

Binding of Ruthenium (II) Polypyridyl Complexes with Quinones in DMF

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Abstract

The binding of $[Ru(bpy)_3]^{2+}$ ($bpy = 2,2'$ - bipyridine) $[Ru(dmbpy)_3]^{2+}$ ($dmbpy = 4,4'$ - dimethyl -2, 2' - bipyridine) complexes with quinones (1,4 - benzoquinone (BQ), 2-methyl -1,4-benzoquinone (MBQ), 2,6-dimethyl - 1,4-benzoquinone (DMBQ)) have been studied in N, N - dimethyl formamide by means of absorption spectral techniques. The complexes have absorption maximum in the range 453 nm to 458 nm. The emission maximum is in the range 603-610 nm. The binding constant (k_b) for these reactions are determined from the Benesi Hildebrand equation using the absorption intensity data. The observed binding constant values are sensitive to the nature of the ligand, as well as the quenchers. Structural effect seems to play an important role on the binding of these quinones with these complexes.

Keywords: Binding, quenching, uminescence, quinones.

Introduction

Quinones are ubiquitous in nature they are electron transfer mediators between PSI and PSII and act as anticancer drugs in medicine [1-4]. They are electron acceptors in nature for variety of reasons. They have predominant application in drugs like antibiotics and as antimalarial agents. The redox behavior of quinones play a vital role in the electrochemical reactions during biological energy storage and transduction. Recent studies provide evidence for quinones utilizers in energy application changes the hybridisation of quinone with various organic and inorganic materials.[5].

Ruthenium (II) polypyridyl complexes have been thoroughly studied due to their unique combination of chemical stability, redox potential, light absorption, and excited state energy. These Ru (II) polypyridine complexes have made an important contribution to the growth of several branches of chemistry including photochemistry, photophysics, photocatalysts, and electrochemistry. These complexes have resulted in wide applications in different areas from solar energy related research to molecular wires, sensors, switches, machines and also as therapeutic agents. The ET reactions of several quinones with excited state $[Ru(NN)_3]^{2+}$ complexes have been reported. previously [6-9]. These ruthenium (II) polypyridyl complexes are potential anticancer drugs. They undergo binding with proteins, DNA, RNA. Herein we report a detailed study on the binding of 1,4-benzoquinone, 2 - methyl -1, 4-benzoquinone and 2,6-dimethyl-1 4- benzoquinone on tris (4,4' - dialkyl -2, 2' - bipyridine) ruthenium (II) complexes in aprotic solvent, DMF.

Experimental

Materials and Methods

The ligands 2,2'- bipyridine , 4,4'- dimethyl -2,2' -bipyridine ,the quinones namely 1,4-benzoquinone, 2- methyl - 1,4 - benzoquinone, 2,6-dimethyl -1, 4- benzoquinone were procured from Sigma Aldrich and were used without any purification. N,N' – dimethyl formamide was purchased from Merck. Binding studies were carried out using N,N- dimethyl formamide. The two $[\text{Ru}(\text{NN})_3]^{2+}$ complexes (where NN= 2,2'- bipyridine (bpy), 4,4'- dimethyl -2,2'- bipyridine (dmbpy)) were synthesized by reacting $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with the corresponding ligands according to the procedure previously described [7].

Spectral measurements

The absorption spectral measurements were recorded using SYSTRONICS 2203 Double Beam Spectrophotometer. Emission studies were recorded using JASCO/FP 8600 Spectrofluorometer. Excited state lifetime of the complex was made with laser flash photophysics techniques using an Applied photophysics SP - Quanta Ray GCR -2 Nd : YAG laser as the excitation source [10]. The structure of the quinones and the ligands used in the present study as shown in figure 1 and 2 respectively. The $[\text{Ru}(\text{NN})_3]^{2+}$ concentration was fixed at 2×10^{-5} M and the quinone concentration was varied between 4×10^{-6} and 2.8×10^{-7} M. The same sample solutions were used for both absorption and emission studies. All the sample solutions used for emission studies were deaerated for ~ 30 min using dry N_2 gas purging by keeping the solutions in cold water to ensure that there was no change in the volume of the solution. All measurements were carried out at room temperature.

