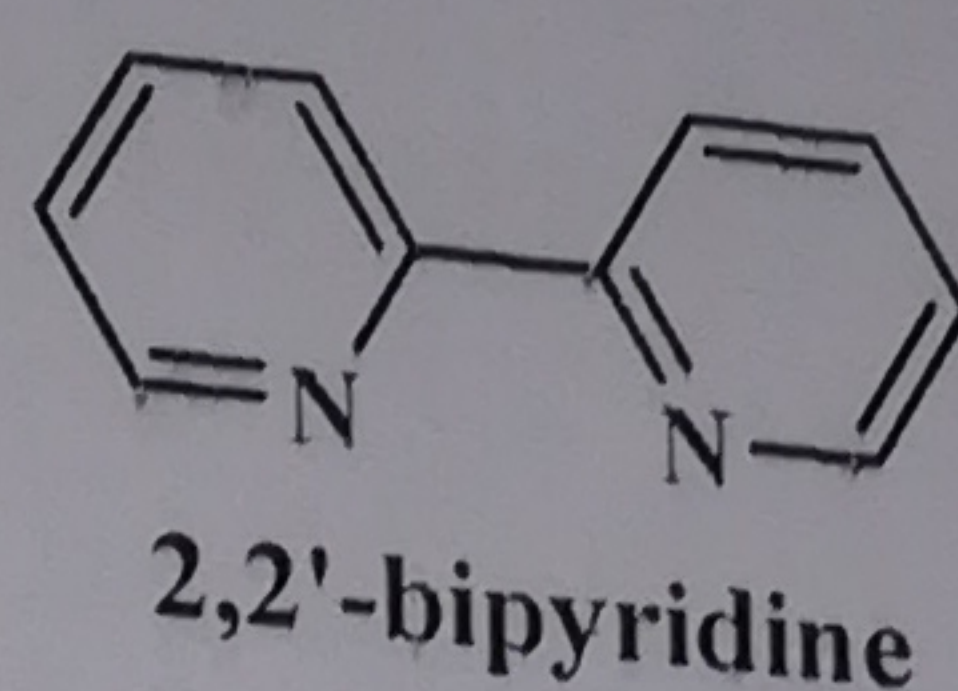
$$I_0 / I = 1 + k_q \tau_0 [Q]$$

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

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Fig. 2
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Quenchers

