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Luminescent Quenching of Tris (4,4'-dinonyl-2,2'-bipyridyl) Ruthenium(II) Cation with Gallic Acid and Quercetin in DMSO and 50 % Aqueous Acetonitrile

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Abstract:

Photo induced electron-transfer reaction of $*[Ru(nbpy)_3]^{2+}$ ($nbpy = 4,4'$ -dinonyl-2,2'- bipyridine) complex with gallic acid and quercetin in DMSO and 50 % aqueous acetonitrile have been studied by luminescent quenching technique. The complex shows emission maximum and excited state lifetime at 625 nm and 804 ns in DMSO and 618 nm and 625 ns in 50 % aqueous acetonitrile. The excited state redox potential of the complex vs Ag/Ag^+ in DMSO and 50 % aqueous acetonitrile are 0.72 and 0.82 V. The static nature of quenching of $[Ru(nbpy)_3]^{2+}$ complex with gallic acid and quercetin in both media is confirmed from the ground state absorption studies. The quenching rate constant, (k_q) is highly sensitive to the nature of the media. The k_q of $*[Ru(nbpy)_3]^{2+}$ complex with the phenolate ions of gallic acid and quercetin in DMSO is higher than that of in aqueous acetonitrile. The reductive quenching of $[Ru(nbpy)_3]^{2+}$ complex with the phenolic quenchers have been confirmed from the transient absorption spectra. Structural effects and $\pi - \pi$ interactions seem to play a vital role on this photoredox reaction.

Keywords: Photo induced electron transfer; Static quenching; Stern-Volmer equation; Structural effects

1. Introduction

The synthesis of Ru(II) 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 [1,2]. Castro *et al.* [3] have successfully designed a sensor for hydrocarbon, based on ruthenium(II)-complex, $[Ru(nbpy)_3]^{2+}$ ($nbpy = 4,4'$ -dinonyl-2,2'-bipyridine) which is able to detect reversibly and to quantify both aromatic and aliphatic hydrocarbons in aqueous samples.

Investigations on the luminescence quenching efficiency of ruthenium (II)- polypyridyl complexes with phenols have been made so far and the present study concentrates on the quenching behaviour of the $[Ru(nbpy)_3]^{2+}$ complex with gallic acid and quercetin in DMSO and 50 % aqueous acetonitrile (pH 11). The photoredox reactions of polyphenols with the $*[Ru(nbpy)_3]^{2+}$ complex proceeds through photo induced electron transfer (PET) reaction in both media and has been studied by luminescent quenching technique. The excited state properties like emission maxima, lifetime, and redox potential of this complex vary with the solvent. The transient absorption spectra confirm the electron transfer nature of $[Ru(nbpy)_3]^{2+}$ complex with polyphenols in DMSO and 50 % aqueous acetonitrile, where quenching process proceeds through the formation of phenolate ions. The absorption spectral studies with the quenchers confirm the static nature of quenching of the $[Ru(nbpy)_3]^{2+}$ complex.

2. Experimental Section

The complex, $[Ru(nbpy)_3] Cl_2$ was synthesized following the procedure of Castro *et al.*, [3]. Then the complex was treated with sodium tetrafluoroborate to get the BF_4^- salt $[Ru(nbpy)_3](BF_4)_2$. Sample solutions of the $[Ru(nbpy)_3]^{2+}$ complex and the quenchers were freshly prepared for each measurement. The absorption and emission spectral measurements were carried out using SYSTRONICS 2203 double beam spectrophotometer and ELICO SL 174 spectrofluorometer. All the sample solutions used for emission and excited state lifetime measurements were de-aerated for about 25 min by dry nitrogen gas purging. All the spectral measurements were carried out at 293 K. Excited state lifetime was made with laser flash photolysis technique using an Applied Photophysics SP-Quanta Ray GCR-2(10) Nd:YAG laser as the excitation source. The redox potential of the complex, $[Ru(nbpy)_3]^{2+}$ and the oxidation potential of gallic acid and quercetin in DMSO and 50 % aqueous acetonitrile (pH 11) were determined by cyclic voltammetric technique using CHI604C electrochemical analyzer.

The photochemical reduction of $[Ru(nbpy)_3]^{2+}$ complex with various concentrations (2×10^{-5} - 1.4×10^{-4} M) of the quenchers in DMSO and 50 % aqueous acetonitrile has been studied by luminescent quenching techniques. 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 than in the case of acetonitrile [4]. This proton transfer yields phenolate

ion, which act as quenchers in the PET reactions. Whereas in 50 % aqueous acetonitrile phenolate ions were prepared by mixing the corresponding polyphenols with NaOH and the pH of the solution maintained at 11 to confirm that the quencher were present as phenolate ions. The change of emission intensity of $^*[Ru(nbpy)_3]^{2+}$ with the quenchers measured at 293 K is shown in Fig. 1. The quenching rate constant, k_q , for the reaction is determined from the Stern-Volmer equation.

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

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 Ru (II) complexes in the absence of quencher.