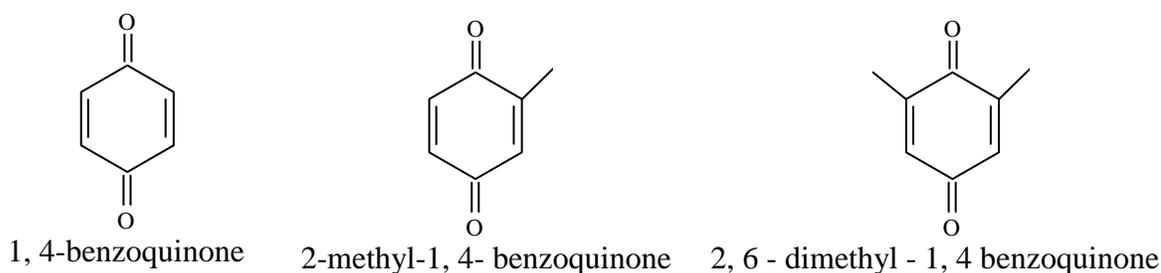


Fig.1: Structure of Quinones



Fig. 2: Structure of the ligands used.

Results and Discussion

The absorption maximum, emission maximum and lifetime of the two complexes in DMF are shown in table 1. The ‘MLCT state of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex has an absorption in the visible region at 453 nm whereas $[\text{Ru}(\text{dmbpy})_3]^{2+}$ complex has the absorption maximum at 458 nm. This red shift may be due to the presence of electron releasing group in the 4,4' position of 2,2'-bipyridine ligand and the change in the absorption spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex in the presence of increasing concentration of 1,4-benzoquinone is shown in figure. 3. There is a slight change in the absorption intensity of MLCT of $[\text{Ru}(\text{NN})_3]^{2+}$, which is more sufficient to determine the binding constant for the binding of quinones with $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{dmbpy})_3]^{2+}$ complexes.

The binding constant (k_b) of the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes with quinones were determined from the Benesi – Hildebrand equation using absorption intensity ratio [eqn.1].

$$\frac{1}{\Delta A} = \frac{1}{k_b} \Delta \epsilon [\text{H}] + \frac{1}{\Delta \epsilon} [\text{Q}] \quad (1)$$

where ΔA is the change in absorbance of the complex with different concentrations ($[\text{Q}]$) of the quinones. The plot of $\frac{1}{\Delta A}$ of verses $\frac{1}{[\text{Q}]}$ give a straight line, k_b can be calculated from the ratio of y - intercept to the slope of the straight line. The binding constants are shown in table 2. The Benesi - Hildebrand plots are shown in figure. 4. The obtained k_b values are in the order of $10^4 - 10^5 \text{ M}^{-1}$.

Table 1: Photophysical properties of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in DMF.

Complex	Absorption maximum (nm)	Emission maximum (nm)	Excited state lifetime (ns)
$[\text{Ru}(\text{bpy})_3]^{2+}$	453	603	912
$[\text{Ru}(\text{dmbpy})_3]^{2+}$	453	608	164

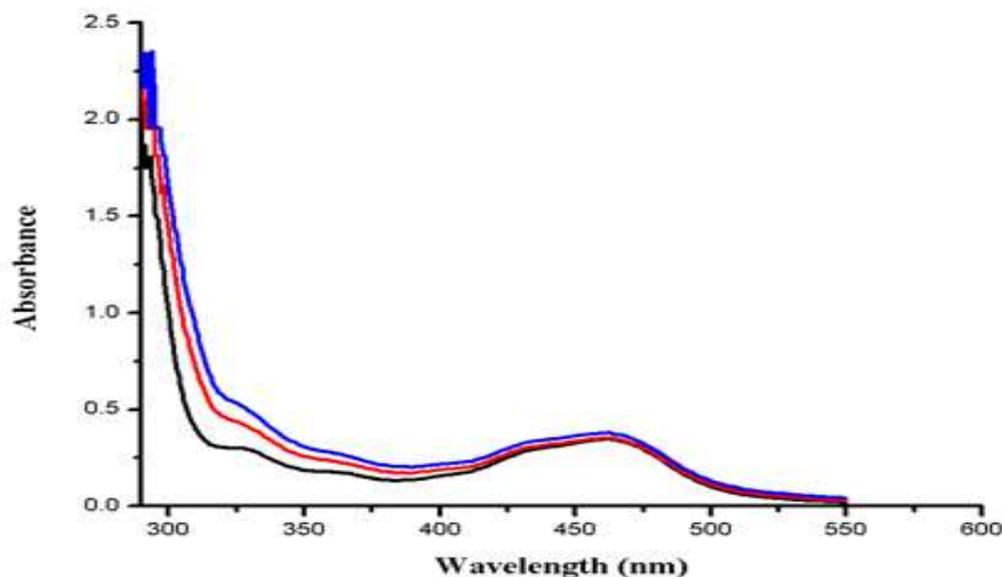


Fig. 3: Absorption spectrum of $[\text{Ru}(\text{dmbpy})_3]^{2+}$ shows with incremental concentration of 1,4-benzoquinone in DMF

