

Binding Studies of Ruthenium (II) Polypyridyl Complex with Quinones in Aprotic Polar Medium

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ABSTRACT: The binding of Ru(II) polypyridyl complex $[\text{Ru}(\text{dmeobpy})_3]^{2+}$ with 2-methyl-1,4- benzoquinone and 2,6-dimethyl -1,4-benzoquinone have been studied in N,N-Dimethyl Formamide by means of absorption spectral technique. The binding constant (K_b) for these reactions are determined from the Benesi-Hildebrand equation using the absorption intensity data. The observed K_b value depends on the nature of the ligand and also on the structure of the quinones. The nature of binding is mainly due to electrostatic interaction between the quinones and ruthenium (II) complex.

KEYWORDS: binding constant, quinones, Benesi-Hildebrand equation , Ru(II) complexes UV/Vis spectroscopy.

I. INTRODUCTION

Quinones are ubiquitous in nature. They have wide application in biology and chemistry. Quinones appear to be electron acceptors in nature due to its favourable redox potential [1]. They serve as an important functional moiety in various biological systems like electron-proton carrier in respiratory chain and its important involvement as electron carrier in photosynthesis. They play an important role in the biochemistry of living cells [2].

In order to understand the electron accepting properties, several photosensitive metal-porphyrin, ruthenium(II) polypyridyl complexes have been designed and electron transfer reactions have been studied. Transition metal complexes have widespread application in the field of pharmaceutical chemistry. Researchers have shown that the activity of a drug molecule is enhanced when it binds to these metallic complexes [3]. The ET reactions of several quinones have been reported by several group of researchers[5-8]. Herein we report the binding of $[\text{Ru}(\text{dmeobpy})_3]^{2+}$ complex with 2-methyl-1,4-benzoquinone and 2,6-dimethyl-1,4-benzoquinone in DMF.

II. EXPERIMENTAL MATERIALS AND METHODS

The ruthenium polypyridyl complex $[\text{Ru}(\text{dmeobpy})_3]^{2+}$ was prepared by reacting $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with the corresponding dimethoxy bipyridine ligand by the known procedures [9-10]. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 4,4'-dimethyl-2,2'-bipyridine (dmbpy) and the quinones were procured from Sigma-Aldrich. N,N-Dimethyl Formamide was purchased from Merck and were used as such.

Absorption spectral measurements were carried out using SYSTRONICS 2203 Double Beam Spectrophotometer. Quartz cuvettes with a pathlength of 1cm were used throughout. The emission intensity measurements were recorded by JASCO/FP-8900 spectrofluorometer with a 1cm path length quartz cell, equipped with a 150w xenon source, a red sensitive photomultiplier tube. All the sample solutions used for the emission measurements were deaerated for 30 minutes by nitrogen gas purging and keeping the solution in cold water to ensure that there is no volume change in the solution. Nitrogen gas was purified by Fieser's solution to remove oxygen present in the solution.

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Excited state lifetime for the complex was made with laser flash photolysis technique using an Applied Photophysics SP-Quanta Ray. GCR-2910) Nd : YAG laser as the excitation source.

III. RESULTS AND DISCUSSION

The structure of quinones used in the present study was shown in **Fig.1**. The binding of $[\text{Ru}(\text{dmeobpy})_3]^{2+}$ complex with various concentrations ($4 \times 10^{-6} - 2.8 \times 10^{-7} \text{M}$) of 1,4-benzoquinone, 2-methyl-1,4-benzoquinone and 2,6-dimethyl-1,4-benzoquinone have been studied by absorption spectral technique. All the sample solutions were freshly prepared using N,N- dimethyl formamide.

The binding constant (K_b) of the $[\text{Ru}(\text{NN})_3]^{2+}$ complex with the quinones were determined from the Benesi- Hildebrand equation using the absorption intensity data [10].

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

Where ΔA is the change in absorption of the complex with different concentration ($[\text{Q}]$) of the quinones. The plot of $1/\Delta A$ versus $1/[\text{Q}]$ gives a straight line. The binding constant K_b is got from the ratio of Y-intercept to the slope of the straight line.

