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Binding of Tris(4,4'-dimethoxy-2,2'-bipyridyl)ruthenium(II) Cation with Quinones in 50% Aqueous Acetonitrile

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ABSTRACT

Binding of tris($2,2^{'}-$ dimethoxy $- 2,2^{'} -$ bipyriyl) ruthenium (II) complex with quinones have been studied in 50% aqueous acetonitrile medium by means of absorption spectral technique. The absorption and emission maximum of $[Ru(dmeObpy)_3]^{2+}$ complex are 468 nm and 606 nm respectively. The binding constants for the reactions of the complex with quinones are determined using the Benesi-Hildebrand plot using the absorption intensity data. The value of K_b is sensitive to the structure and nature of the quenchers used. Structural effect also plays a significant role on the binding of the complex with quinones.

1. Introduction

Quinones are organic compound well known for their widespread application in various fields of chemistry and medicine. They act as electron acceptors in photosynthesis and in the biological proteins and are ultimate acceptor of electron in the photosynthetic reaction centers [1-5]. In order to understand the electron accepting properties of quinones, many model photosensitizers have been designed by researchers and ET reactions with quinones have been studied [6-10]. Quinone derivatives are used as electron mediators [11] in the energy conversion system. Biological role of quinones are utilized for the development of many storage systems.

Ruthenium (II)polypyridyl complexes are also used to mimic ET behavior of the PSII reaction centres [12]. They act as good electron donors. The main advantage of ruthenium complexes is that their excited state properties can be dramatically changed by introducing electron releasing and electron with-drawing moieties in the $4,4^{'-}$position of $2,2^{'} -$ bipyridine ligand. On excitation of $[Ru(NN)_3]^{2+}$ complex by a photon, a triplet metal to ligand charge transfer (^{3}MLCT) excited state is formed and the excited electron gets transferred to an electron acceptor (quinones). The oxidized Ru^{3+} state may get reduced back to the Ru^{2+} state by back electron transfer from the quinones. Based on the literature survey, the present study concentrates on the binding of $[Ru(dmeObpy)_3]^{2+}$ complex with quinone derivatives in 50% aqueous acetonitrile medium.

2. Experimental Methods

$RuCl_3H_2O$ & $4,4^{'} -$ dimethoxy $- 2,2^{'} -$ bipyridine (dmeObpy) and the quenchers were procured from Sigma Aldrich. Acetonitrile was purchased from Merck. The solvent and the quenchers were used as such without any purification. $[Ru(dmeObpy)_3]^{2+}$ complex was prepared by reacting $RuCl_3{\cdot}H_2O$ with the corresponding $4,4' -$ dimethoxy $- 2,2' -$ bipyridine ligand as given from the known procedure [13]. Double distilled deionized water was used for the binding studies.

SYSTRONICS 2203 double beam spectrophotometer was used to carry out the absorption spectral measurements. Quartz cuvette of path length 1 cm was used throughout. Emission intensity measurements were done and the emission spectra were measured using JASCO FP 8600 spectrofluorometer. Excited state lifetime measurements of the complex were made using a laser flash photolysis technique. This technique uses an Applied Photophysics SP-Quanta Ray GCR – 2(10) Nd:YAG laser as the excitation source. For the absorption measurements, the complex concentration was fixed as 4×10^{-5} M. The quencher concentrations were varied between 4×10^{-6} M and 2.8×10^{-7} M.

Binding studies were carried out for $[Ru(dmeObpy)_3]^{2+}$ complex with different concentrations of quenchers by absorption spectral technique. The binding constants were calculated from Benesi-Hildebrand equation using absorption intensity data [14],

$$\frac{1}{\Delta A} = \frac{1}{K_b} \Delta\varepsilon[\Delta] + \frac{1}{\Delta\varepsilon}[Q]$$

where, ΔA refers to the change in the absorbance of the complex with varying concentration ([Q]) of quinones. The plot of $\frac{1}{\Delta A}$ verses $\frac{1}{[Q]}$ gives a straight line and K_b was obtained from the ratio of Y-intercept to the slope of the straight line.

3. Results and Discussion

The structure of the ligand and the quenchers are shown in Fig. 1. The absorption maximum, emission maximum and excited state lifetime of $[Ru(dmeObpy)_3]^{2+}$ complex in 50% aqueous acetonitrile are shown in Table 1.

