

A Study on the Binding Interaction of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with quinones in neutral micellar medium

T. Sumitha Celin and G. Allen Gnana Raj*

Department of Chemistry & Research Centre, Scott Christian College(Autonomous),
Nagercoil, Tamilnadu, India .

Abstract

The binding interaction of the ruthenium polypyridyl complex with *para* - quinones have been studied by absorption spectral technique. The metal complex shows an absorption maximum of 451 nm and the emission maximum of the complex is 595 nm in Triton X-100 medium. The binding constant (K_b) of the complex is determined from the Benesi-Hildebrand equation using the absorption intensity data. Structural effect plays an important role in the binding of the quinones with the complexes.

Keywords: *Ru polypyridyl complex, quinones, binding, Benesi Hildebrand plot, hydrophobic interaction*

Introduction

The photochemistry of organic and inorganic metal complexes has been an active area of research for many years. The monographs of Balzani and Carassiti on the photochemistry of coordination compounds [1] show that transition metal complexes are capable of utilizing visible light to engage organic molecules in redox chemistry. Of these, ruthenium polypyridyl complexes have been thoroughly studied for the past 30 years, due to their remarkable stability and photophysical properties [2]. Extensive work have been done after the discovery of the luminescence of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy- bipyridyl) in 1959 by Paris and Brandt [3]. These complexes have potential application in the development of electron and energy transfer, luminescence and solar energy conversion [4-6]. These luminescent complexes have applications such as photocatalyst [7-9], sensors for biomolecules [10-12], phototherapeutic agents [13, 14]

Quinones are important molecules in biological electron transport. They have very high toxicological and pharmacological effects. In order to understand the electron transfer properties of quinones, several

photosensitizers have been designed. Quinones possess favorable redox potentials and can be converted to stable reduction products in a stepwise manner. Many attempts have been made in recent years to design and synthesize molecules to mimic important light driven process, photosystem II [15-19]. A wide range of functions are performed by the biological membranes and membrane proteins. These have motivated researchers to look for simple model systems [20]. The typical examples of such membranes biometric models are micelles. Micelles are organized assemblies of surfactants in aqueous solvents. The structures of micelles depend on the structure of the surfactant molecule, the concentration of the surfactant, additives and the temperature of the solution. The organized media like micelles are well documented as a novel environment for photochemical conversion as these micellar systems can promote ET from electron donor to acceptor by concentrating them. In this work a comprehensive study was carried out to understand the binding interaction of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with *p*-quinones in neutral micellar medium by using absorption spectral techniques.

Material and Methods

The ligand 2,2'- bipyridine, and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ were purchased from Sigma Aldrich. All the quenchers used in the present study were procured from Sigma Aldrich and were used as such without purification. The surfactant namely Triton X-100 was procured from Merck. The solvents namely acetonitrile was purchased from Merck. The quenching studies were carried out using double distilled deionized water.

Absorption and Emission spectral measurements

The absorption spectra of the metal complex in aqueous and Triton X-100 media were recorded using SYSTRONICS 2203 double beam spectrometer. Emission spectral measurements were carried out using JASCO-FP 8900 spectrofluorometer. Freshly prepared sample solutions of the metal complexes and quenchers were used for each measurement. All the sample solutions used for the emission measurements were deaerated for 30 min with dry nitrogen gas purging keeping the solution in cold water to ensure that there was no change in the volume of the solution.

Transient absorption measurements and excited state lifetime

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. 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 (pulse Xenon lamp of 250W) the absorbance change.

Synthesis of Tris (2,2'- bipyridine) Ruthenium (II) Chloride, [Ru(bpy)₃]Cl₂

RuCl₃ · 3H₂O (0.5g) and 2, 2'- bipyridine (0.6g) were dissolved in 25 ml of ethanol and the solution was refluxed for 20 hours. The resultant orange red complex formed remained in the ethanol solution. The crude product was purified on a silica gel column using n-propanol as eluent. The pure complex was recovered after subsequent evaporation. The absorption maximum ($\lambda_{\text{abs}}^{\text{max}}$) and emission maximum ($\lambda_{\text{em}}^{\text{max}}$) of the complex in acetonitrile are 448 nm and 596 nm respectively. These values were in agreement with the reported values [21].