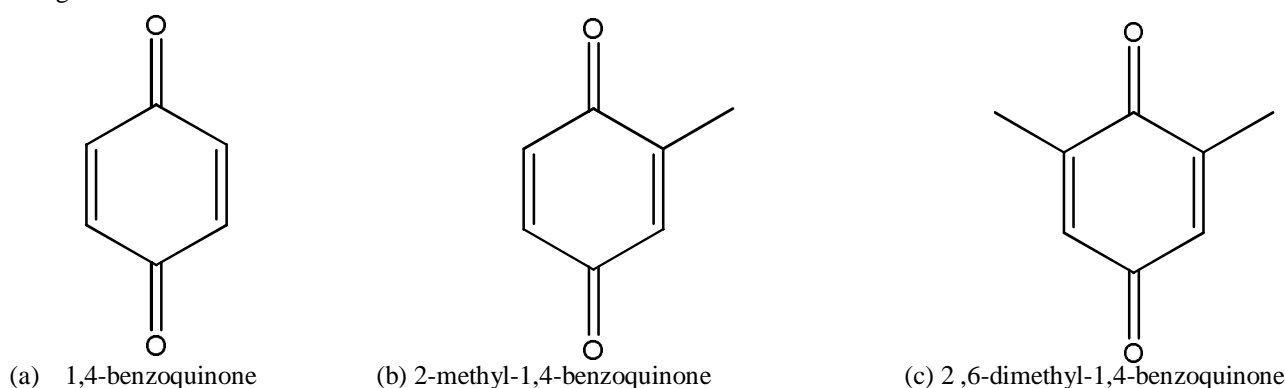


Fig 1. Structure of the quinones.

The UV/Visible absorption spectra of the $[\text{Ru}(\text{dmeobpy})_3]^{2+}$ complex shows a ligand centred (LC) absorption peak of high energy at 268 nm and a metal to ligand charge transfer (MLCT) peak at 468 nm in DMF (**Fig. 2**). The transition at 468nm corresponds to the $d\pi-\pi^*$ transition and 250-300 nm corresponds to the $\pi-\pi^*$ transition respectively.

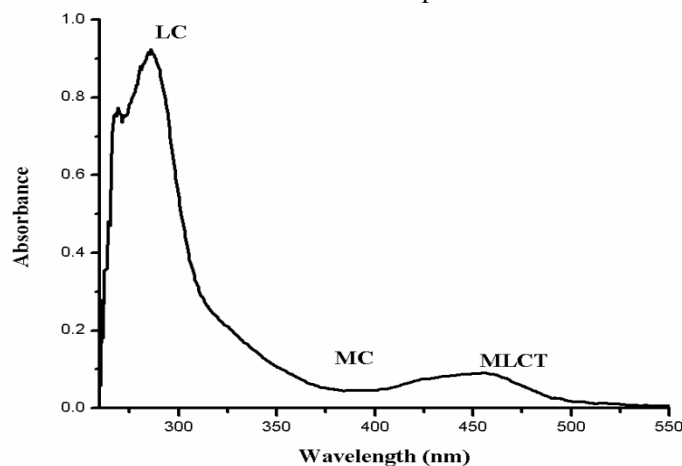


Fig. 2. Absorption spectrum of $[\text{Ru}(\text{dmeobpy})_3]^{2+}$ complex in DMF.

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The absorption spectral studies of $[\text{Ru}(\text{dmeobpy})_3]^{2+}$ with an incremental addition of 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2,6-dimethyl-1,4-benzoquinone show a steady state increase in the LC and MLCT absorption maximum, indicate the formation of ground state complex (Fig.4). Addition of 1,4-benzoquinone to the metal complex increases the absorbance at 268 nm and 468 nm, indicates the binding of quinones with the Ru polypyridyl complex. The absorption maximum, emission maximum and excited state lifetime of the complex are shown in Table 1.

Table .1 Absorption maximum, emission maximum and lifetime of $[\text{Ru}(\text{NN})_3]^{2+}$ in DMF.

Complex	Absorption maximum (nm)	Emission maximum (nm)	Lifetime (ns)
$[\text{Ru}(\text{dmeobpy})_3]^{2+}$	468	608	207

The emission spectrum of the $[\text{Ru}(\text{dmeobpy})_3]^{2+}$ complex in DMF was recorded at room temperature by the excitation of the MLCT band. The emission spectrum of the complex occurs at 468 nm. The complex has a lifetime of 207 ns.