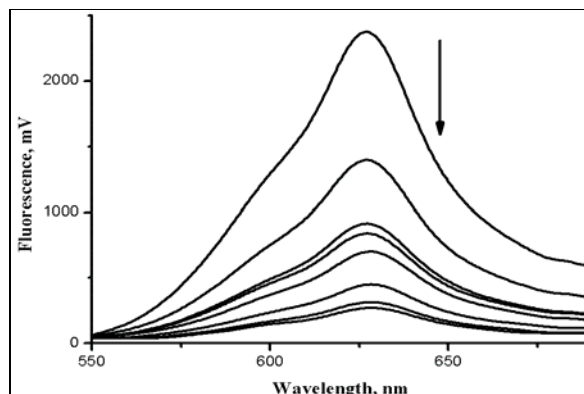


Figure 1: The change in emission intensity of $^*[Ru(nbpy)_3]^{2+}$ with different concentrations of gallic acid in DMSO

3. Results and Discussion

The absorption maximum of $[Ru(nbpy)_3]^{2+}$ complex in both media is 457 nm. The complex shows emission maximum and excited state lifetime at 625 nm and 804 ns in DMSO and 618 nm and 625 ns in 50 % aqueous acetonitrile.

The emission intensities of $[Ru(nbpy)_3]^{2+}$ complex are efficiently quenched in the presence of quenchers in both media. The absorption spectral studies of $[Ru(nbpy)_3]^{2+}$ complex with the incremental addition of gallic acid and quercetin shows a slight increase in the metal to ligand charge transfer absorption maximum, indicates the formation of ground state complex. The ground state interaction between the quenchers and the ligands of $[Ru(nbpy)_3]^{2+}$ complex are hydrophobic or π -stacking in nature and the extent of binding depends on the π - π stacking interactions. The Stern-Volmer plots for gallic acid and quercetin in both media are linear but the absorption spectral data confirms the static nature of quenching.

Quercetin has two different pharmacophores, the catechol group and the benzo- γ -pyrone derivative, of which the catechol moiety is the most reactive one where deprotonation occurs easily [5]. Steric hindrance exerted by the benzo- γ -pyrone derivative at *para*-position of the catechol reduces its quenching efficiency when compared to gallic acid. The radius of gallic acid and quercetin are 4.1 and 5.93 Å Quercetin exerts greater electron transfer distance than gallic acid due to its high radius and it reduces the quenching rate constant (k_q) in both media.

Quencher	Quenching rate constant, k_q ($M^{-1}s^{-1}$)	
	DMSO	50 % aqueous acetonitrile
Gallic acid	6.2×10^9	4.6×10^9
Quercetin	2.5×10^9	1.4×10^9

Table 1: Quenching rate constants (k_q), for the reductive quenching of $[Ru(nbpy)_3]^{2+}$ with the quenchers in DMSO and 50 % aqueous acetonitrile

The PET reaction of $[Ru(nbpy)_3]^{2+}$ with polyphenols proceeds through the same mechanism in DMSO and 50 % aqueous acetonitrile (Table 1). The polarity of DMSO is 47.2 and that of 50 % aqueous acetonitrile is 55.63 [6]. This photoredox reaction is highly sensitive to the change of polarity of the medium. Thus the k_q values in DMSO are higher than that of 50 % aqueous acetonitrile. Previtali have studied the solvent effect on the excited state quenching of $[Ru(bpy)_3]^{2+}$ complex by aromatic amines and nitrobenzenes in methanol and acetonitrile and reported higher k_q for methanol than acetonitrile [7]. This results are in accordance with the k_q of $[Ru(nbpy)_3]^{2+}$ with phenols in both media.

The reductive quenching of $^*[Ru(nbpy)_3]^{2+}$ by the phenolate ions have been confirmed from the transient absorption spectrum (Fig.2) The band at 400 and 510 nm in the transient absorption spectrum of the $[Ru(nbpy)_3]^{2+}$ complex with gallic acid confirms the formation of gallate radical and $[Ru(nbpy)_3]^+$ as transient species.

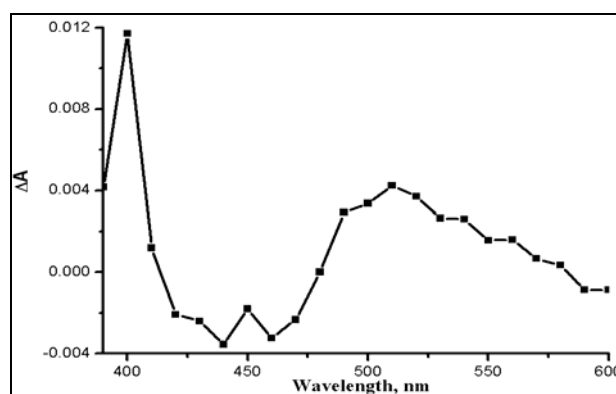


Figure 2: Transient absorption spectrum of $[Ru(nbpy)_3]^{2+}$ in the presence of $8 \times 10^{-5} M$ gallic acid recorded at $1 \mu s$ in 50 % aqueous acetonitrile

4. Conclusion

The $[Ru(nbpy)_3]^{2+}$ complex, in the excited state undergoes facile ET reaction with polyphenols in DMSO and 50 % aqueous acetonitrile (pH 11) and the k_q is sensitive to the polarity of the medium. Gallic acid behaves as an efficient quencher in both media, due to lesser electron transfer distance. The transient absorption spectra confirm the reductive quenching nature of this complex with the quenchers in both media. This study confirms the structural effects and the $\pi - \pi$ stacking interactions on the electron transfer reactions of biologically important phenolate ions with the excited state $[Ru(nbpy)_3]^{2+}$.

5. References

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