The binding of [Ru(bpy)₃]²⁺ with various concentrations (4×10^{-6} – 2.8×10^{-7} M) of quinones have been studied by absorption spectral techniques. The binding constant (K_b) of the [Ru(bpy)₃]²⁺ complex with quinones were determined from Benesi-Hildebrand equation [22] using absorption intensity data .

$$1/\Delta A = 1/K_b \Delta \epsilon [H] + 1/\Delta \epsilon [Q]$$

Where ΔA is the change in the absorption of the complex with various concentrations of (ΔG) of the quinones. The plot of $1/\Delta A$ versus $1/[Q]$ gives a

straight line and the binding constant K_b is calculated from the ratio of y intercept to the slope of the straight line.

Results and Discussion

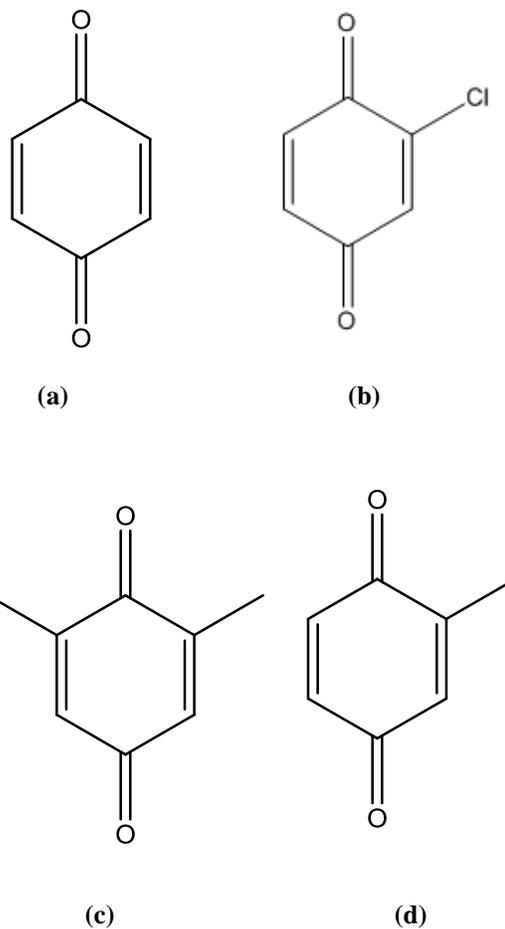


Figure 1. Structure of the Quenchers

(a) 1,4-benzoquinone (b) 2-chloro-1,4-benzoquinone (c) 2,6-dimethyl-1,4-benzoquinone (d) 2-methyl-1,4-benzoquinone

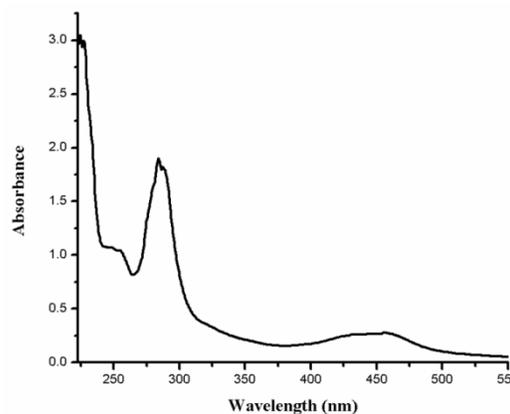
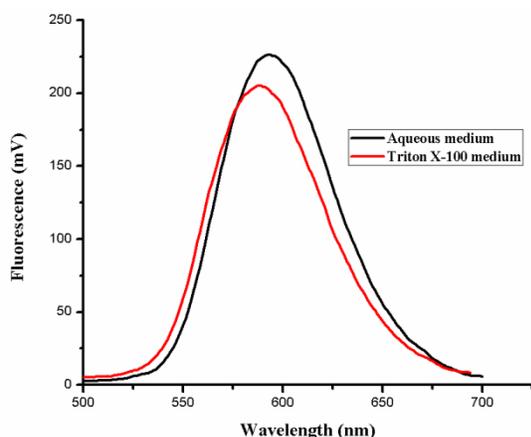