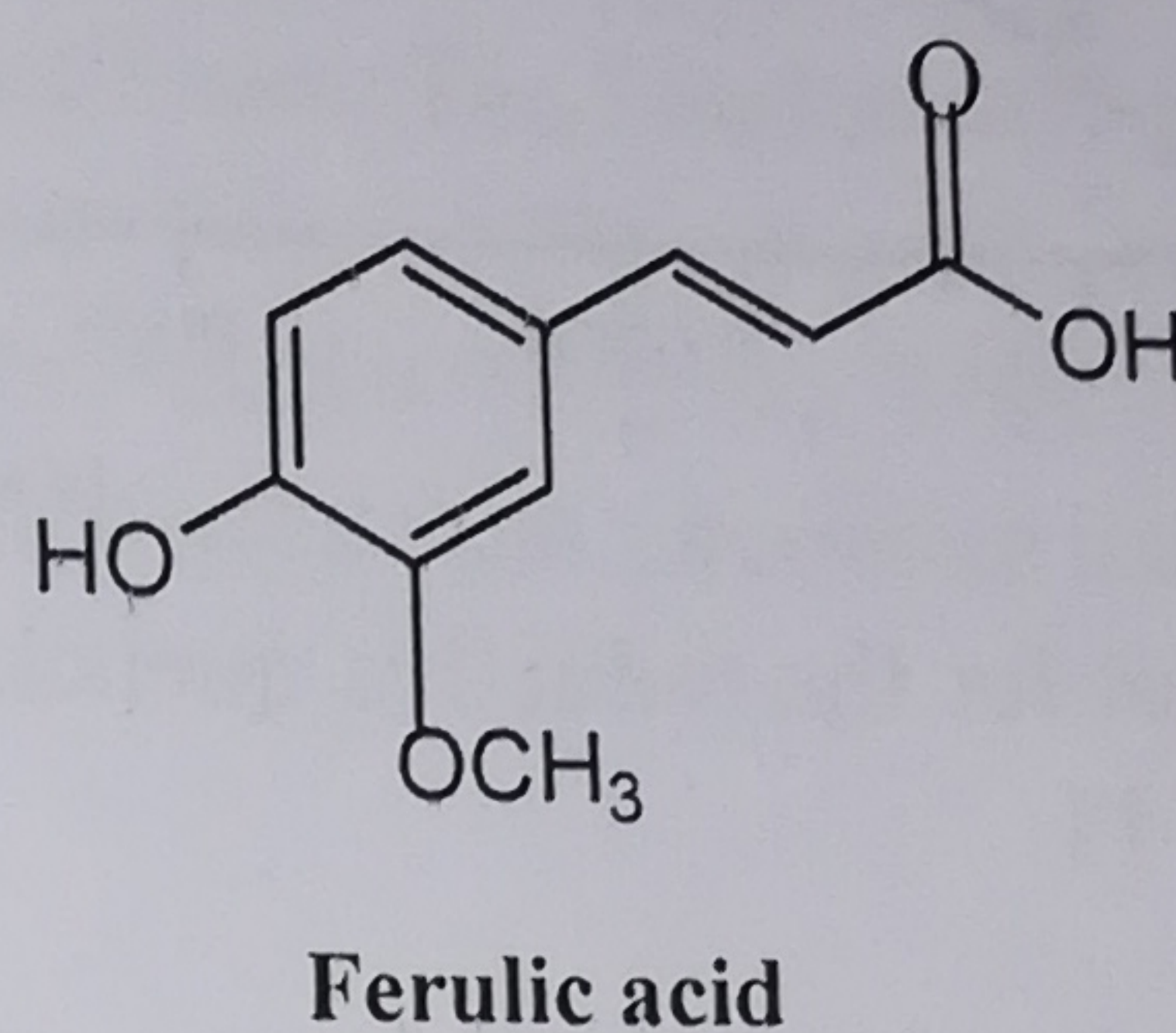
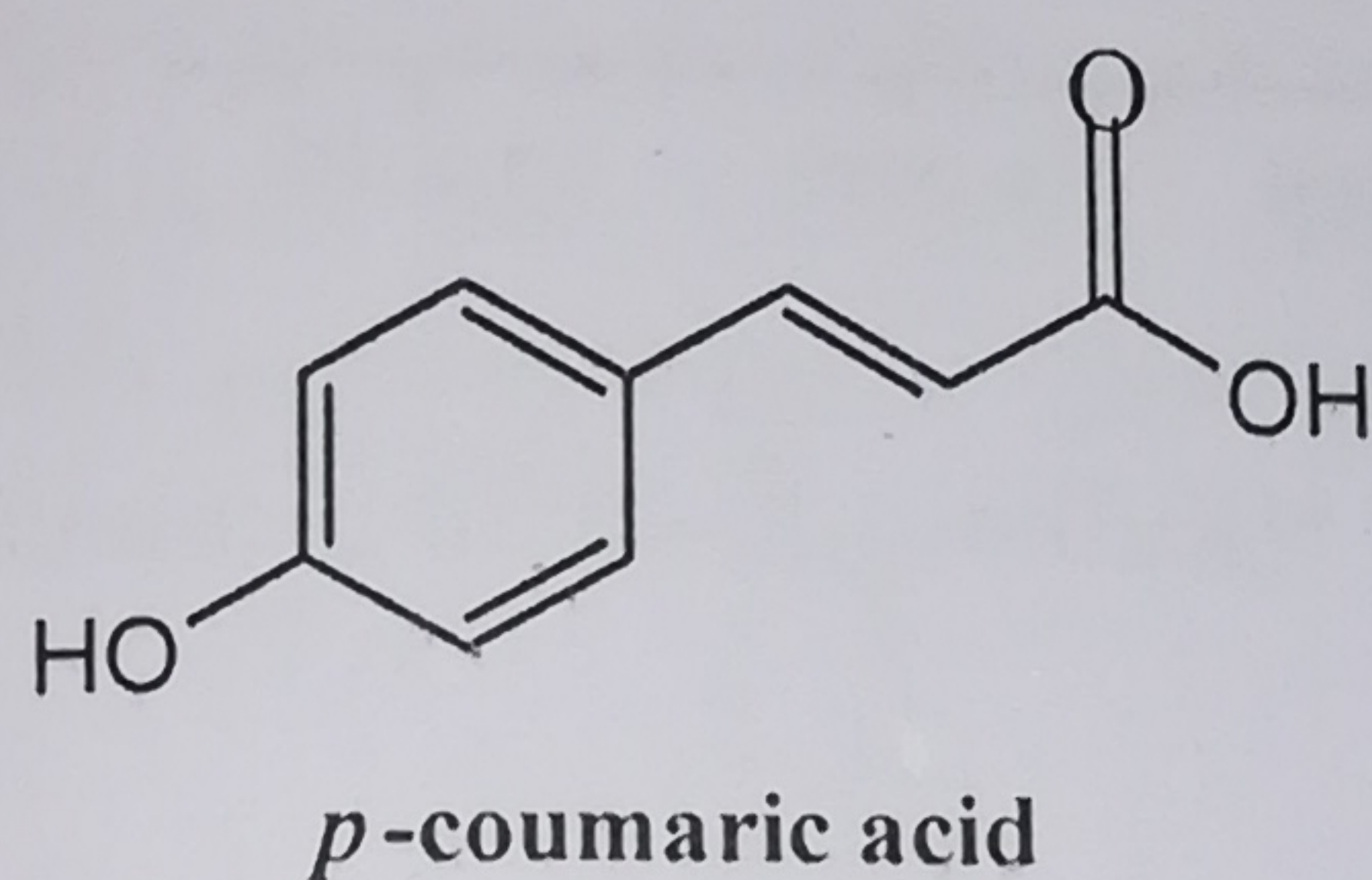
