ROLE OF OXYGEN ON THE PHOTOINDUCED ELECTRON TRANSFER REACTIONS OF Ru(II) POLYPYRIDINE COMPLEXES WITH AROMATIC AMINES

T. Rajendran[1,2], G. Balakrishnan[3], K. Senthil Murugan[3], P. Kathiravan[4], P. Jayaprakash[4],

V. K. Sivasubramanian[5], M. Ganesan[5]

Professor, Department of Chemistry, PSNA College of Engineering & Technology, Dindigul-624 622, India[1]

Research Scholar, Department of Chemistry, Vivekananda College, Tiruvedagam West, Madurai 625 234, India[3]

P.G Student, Department of Chemistry, Vivekananda College, Tiruvedagam West, Madurai 625 234, India[4]

Associate Professor, Department of Chemistry, Vivekananda College, Tiruvedagam West, Madurai 625 234, India[2,5]

Abstract: The present work involves an attempt to prepare two Ruthenium(II) complexes [Ru(bpy)3]2+ (I) and [Ru(phen)3]2+ (II) by simple and effective one-pot synthesis in a greener way and we have succeeded in achieving the target compounds in very good yields. Furthermore, we have studied extensively the photochemical reduction of complex I and II , *[Ru(NN)3]2+ in their excited states with various aromatic amines in the absence and presence of oxygen molecules by the luminescence quenching technique. The quenching rate constants, kq for each photoredox reactions have been determined using Stern - Volmer analysis. The results exhibit an interesting trend which depends on the nature of the quencher. In particular, the result proves the efficient interacting mechanism of oxygen with the excited state of $*[Ru(NN)_3]^{2+}$.

Keywords: One-pot synthesis, Fluorescence-quenching studies, role of oxygen, Stern-Volmer analysis, aromatic amines.

I. INTRODUCTION

Electron transfer is an active topic in chemical research, particularly in solar energy conversion and photosynthetic process [1, 2]. It is well-know that medium effects, such as solvent polarity, heterogeneity of the microenvironment and the addition of salts, have an important influence on the dynamics of photoinduced electron transfer between donor and acceptor in solutions [3]. Ruthenium (II) complexes based on bipyridine ligands are highly interesting due to their photophysical and redox properties [4]. The ruthenium (II) ion offers a series of advantages: (a) due to the octahedral complex geometry, specific ligands can be introduced in a controlled manner; (b) the photophysical, photochemical and the electrochemical properties of these complexes can be tuned in a predictable way; (c) the ruthenium metal ion possesses stable and accessible oxidation states ranging from I to III. (d) Ruthenium (II) forms kinetically stable bonds with bipyridine, facilitating the synthesis of heteroleptic compounds in good yields.

The rate of electron transfer (ET) from a donor to an acceptor molecule is influenced by exothermicity, reorganization energy and distance [5-8]. During the past three decades numerous theoretical and experimental studies have been directed towards understanding the above factors that affect the rate of photoinduced ET reactions of Ru(II) complexes [9-15]. To a large extent the ligands of [Ru(NN)3]2+ (NN being the polypyridine ligand) and the nature of the quencher determine the distance over which the ET occurs[16-18]. The distance dependence of ET has become increasingly important as attempts are made to unravel the complexities of ET reactions in biological systems and in natural and synthetic solar energy conversion systems [19, 20]. In particularly, the study of ET from amines (donor) to an acceptor (d6 – metal complex) is a highly important topic owing to the application of cell imaging,

photopolymerization and also used in the synthesis of amino acids, alkaloids and several other nitrogen-containing compounds of biological and pharmaceutical importance [21]. Base on the future application, we are much interested to investigate the ET transfer reaction of ruthenium (II) complexes with different aromatic amines.

Reports on the solvothermal one-pot greener synthesis and fluorescence quenching studies of different metal complexes with various biologically important quenchers have been already reported from our research group [22]. Herein we report a detailed study on the photoinduced electron transfer reactions of two Ru(II) polypyridyl complexes (I and II) with aromatic amines in the absence and presence of oxygen molecule in acetonitrile medium.