Figure 2. Absorption spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ in Triton X-100 medium

 Table 1. Photophysical properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex

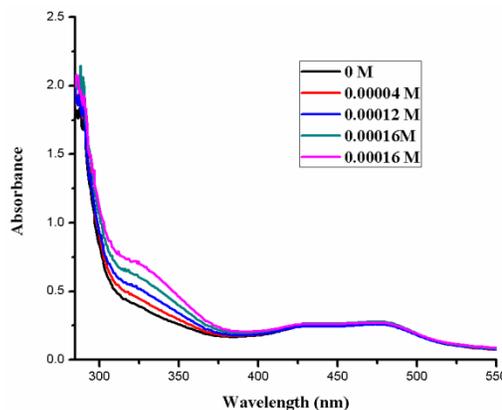
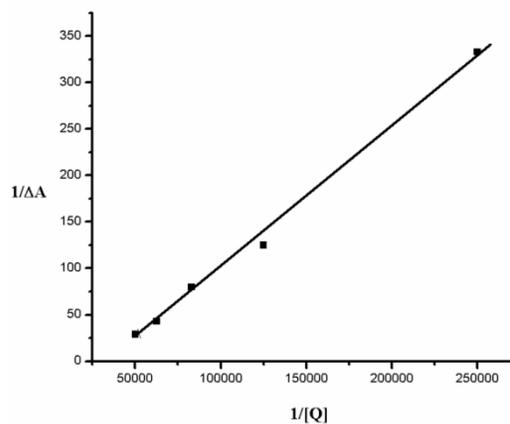
Complex	Absorption maxima (nm)		Emission maxima (nm)		Lifetime (ns)	
	Aqueous	Triton X-100	Aqueous	Triton X-100	Aqueous	Triton X-100
$[\text{Ru}(\text{bpy})_3]^{2+}$	448	451	596	595	650	600

The structure of the ligand and the quenchers used for the present study are shown in figure 1. The electronic absorption spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ in Triton X-100 medium is shown in Figure 2. The bands at 285 nm is due to the $\pi \rightarrow \pi^*$ transition. The two intense bands at 240 nm and 450 nm have been assigned to MLCT $d \rightarrow \pi^*$ transition. The two shoulders at 322 nm and 344 nm might to due to MC $d \rightarrow d$ transition. The photophysical properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ arise from the population of MLCT state. Triton X-100 is a neutral micelle with CMC = 0.32 mM. The addition of neutral surfactant to the complex resulted in red shift to the tune of 3 nm at the absorption maximum.


Figure 3. Emission spectrum of complex in aqueous and Triton X-100 medium.

The complex $[\text{Ru}(\text{bpy})_3]^{2+}$ has the emission maximum at 596 nm in aqueous medium. Figure 3 shows the emission spectrum of the complex in aqueous and Triton X – 100 medium. This long lived excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ can transfer its energy to another molecule (a quencher), either by electron transfer or energy transfer. The absorption spectral studies of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with the incremental addition of 1,4-benzoquinone, in Triton X-100 medium are shown in figure 4. There is no shift in the MLCT absorption

maximum of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with the addition of 1,4-benzoquinone. This shows the dynamic nature of quenching of the complex in the present experimental condition.


Figure 4. Electronic absorption spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ with incremental concentration of 2-methyl-1,4-benzoquinone in Triton X-100 medium

Figure 5. Benesi-Hildebrand plot on MLCT absorption of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with incremental addition of 1,4-benzoquinone in Triton X-100

The binding constant of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with the quinones in Triton X-100 medium calculated from Benesi-Hildebrand) plot (figure. 5) are shown in Table 2. The K_b obtained for the quenchers with $[\text{Ru}(\text{bpy})_3]^{2+}$ complex are in the order $10^3 - 10^4 \text{ M}^{-1}$. The first order rate constant (k_{red}) values for the quinones in Triton X – 100 are in the order $10^3 - 10^4 \text{ s}^{-1}$.