Table 1 Photophysical properties of $[Ru(dmeObpy)_3]^{2+}$ complex in 50% aqueous acetonitrile and aqueous medium

Medium	Absorption maximum (nm)	Emission maximum (nm)	Excited state lifetime (τ) ns
50% aqueous Acetonitrile	448	606	246
Aqueous	448	595	232

The complex give rise to different absorption maxima corresponding to the ligands coordinated to the metal centre $[Ru(dmeObpy)_3]^{2+}$. The low energy absorption in the 448 nm region is assigned to the $d_{\pi\text{-}\pi^*}$ MLCT transition (Fig. 2). The emission maximum of Ru(II) complexes originates from the dπ-π* ^{3}MLCT transition. The emission intensity of $[Ru(dmeObpy)_3]^{2+}$ complex shows a bathochromic shift of about 5 nm on changing the medium (Fig. 3).

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The absorption spectral studies of $[Ru(dmeObpy)_3]^{2+}$ complex with incremental addition of 1,4-benzoquinone, 2-methyl-1,4-benzoquinone (4×10^{-10} M to 2.8×10^{-7} M) are performed to check the formation of ground state complex. The absorption spectra of the mixture of quinones and $[Ru(dmeObpy)_3]^{2+}$ are shown to be the sum of the component spectra. There is a shift in the MLCT absorption maximum of the complex with the addition of quinones. This shows the formation of ground state complex under the experimental condition. This observation concludes the static nature of quenching of the complex in the present experimental study. Fig. 4 shows the absorption spectra of $[Ru(dmeObpy)_3]^{2+}$ with the incremental addition of the 1,4-benzoquinone.

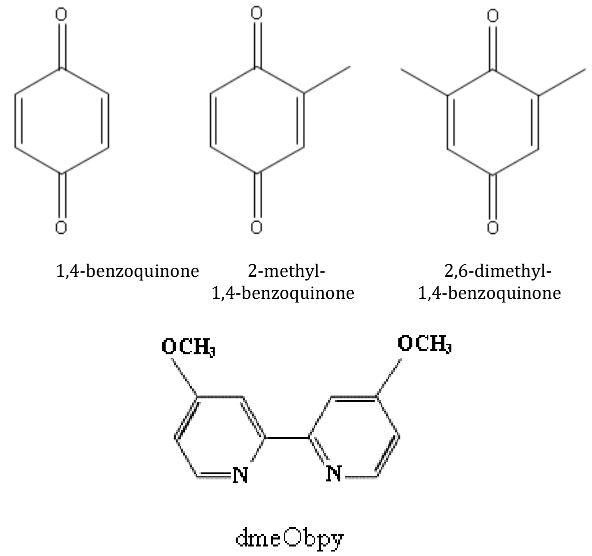

Fig. 1 Structure of quinones and the ligands

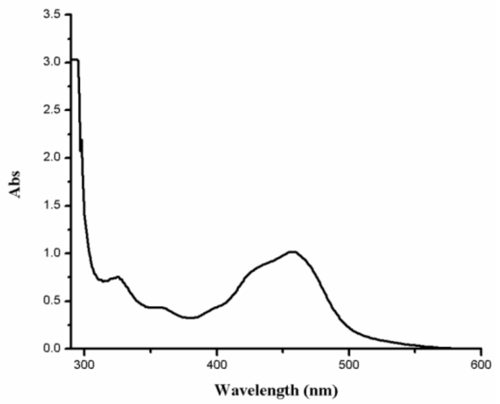

Fig. 2 Absorption spectrum of $[Ru(dmeObpy)_3]^{2+}$ complex in 50% aqueous acetonitrile medium

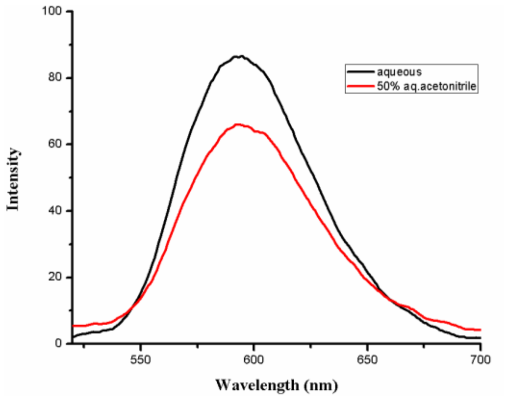

Fig. 3 Emission spectrum of $[Ru(dmeObpy)_3]^{2+}$ complex in 50% aqueous acetonitrile and aqueous medium