II. EXPERIMENTAL

All chemicals, 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and RuCl3.3H2O were purchased from Sigma Aldrich and used as received. The aromatic amines used in this study were obtained from Merck and Alfa Aesar. Solvent were dried by distillation over appropriate drying agents, distilled and stored under dinitrogen.

Absorption spectra were recorded using JASCO V-530 UV-visible Spectrophotometer. The emission spectra were recorded using JASCO FP-6200 Spectrofluorimeter. All the sample solutions used for the deaerated emission measurements were purged with dry N2 purging for about 30 min, by keeping solution in cold water to ensure that there is no change in the volume of the solution. All the measurements were done at room temperature. Both the absorption and emission titrations were carried out by keeping the concentration of complexes as constant (1×10^{-5} M) while varying the concentration of aromatic amines.

A suspension containing a mixture of 0.261g RuCl3.3H2O (1.0 mmol) and α-diimine (3.2 mmol) in 10 ml of ethanol in a 15 ml Teflon flask was placed in a steel bomb. The bomb was placed in an oven maintained at 1600C for 48h and then cooled to 300C. Good quality, red orange colored crystals were separated by filtration and washing with hexane. The solvent from the reaction mixture was removed by vacuum distillation and the residue was recrystallized by ethanol. Yield ~ 89 % for (I) and~ 84 % for (II) . 1H NMR spectra of the two Ru(II) complexes have good agreement with the previously published reports [5].

III. RESULTS AND DISCUSSION

The structures of the ruthenium complex $[Ru(bpy)_3]^{2+}$ (**I**) and $[Ru(phen)_3]^{2+}$ (II) and aromatic amines used in the present study are shown in Chart 1 and 2.

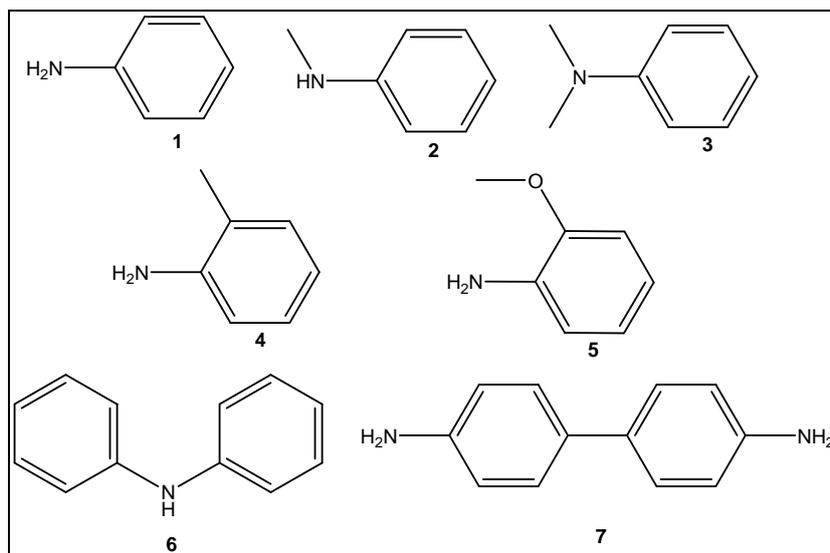Chart 1: Structure of Ru(II) polypyridyl complexes
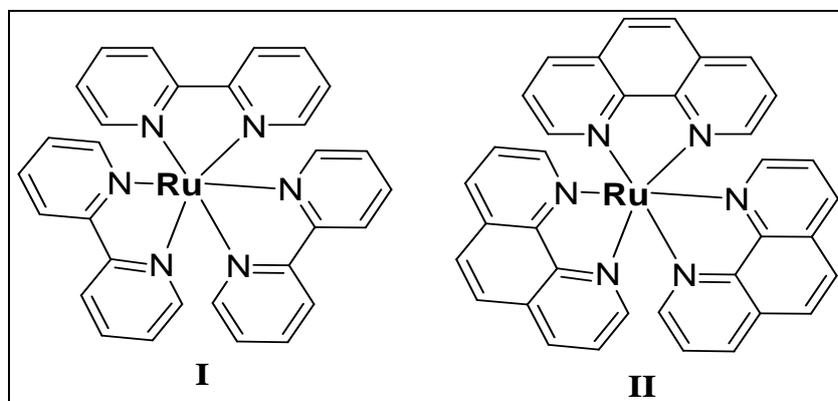
Chart 2: Structure of aromatic amines