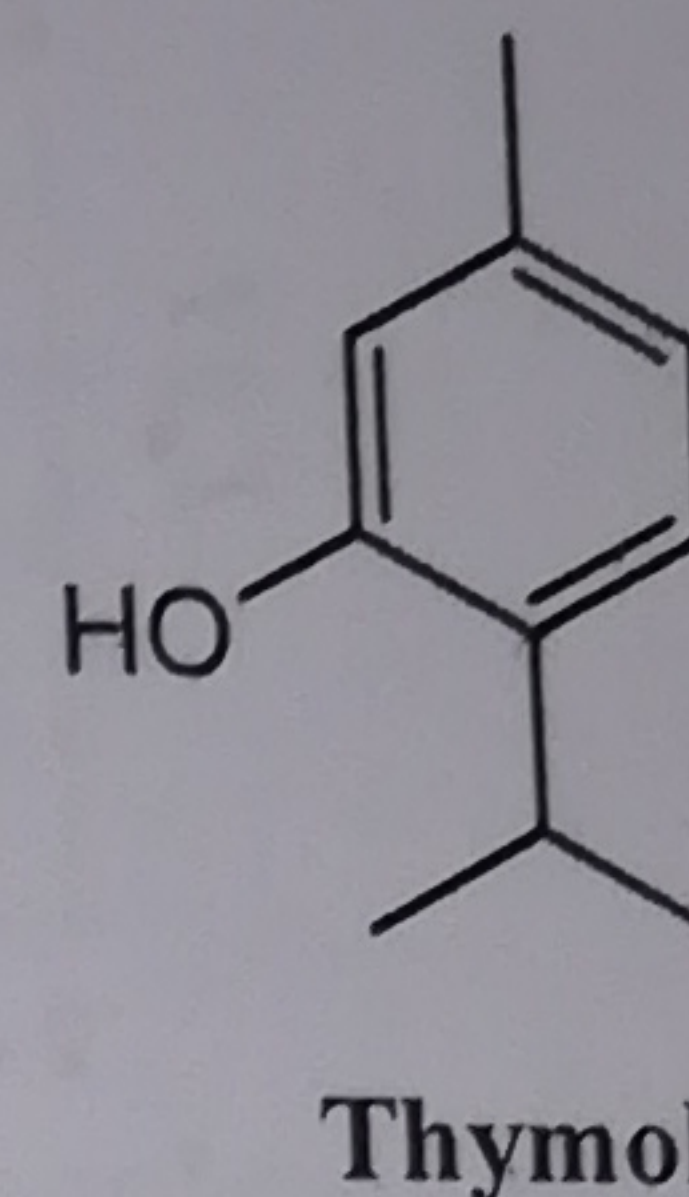