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})	
	$[Ru(bpy)_3]^{2+}$	$[Ru(dmbpy)_3]^{2+}$
1,4 - benzoquinone	4.14×10^4	4.91×10^4
2- methyl -1,4 - benzoquinone	9.31×10^4	9.77×10^4
2,6 - dimethyl -1,4 - benzoquinone	1.04×10^5	1.24×10^5

The ground state interaction between quinones and the bipyridyl ligands of $[Ru(NN)_3]^{2+}$ complexes are hydrophobic or π - stacking in nature. The binding becomes stronger when the π - π stacking interactions exist between the ligands of Ru(II) complexes and the quinones. The hydrophobic nature increases from $[Ru(bpy)_3]^{2+}$ to $[Ru(dmbpy)_3]^{2+}$ complex due to the presence of alkyl substituted ligand. As the hydrophobic nature of the ligands increase, the binding constant k_b values also increases. This results clearly indicates that k_b value depends on the hydrophobic nature of the ligands.

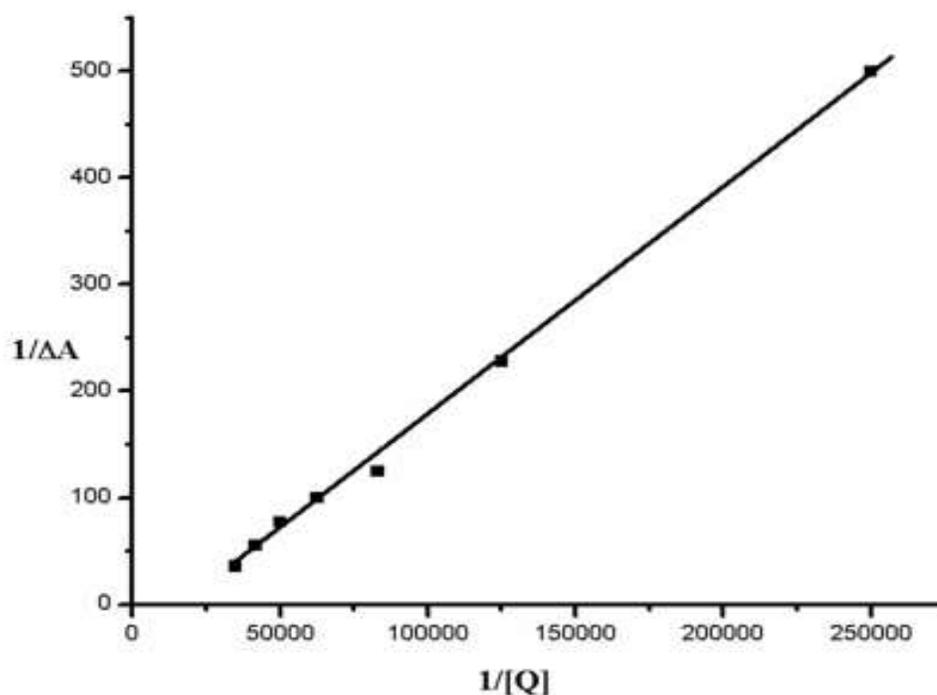


Fig. 4: Benesi – Hildebrand plot on MLCT absorption $[Ru(bpy)_3]^{2+}$ complex with incremental addition of 2,6 - dimethyl -1,4 benzoquinone in DMF.

$[Ru(bpy)_3]^{2+}$ complex, the binding constant values k_b is in the order DMBQ > MBQ > BQ. $[Ru(dmbpy)_3]^{2+}$ has also the same order for all the quenchers, showing that the k_b values depend on the size of the quinones. This indicates that the k_b is not only sensitive to the nature of the ligand, but also on the structure of the quinones. Thus k_b depends on the substituents present in the ligands and the quinones.

Conclusion

The binding of 1,4-benzoquinone, 2 - methyl -1,4 - benzoquinone, 2, 6- dimethyl-1,4-benzoquinone with $[\text{Ru}(\text{NN})_3]^{2+}$ complexes in DMF medium has been studied by absorption spectral techniques. The binding constants are determined by using Benesi - Hildebrand plot. The binding constants depend on the hydrophobic nature of the ligands. Structural effect also influence the binding of quinones with $[\text{Ru}(\text{NN})_3]^{2+}$ complexes.

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