1. Aniline 2. N-Methylaniline 3. N,N'-Dimethylaniline 4. *o*-toluidine 5. *o*-Anisidine 6. Diphenylamine 7. Benzidine	

To confirm this the authors have recorded both the absorption and the emission spectra of Ru(II) complexes I and II in acetonitrile medium (Figure 1 and 2). Table 1 summarizes the electronic absorption and emission spectral data and excited-state lifetime data of complex.
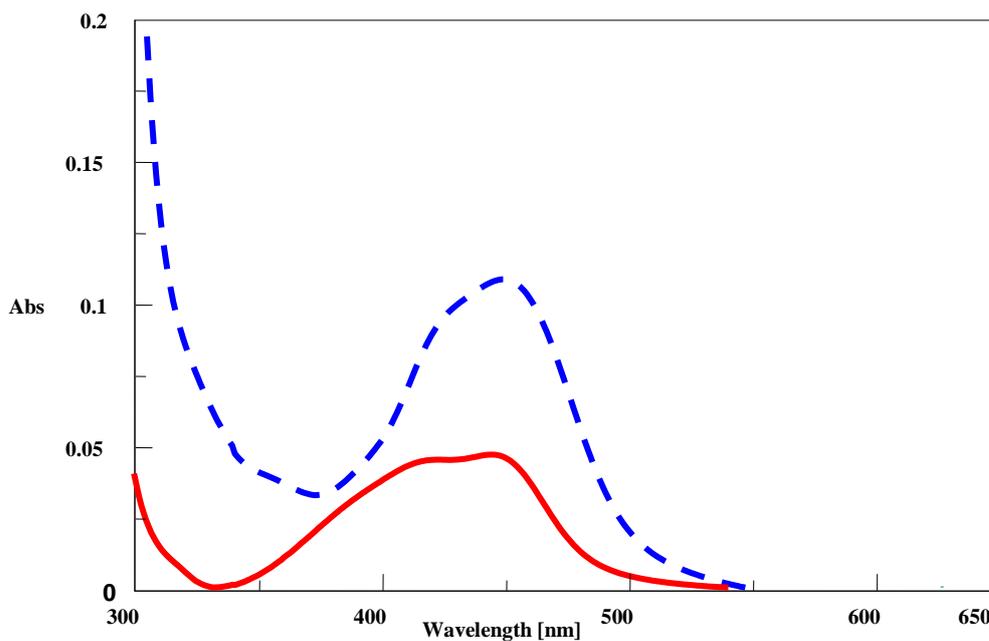