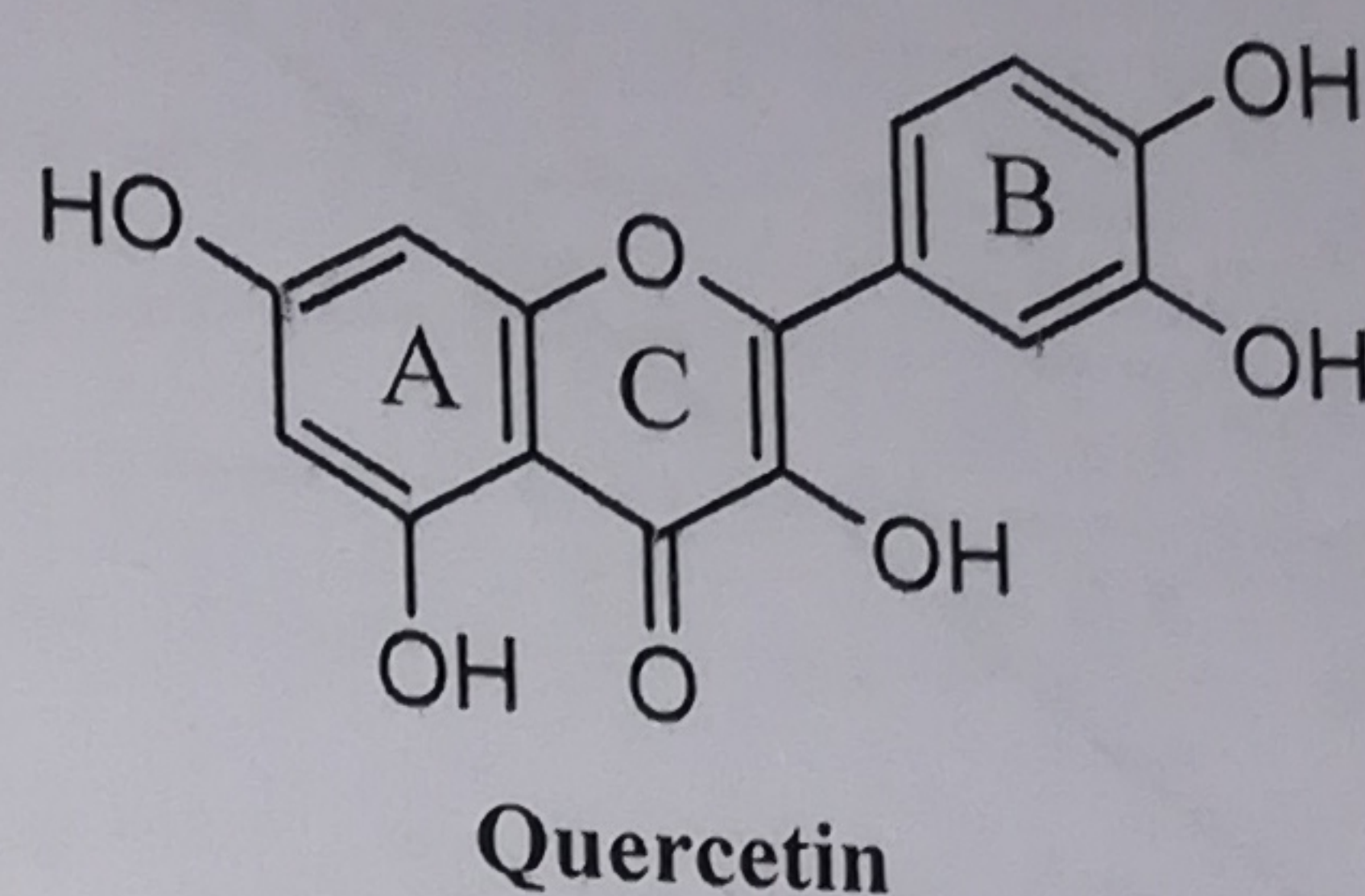
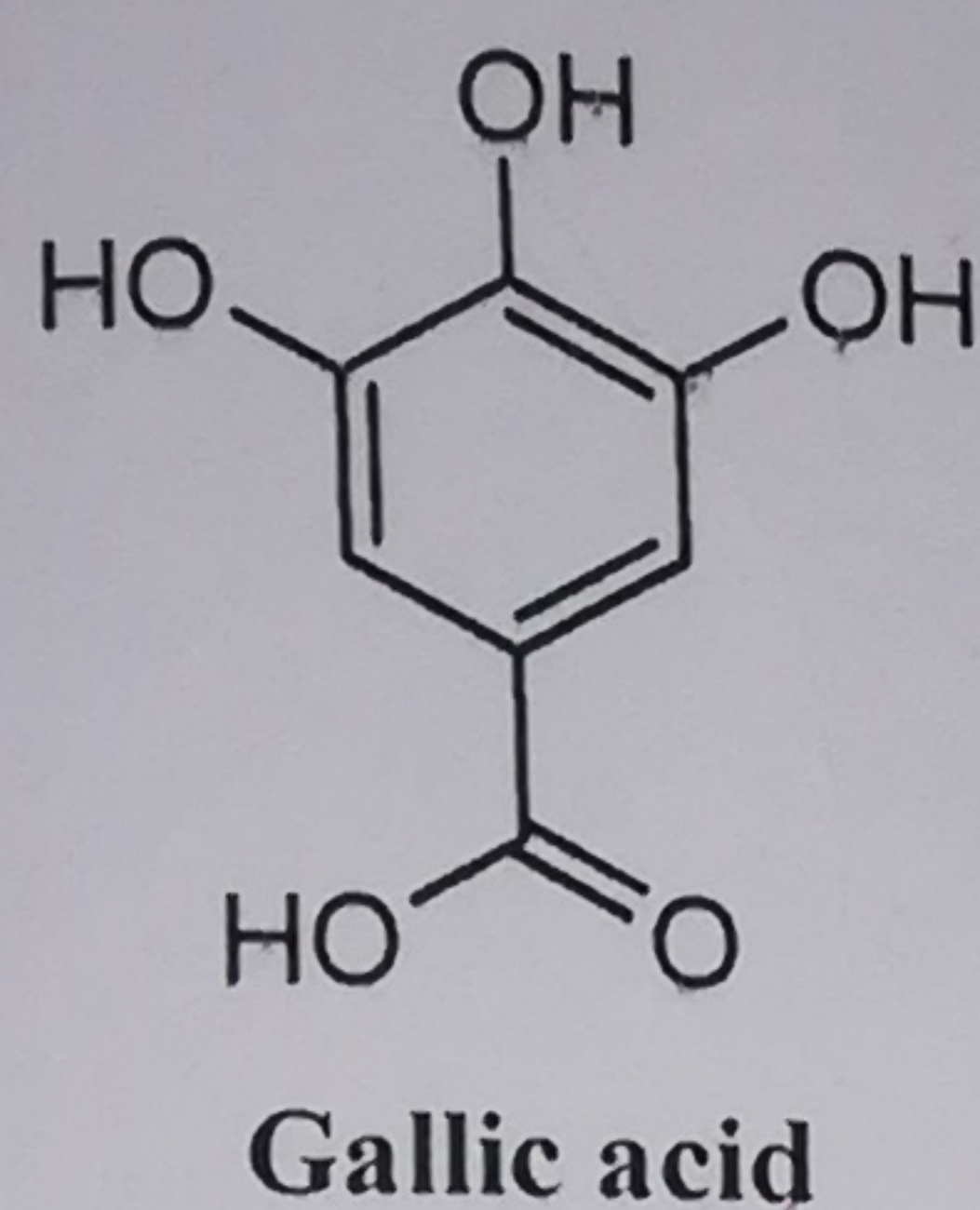