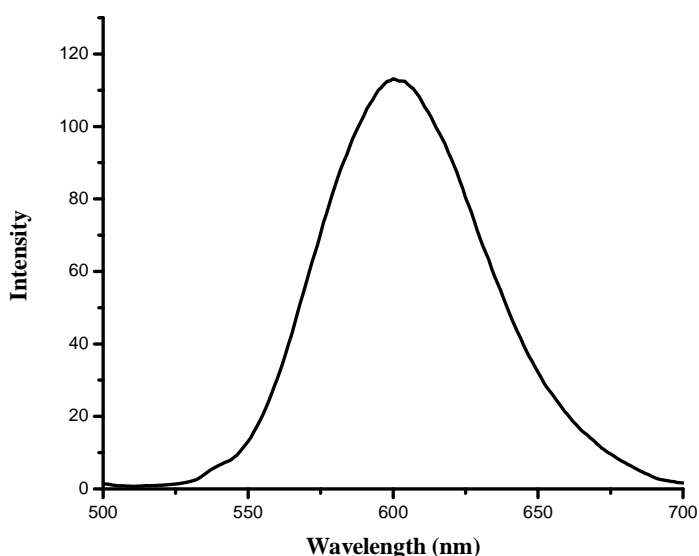


Fig 3. Emission spectrum of $[\text{Ru}(\text{dmeobpy})_3]^{2+}$ complex.

Benesi-Hildebrand plot on MLCT absorption of $[\text{Ru}(\text{dmeobpy})_3]^{2+}$ complex with incremental addition of 1,4-benzoquinone in DMF medium is shown in Fig.5. The plot of $1/\Delta A$ versus $1/[\text{Quinone}]$ gives a straight line. The binding constant K_b is got from the ratio of Y-intercept to the slope of the straight line.

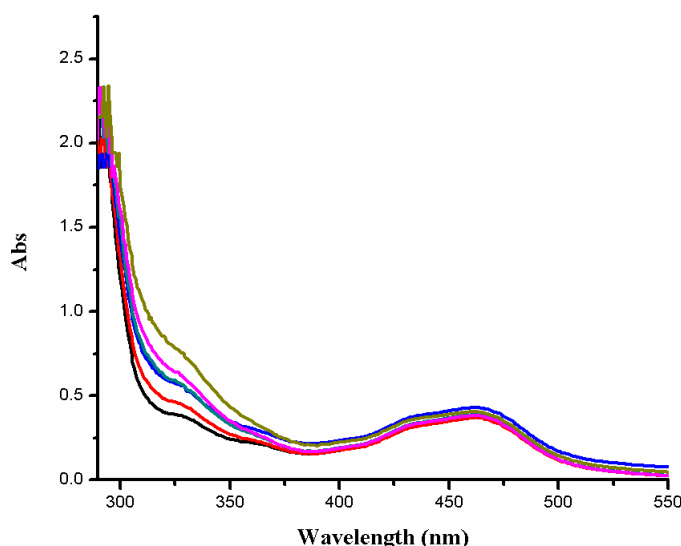


Fig 4. Absorption spectrum of $[Ru(dmeobpy)_3]^{2+}$ complex with incremental addition of 2,6-dimethyl-1,4-benzoquinone in DMF.

The K_b of $[Ru(NN)_3]^{2+}$ complexes with the quinones in DMF medium calculated from Benesi-Hildebrand plot is shown in Table.2. The K_b obtained for these quinones with $[Ru(NN)_3]^{2+}$ complex are in the order $10^3 - 10^4 M^{-1}$.

Table 2. Binding constant, $K_b (M^{-1})$ for 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, and 2,6-dimethyl-1,4-benzoquinone with $[Ru(dmeobpy)_3]^{2+}$ complex in DMF.