The binding constant of $[Ru(dmeObpy)_3]^{2+}$ complex with the quinones in 50% aqueous acetonitrile medium calculated from Benesi-Hildebrand plot (Fig. 5) are shown in Table 2. The K_b obtained for the quenchers with $[Ru(dmeObpy)_3]^{2+}$ complex are in the order 10^3 -10^5 M^{-1}.

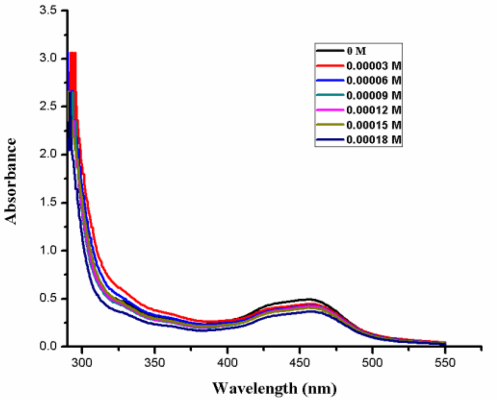

Fig. 4 Absorption spectrum of $[Ru(dmeObpy)_3]^{2+}$ complex in 50% aqueous acetonitrile medium with incremental concentration of 1,4-benzoquinone

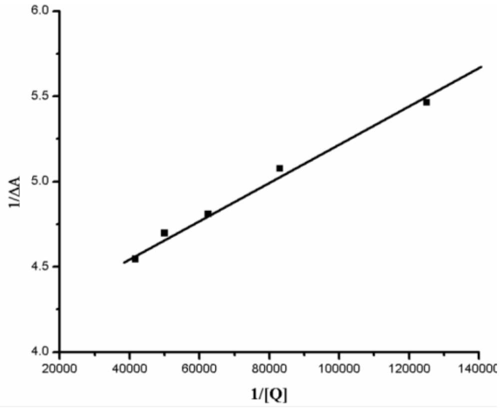

Fig. 5 Benesi–Hildebrand plot on luminescence quenching data of $^*[Ru(dmeObpy)_3]^{2+}$complex with incremental addition of 2,- methyl -1,4-benzoquinone

Table 2 The binding constant of $[Ru(dmeObpy)_3]^{2+}$ complex with the quinones in 50% aqueous acetonitrile medium

Quencher	Binding constant K_b (M^{-1})
1, 4 - benzoquinone	6.20×10^3
2 - methyl -1,4- benzoquinone	3.70×10^4
2, 6 - dimethyl -1,4 - benzoquinone	1.75×10^5

The interaction between the bipyridyl ring of $[Ru(dmeObpy)^{3+}]^{2+}$ complex and that of the quinones are hydrophobic or π stacking in nature [15]. It is seen from the table that the binding constant increases as the size of the quencher increases. Thus, the binding constant values are in the order 1,4–benzoquinone, 2, 6-dimethyl–1,4–benzoquinone > 2-methyl-1,4-benzoquinone. Thus the results show that the value of K_b is sensitive to the hydrophobicity of the quenchers. Thus 2,6-dimethyl- 1,4-benzoquinone undergoes strong binding with the Ru(II) polypyridyl complex.

4. Conclusion

The binding of quinones with $[Ru(dmeObpy)_3]^{2+}$ complex in 50% aqueous acetonitrile medium has been studied by absorption spectral technique. The binding constants of the Ru(II) complex with the quinones are determined from the Benesi-Hildebrand plot. As the substituent in the quinone increases, the binding constant also increases. 2,6-dimethyl-1,4-benzoquinone shows the higher binding constant due to the bulkiness of the substituent present in the side chain of 1,4-benzoquinone. The present study confirms the structural effects of binding of quinones with $[Ru(dmeObpy)_3]^{2+}$ complex.

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