Fig. 1 Structure of the ligand and the quenchers

3 Results and Discussion

The absorption spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ shows a high energy absorption at 286 nm corresponding to the ligand centered $\pi - \pi^*$ transition and a low energy absorption at 450 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 centred acceptor π^* orbitals (ligand). The $[\text{Ru}(\text{bpy})_3]^{2+}$ complex shows an emission maximum at 625 nm in aqueous medium. The excited state life time of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex in aqueous medium at pH 11 is 614 ns.

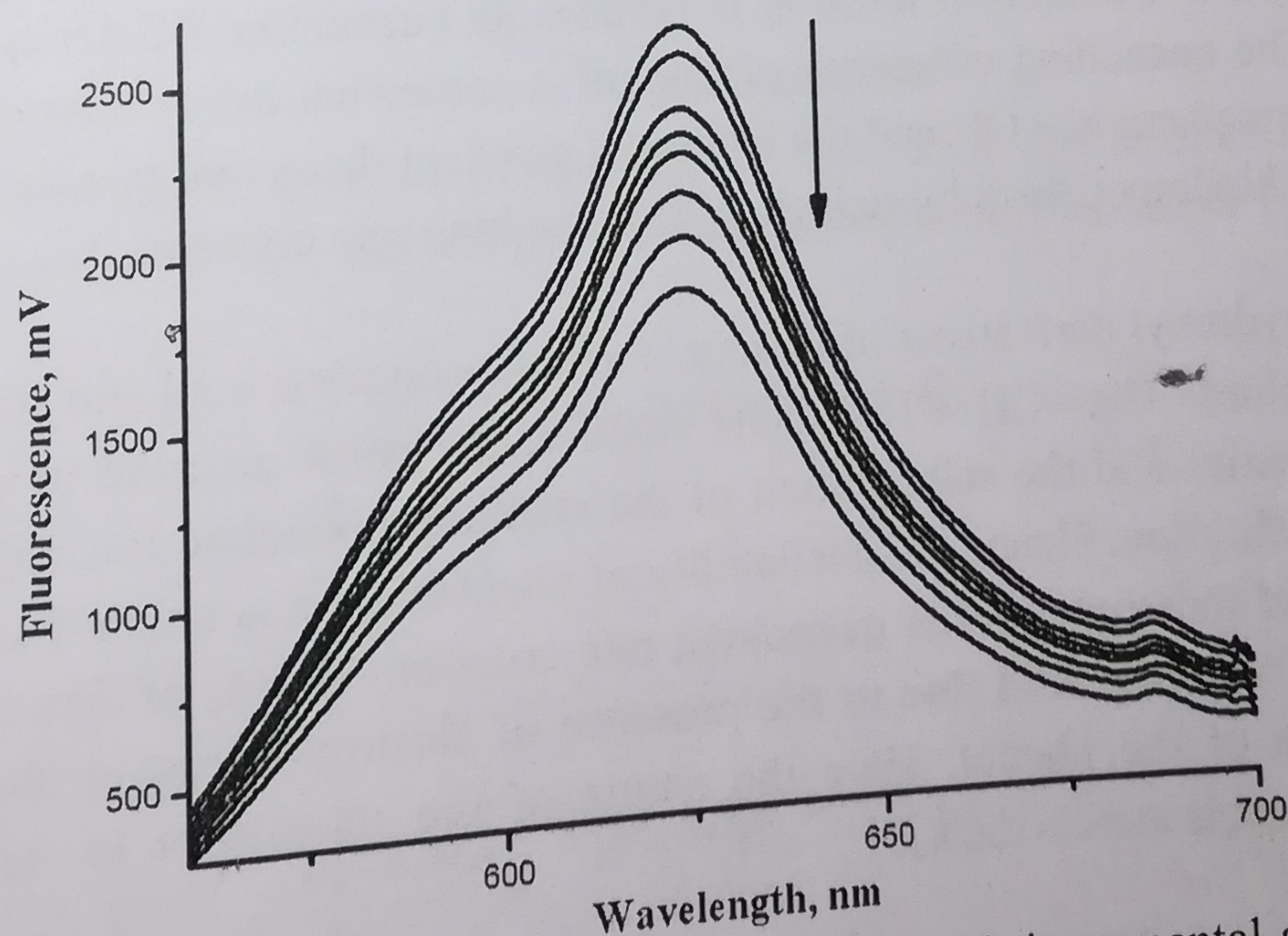


Fig. 2 The change in emission intensity of $^*[\text{Ru}(\text{bpy})_3]^{2+}$ with incremental addition of ferulic acid ($2 \times 10^{-4} - 1.4 \times 10^{-3} \text{ M}$) in aqueous medium at pH 11