 Table 2. Binding constant, $K_b (\text{M}^{-1})$ from absorption spectral data for the quinones with $[\text{Ru}(\text{bpy})_3]^{2+}$ in Triton X – 100 medium

Quinones	Binding constant, K_b (M^{-1})
2-chloro-1,4-benzoquinone	2.264×10^4
1,4-benzoquinone	5.59×10^4
2-methyl-1,4-benzoquinone	6.738×10^4
2,6-dimethyl-1,4-benzoquinone	9.13×10^4

The results clearly indicate the hydrophobic interaction of Ru(II) polypyridyl complex. Photoluminescence studies have shown that the binding between $[Ru(bpy)_3]^{2+}$ and Triton X-100 micelles is probably Vander Waals or hydrophobic in nature. Therefore, binding is by competition between water and the micelles for solvation of the complexes [22]. In Triton X-100, the central micelle core is relatively dry and consists of the phenyl groups and the aliphatic chain. The remainder of the micelle is relatively wet outer sheath of partially hydrated polar ethoxy units. Binding of the sensitizers occurs predominantly at the interface of the dry core and the wet ethoxy region of the micelle.

The ground state interaction between the quinones and the bipyridine ring of $[Ru(bpy)_3]^{2+}$ complexes are hydrophobic and π -stacking in nature. π - π stacking interactions exist between the ligands of the Ru(II) complex and the quinones, so the binding also becomes stronger. Binding occurs in the LC and in the MLCT absorption maximum of the complex in the ground state. The K_b calculated for the quinones shows that, the $[Ru(bpy)_3]^{2+}$ complex bind strongly to 2,6-dimethyl-1,4-benzoquinone than the other quinones. This shows that binding increases with the size of the quinones.

Conclusion

In this work, an attempt was made was carried out to the binding interaction of $[Ru(bpy)_3]^{2+}$ complex with *p*-quinones in Triton X-100 medium by using absorption spectral techniques. The binding constants were calculated using Benesi – Hildebrand plot. The experimental results show that the binding of the $[Ru(bpy)_3]^{2+}$ complex with *p*-quinones depend on the size of the ligand as well as the quinones. The binding of $[Ru(bpy)_3]^{2+}$ complex with 2,6-dimethyl-1,4-benzoquinone shows a high value of binding constant $9.13 \times 10^4 M^{-1}$ which shows that this interaction is stronger than the other quinones. This may be attributed due to the bulkiness of the quinones.

References

- [1] Balzani V and Carassiti V, 'Photochemistry of Coordination Compounds', Academic Press, New York, 1970.
- [2] Juris A Balzani F Campagna S Belzer P and Von Zelewsky A, Coordination Chemical Review, Vol. 84, 85-277, 1988.
- [3] Paris JP and Brandt WW, 'Charge transfer luminescence of a ruthenium(II) chelate', Journal of American Chemical Society, Vol. 81, 5001-5002, 1959.
- [4] Gratzel M, 'Photochemical Cells', Nature, Vol. 414, 338-344, 2001.
- [5] Gratzel M, 'Solar energy conversion by dye sensitized photovoltaic cell', Inorganic Chemistry, Vol. 44, 6841-6851, 2005.
- [6] Giri Babu L Singh VK Vijay Kumar C Soujanya Y Gopal Reddy V and Yella Reddy P, 'Organic Ruthenium (II) Polypyridyl Complex Based Sensitizer for Dye Sensitized Solar Cell Applications', Advances in OptoElectronics, 8, doi:10.1155/2011/294353.
- [7] Lela Duan FB Mandal S Stewart B Privalov T Liobet A and Sun L, 'A molecular ruthenium catalyst with water - oxidation activity comparable to that of photosystem II', Nature Chemistry, Vol. 4, 418-423, 2012.
- [8] Chen Z Chen C Weinberg DR Kang P Concepcion JP Harrison DP Brookhart MS and Meyer TJ, 'Electrocatalytic reduction of CO₂ to CO by polypyridyl Ruthenium complexes', Chemical Communications, Vol. 47, 12607-12609, 2011.
- [9] Ohzu S Ishizuko T Hirai Y Fukuzum S and Kojima T, 'Photocatalytic oxidation of organic compounds in water by using Ruthenium polypyridylamine complexes as catalysts with high efficiency and selectivity', Chemistry - An European Journal, Vol.19, 1563-1567, 2013.
- [10] Muthu Mareeswaran P Babu E and Rajagopal S, 'Optical recognition of anions by ruthenium (II) bipyridine - calyx [4] arene system' Journal of Fluorescence, Vol. 23, 997-1006, 2013.
- [11] Babu E Muthu Mareeswaran P and Rajagopal S, 'Highly sensitive optical biosensor for thrombin based on structure switching aptamer luminescent silica nanoparticles', Journal of Fluorescence, Vol. 23, 137-146, 2013.
- [12] Muthu Mareeswaran P Maheshwara D Balu E and Rajagopal S, 'Binding and Fluorescence, resonance energy transfer (FRET) of Ruthenium(II)bipyridine - calixarene system with proteins - experimental and docking studies', Journal of Fluorescence, Vol. 22, 1345-1356, 2012.