Quinones	Binding constant, $K_b (M^{-1})$
1,4 benzoquinone	5.33×10^3
2-methyl -1,4 - benzoquinone	2.96×10^4
2,6 –dimethyl -1,4- benzoquinone	3.003×10^4

From the absorption spectrum of 2-methyl-1,4-benzoquinone and 2,6-dimethyl-1,4-benzoquinone in DMF (Fig 5), it is seen that the quinones have weak absorption near the MLCT of the complex, it is seen that the quinones bind with the LC and MLCT absorption peak of the $[Ru(dmeobpy)_3]^{2+}$ complex in the ground state. The ground state interaction between quinones and the bipyridine ring of the $[Ru(dmeobpy)_3]^{2+}$ complex are hydrophobic or π -stacking in nature. The more the π - π stacking interaction occurs between the ligands of the $[Ru(dmeobpy)_3]^{2+}$ complex and the quinone, stronger will be the binding. The calculated K_b shows that 2,4-dimethyl-1,4-benzoquinone binds to the complex more strongly than that of 1,4-benzoquinone and 2-methyl-1,4-benzoquinone.

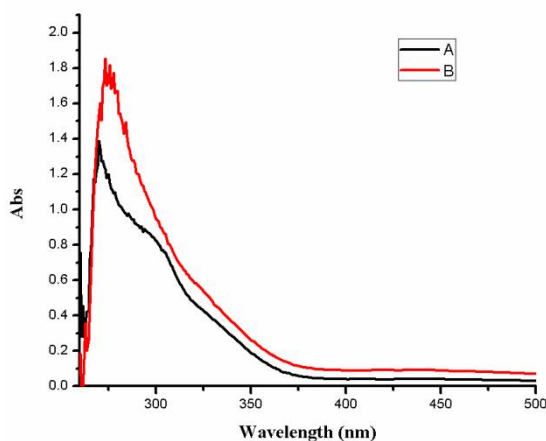


Fig.5 Absorption spectrum of A. 2-methyl -1,4 benzoquinone B. 2,6 –dimethyl -1,4 -benzoquinone in DMF.

The binding interaction of the complex with the incremental addition of 2-methyl-1,4 -benzoquinone in DMF is shown using Benesi-Hildebrand plot (**Fig.6**).

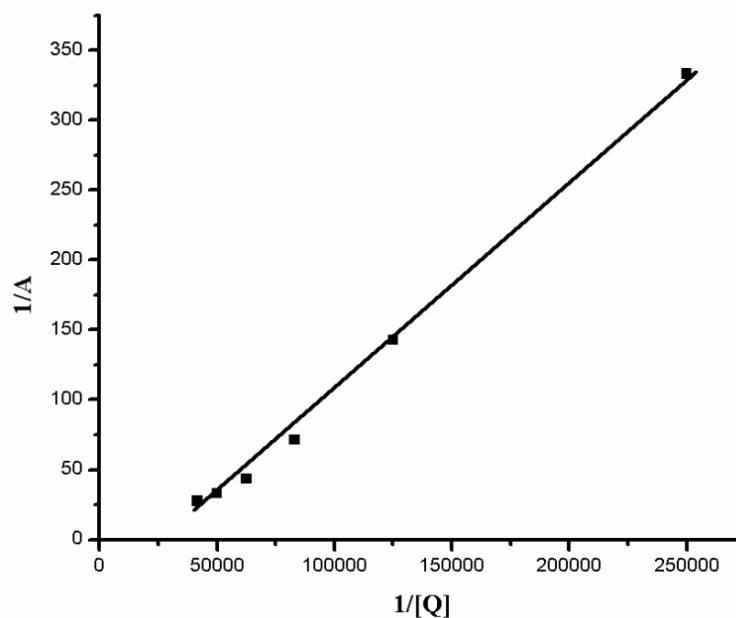


Fig.6. Benesi –Hildebrand plot on MLCT absorption of $[Ru(dmeobpy)_3]^{2+}$ complex with incremental addition of 2-methyl -1,4 benzoquinone in DMF.

The K_b value of 2,4-dimethyl-1,4-benzoquinone is $3.003 \times 10^4 M^{-1}$ whereas it is $2.96 \times 10^4 M^{-1}$ for 2-methyl-1,4-benzoquinone. Binding of 1,4-benzoquinone with $[Ru(dmeobpy)_3]^{2+}$ complex shows a binding constant of $5.33 \times 10^3 M^{-1}$. From the results we infer that nature and size of the substituent of the quinones play an important role in binding. As the size of the substituent in the quinone increases, the binding efficiency also increase. Satish et al [11] have reported that binding efficiency of ruthenium polypyridyl complexes with DNA is enhanced with the size of the ligands.