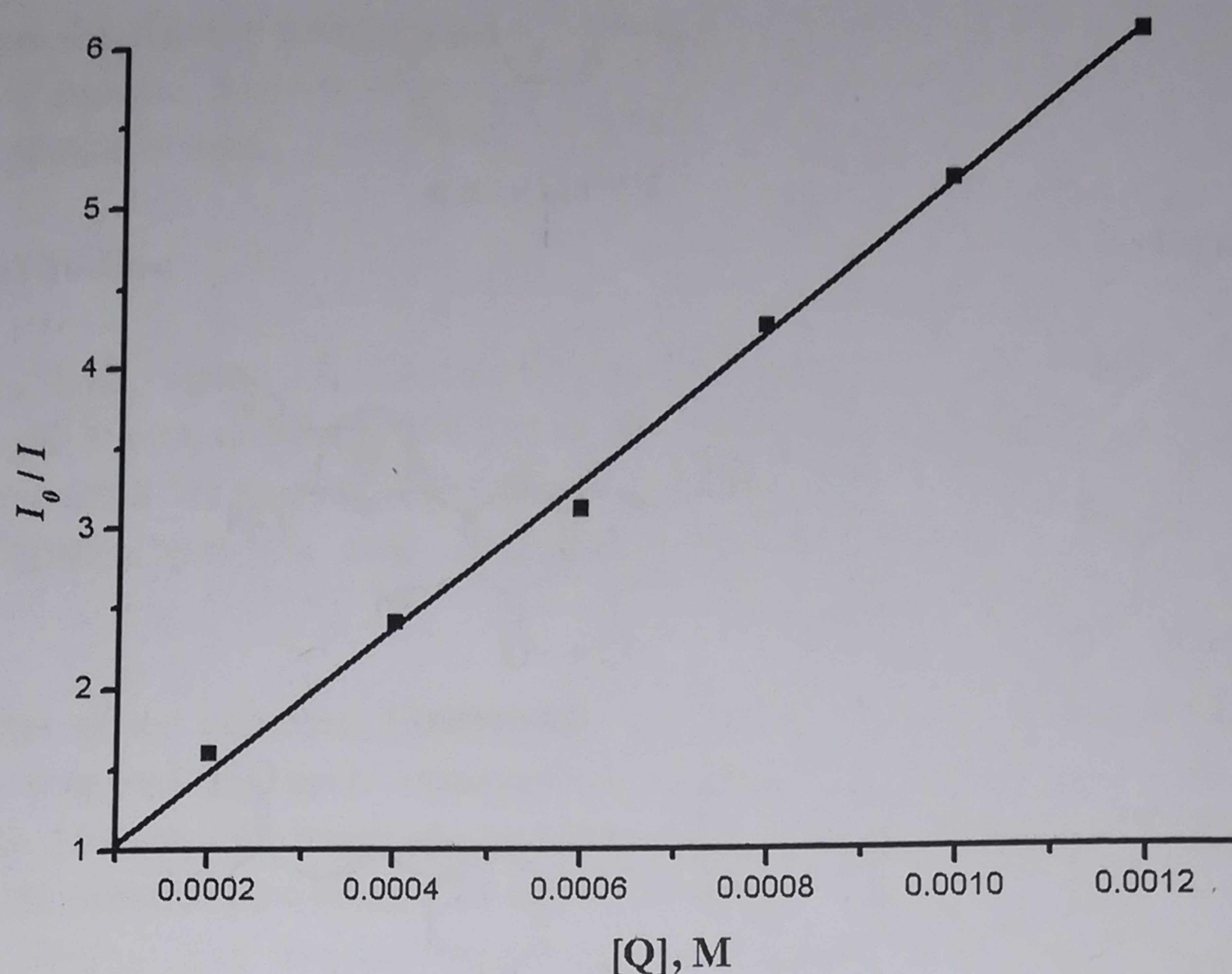


Fig. 3 Stern-Volmer plot for the reductive quenching of $^*[Ru(bpy)_3]^{2+}$ with *p*-coumaric acid in aqueous medium at pH 11

The experimental bimolecular quenching rate constant (k_q) of $^*[Ru(bpy)_3]^{2+}$ complex in aqueous medium at pH 11 are shown in **Table 1**. The k_q values for gallic acid, quercetin and thymol are 8.8×10^9 , 6.3×10^9 and $2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively, whereas ferulic acid and *p*-coumaric acid records 1.7×10^9 , $5.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. For the sake of comparison of the substituent effect of the polyphenols with $[Ru(bpy)_3]^{2+}$ complex, this luminescent study has done with phenol also and the results are discussed here. Phenol shows least k_q of $4.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The availability of phenolate ions is more with respect to gallic acid due to the presence of three phenolic -OH groups, acts as an efficient quencher compared to the other polyphenols taken in the present study. 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 ^[10]. Steric hindrance exerted by the benzo- γ -pyrone derivative at *para*- position of the ring B reduces its quenching efficiency when compared to gallic acid. 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 smallest k_q values. The $-\text{CH}=\text{CH}-\text{COOH}$ 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 reduces the quenching rate constant. The k_q 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 in the *ortho*- and *para*- positions of phenols affects the k_q .

Table 1 Quenching rate constants (k_q), of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with the quenchers in aqueous medium at pH 11

Quencher	$k_q (\text{M}^{-1}\text{s}^{-1})$
Phenol	4.6×10^8
<i>p</i> -coumaric acid	5.7×10^8
Ferulic acid	1.7×10^9
Thymol	2.9×10^9
Quercetin	6.3×10^9
Gallic acid	8.8×10^9

The reductive quenching of $^*[\text{Ru}(\text{bpy})_3]^{2+}$ complex by the phenolate ions have been confirmed from the transient absorption spectrum. The band at 400 and 510 nm in the transient absorption spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with 0.0008 M gallic acid confirms the formation gallate radical and $[\text{Ru}(\text{bpy})_3]^+$ as transient species (**Fig. 4**). Thus, the present study confirms the reductive quenching of $^*[\text{Ru}(\text{bpy})_3]^{2+}$ complex with phenolate ions.