- [13] Taheri S Behzad M Nazari H and Khaleghian A, 'Synthesis, characterization and biological studies of new Ruthenium polypyridyl complexes containing noninnocent ligands', *ISRN Inorganic Chemistry*, Vol. 2013, 1-6, 2013.
- [14] Gill MR and Thomas JR, 'Ruthenium (II) Polypyridyl complexes and DNA - from structural probes to cellular imaging and therapeutics', *Chemical Society Reviews*, Vol. 41, 3179-3192, 2012.
- [15] Virginia W Manner and James M Meyer, 'Concerted Proton - ET in a Ruthenium Terpyridyl-Benzoate System with a Large Separation between the Redox and Basic Sites', *Journal of American Chemical Society*, Vol. 131(issue 29), 9874-9875, 2009.
- [16] James Barber, 'Crystal Structure of the Oxygen-Evolving Complex of Photosystem II', *Inorganic Chemistry*, Vol. 47(issue 6), 1700-1710, 2008.
- [17] Nizamuddin Shaikh, Olof Johansson, Magnus F Anderlund, Stenjorn Styring, Bjorn Akermark, Ann Magnuson and Leif Hammarstrom, 'Light Induced Manganese Oxidation and Long-Lived Charge Separation in a $Mn_2^{II,II}-Ru^{II}(bpy)_3$ -Acceptor Triad, Magnus Borgström', *Journal of American Chemical Society*, Vol. 127(issue 49), 17504-17515, 2005.
- [18] Claudio Carra, Nadialka Iordanova and Sharon Hammes-Schiffer, 'Proton-Coupled ET in a Model for Tyrosine Oxidation in Photosystem II', *Journal of American Chemical Society*, Vol. 125, (issue 34), 10429-10436, 2003.
- [19] Licheng Sun, Leif Hammarstrom, Bjorn Akermark and Stenjorn Styring, 'Towards artificial photosynthesis: ruthenium-manganese chemistry for energy production', *Chemical Society Reviews*, Vol. 30, 36-49, 2012.
- [20] Balzani V, 'Electron Transfer in Chemistry', Wiley,-VCH, Verlag GmbH, Weinheim, Germany, 2001.
- [21] Kalaiyar Swarnalatha, Eswaran Rajkumar S Rajagopal R Ramaraj I Sadhiya Banu and Perumal Ramamurthy, 'Proton coupled ET reaction of phenols with excited state ruthenium(II) Polypyridyl complexes', *Journal of Physical Organic Chemistry*, Vol. 24, (issue1), 14 - 21, 2011.
- [22] Saha B and Stanbury D.M, *Inorg. Chem.*, Vol 39, 1294-1300, 2000.