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IV. CONCLUSION

The binding of 1,4-benzoquinone, 2-methyl-1,4-benzoquinone and 2,6-dimethyl-1,4-benzoquinone with $\text{Ru}(\text{dmeobpy})_3^{2+}$ complex in DMF medium have been studied by absorption spectral techniques. The K_b value of $\text{Ru}(\text{dmeobpy})_3^{2+}$ complex with the quinones are determined from Benesi – Hildebrand plots. The K_b of 1,4-benzoquinone and 2-methyl-1,4-benzoquinone with $\text{Ru}(\text{dmeobpy})_3^{2+}$ complex are $5.33 \times 10^3 \text{ M}^{-1}$ and $2.96 \times 10^4 \text{ M}^{-1}$ respectively. Among the three quinones reported in this study 2,6-dimethyl-1,4-benzoquinone has the highest binding constant of $3.003 \times 10^4 \text{ M}^{-1}$. This study confirms that structural effect plays an important role in the binding of $\text{Ru}(\text{dmeobpy})_3^{2+}$ complex with quinones. Thus binding constant depends on the nature of the substituent present in the biologically important quinones with $\text{Ru}(\text{dmeobpy})_3^{2+}$ complex in the ground state.

REFERENCES

- [1] Kurreck, H., and Huber, M., "Model Reactions for Photosynthesis-Photoinduced Charge and Energy Transfer between Covalently Linked Porphyrin and Quinone Units", *Angew. Chem. Int. Ed. Engl.*, Vol. 34, pp. 849, 1995.
- [2] Partha Sarathi Guin, Saurabh Das, and Mandal, P.C., "Electrochemical reduction of Quinones in Different Media :A Review", *Int. Journal of Electrochemistry*, Vol 2011, 2011.
- [3] Rajeshire, M., Shah, R., Yadav, P., and Purohit, N.V., "Synthesis and antioxidant activity of metal (II) complexes of isocoumarin derivatives", *Der Pharmacia Sinica*, Vol. 3 No.2, pp. 239-248, 2012.
- [4] Arno G. Siraki, Tom S. Chan, and Peter, J.O. Bren, "Application of Quantitative structure –Toxicity relationship for the comparison of the cytotoxicity of p- Benzoquinone Congeners in primary cultured Rat Hepatocytes verses PC12 Cells", Vol. 18, pp. 148-159.
- [5] Szrebawaty, P., and Kapturkiewicz, "Free energy dependence on tris (2,2'-bipyridine)ruthenium(II) electrochemiluminescence efficiency". *A. Chem. Phys. Lett.*, Vol. 160, pp. 328, 2000.
- [6] Bae, E., and Choi, W., "Effect of the anchoring group (carboxylate vs phosphonate) in Ru-complex – sensitized TiO_2 on hydrogen production under visible light", *J. Phys. Chem. B*, Vol .110, No.30. pp. 14792-99.
- [7] Hayashi, S., and Kato, S., "The Synthesis of New Porphyrin–Quinone Dyad Systems", *J. Phys. Chem. A*, Vol. 102, pp. 3333, 1998.
- [8] Rosokha, S.V., and Kochi, J. K., "X-ray structures and electronic spectra of the p-halogen complexes", *Acc. Chem. Res.*, Vol. 41, pp. 41, 2008.
- [9] Connors, K.A., "Binding Constants : The measurement of Stability", John Wiley & Sons, Ltd Chichester, U. K., 1987.
- [10] Swarnalatha, K., and Sornalatha, S., "Spectroscopic characterization of p-quinones with ruthenium (II) complex of 1, 10 phenanthroline family of ligands", *Int. Journal of Advanced Research* Vol. 4 , No.2, pp. 235-241, 2016.
- [11] Satish S. Bhat, Vidyannand K. Revangar, Ayesha Khan, Raymond J., Butcher, and Krishnachary Thatipamula, "Supramolecular Architecture and photophysical and biological properties of ruthenium(II) polypyridyl complexes", *The Royal Society of Chemistry and the Centre National de l Recherche Scientifique*, Vol 39, pp 3646-3657, 2015.