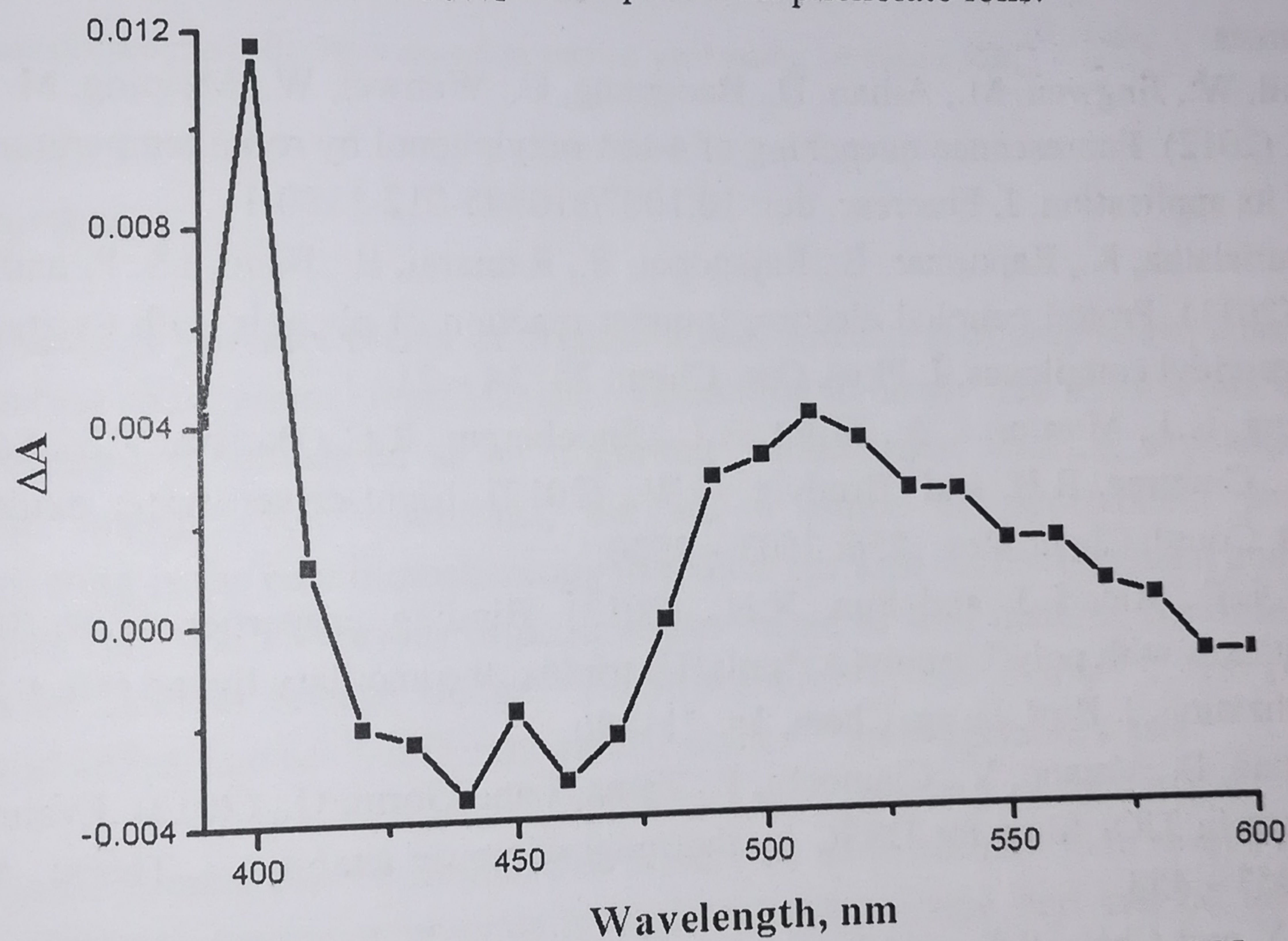
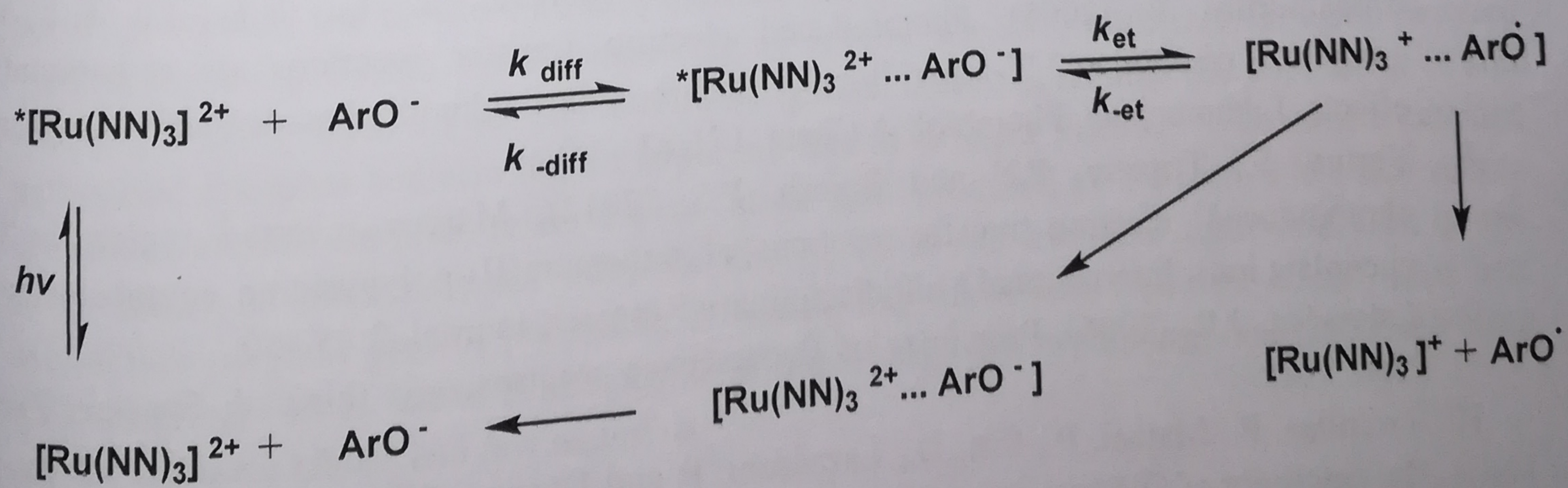


Fig. 4 Transient absorption spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex at 100 ns after 355 nm laser flash photolysis in the presence of 0.0008 M gallic acid in aqueous medium at pH 11



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

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 $[*Ru(NN)_3^{2+} \dots ArO^-]$ 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 electron transfer to the formation of the original reactants.

4. Conclusion

The present study clearly establishes the luminescence quenching of $[*Ru(bpy)_3]^{2+}$ complex with the polyphenols in aqueous medium at pH 11. The k_q depends on the availability of phenolate ions and the nature of the substituent present in the *ortho*- and *para*- positions of the polyphenols. Gallic acid behaves as an efficient quencher compared to that of the other polyphenols due to the availability of more number of phenolate ions. The detection of gallate radical and $[Ru(bpy)_3]^+$ as transient in the transient absorption spectra confirms the electron transfer nature of the reaction. This study confirms the structural effect on the electron transfer reactions of biologically important phenolate ions with the excited state $[*Ru(bpy)_3]^{2+}$ complex.

References

1. Huili, W., Jingwen, M., Ailian, D., Baoguang, C., Wenwei, W., Meiping, M. and Xuedong, W., (2012). Fluorescence quenching of 4-tert-octylphenol by room temperature ionic liquids and its application. *J. Fluoresc.* doi: 10.1007/s10895-012-1150-1
2. Swarnalatha, K., Rajkumar, E., Rajagopal, S., Ramaraj, R., Banu, I.S. P. and Ramamurthy, P., (2011). Proton coupled electron transfer reaction of phenols with excited state Ru(II)-polypyridyl complexes. *J. Phys. Org. Chem.* 24: 14 – 21.
3. Young, K.J., Martini, L.A., Milot, R.L., Snoeberger, R.C., Batista, V.S., Schmittenmaer, C.A., Crabtree, R.H. and Brudvig, G.W., (2012). Light-driven water oxidation for solar fuels. *Coord. Chem. Rev.* 256: 2503 – 2520.
4. Tan, L.F., Xie, L.J. and Sun, X.N., (2013). Binding properties of Ru(II) polypyridyl complexes with poly(U)•poly(A)*poly(U) triplex: the ancillary ligand effect on third-strand stabilization. *J. Biol. Inorg. Chem.* 18: 71 – 80.
5. Sannino, D., Vaiano, V., Ciambelli, P., Zama, I and Gorni, G., (2013). Evaluation of N719 amount in TiO₂ films for DSSC by thermogravimetric analysis. *J. Therm. Anal. Calorim.* 111:453 – 458.
6. Chi, Y and Chou, P.T. (2010). Transition-metal phosphors with cyclometalating ligands: fundamentals and applications. *Chem. Soc. Rev.* 39: 638 – 655.
7. Swarnalatha, K., Rajkumar, E., Rajagopal, S., Ramaraj, R., Lu, Y.L., Lu, K.L and Ramamurthy, P. (2005). Photoinduced electron transfer reactions of ruthenium(II) complexes containing 2,2'-bipyridine-4,4'-dicarboxylic acid with phenols Steric and charge effects. *J. Photochem. Photobiol. A Chem.* 171:83 – 90.
8. Verma, S., Tripathi, P.N and Rajesh, P.S. (2012). Marcus inverted region in the photoinduced electron transfer reactions of ruthenium(II)-polypyridine complexes with phenolate ions. *International Multidisciplinary Research Journal*, 2:45 –50.
9. Lakowicz, J.R. (2006). Principles of fluorescence spectroscopy, third ed. Springer Press, New York.
10. Trouillas, P., Marsal, P., Siri, D., Lazzaroni, R and Duroux, J.L. (2006). A DFT study of the reactivity of OH groups in quercetin and taxifolin antioxidants: The specificity of the 3-OH site. *Food Chem.* 97: 679 – 688.