Fig. 1 Overlay absorption spectrum of complexes (I and II) in CH3CN at 298K
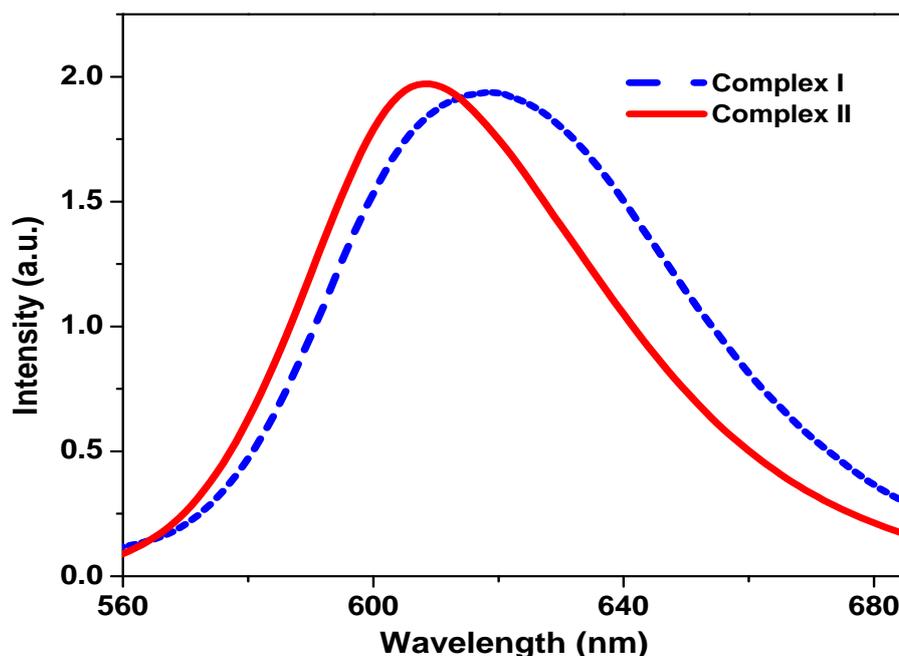
Fig. 2 Overlay emission spectrum of complexes (I and II) in CH3CN at 298K

TABLE I
Photphysical analytical data for complexes $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ in acetonitrile at 298K

S.No	$[Ru(NN)_3]^{2+}$	Absorption[a]	Emission[a]	τ (µs)
1	$[Ru(bpy)_3]^{2+}$	449, 286	620	0.86
2	$[Ru(phen)_3]^{2+}$	420, 262	604	0.46

*τ taken from the publised report [26]

To study the quenching of these complexes with various aromatic amines incremental addition of various aromatic amines have been added and the fluorescence spectra were recorded. The change in the luminescence intensity of the excited states of the complexes I and II with aniline and N,N-dimethylaniline in deaerated condition are shown in Figures 3a and 4a. The quenching rate constant, k_q, values were determined from the Stern-Volmer equation[22].

$$I_0/I = 1+ K_{SV}[Q] = 1+kq\,\tau_0[Q] \tag{1}$$

Where I_0 and I are the steady-state fluorescence intensities in the absence and presence of quencher, respectively, K_{SV} is the Stern−Volmer quenching constant, $[Q]$ is the total concentration of quencher, k_q is the bimolecular quenching constant, and τ_0 is the average lifetime of complex in the absence of quencher.
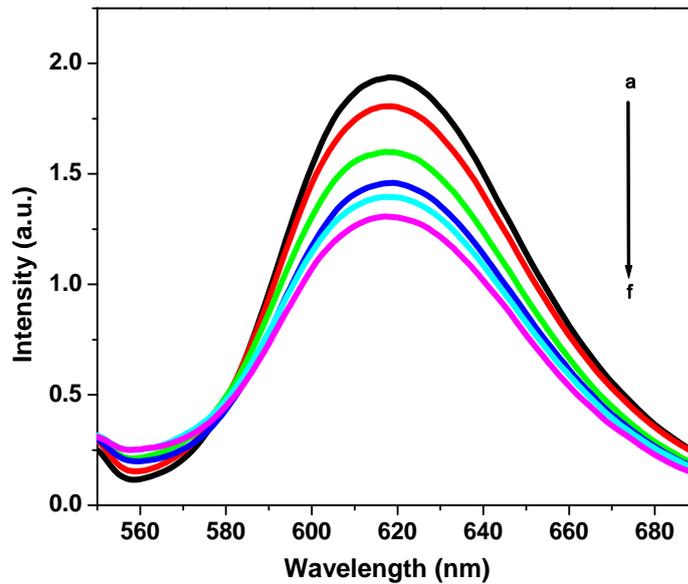
Fig. 3 (a) Overlay emission spectra of I (2 x 10^{-5} M) with different concentration of Aniline in aerated acetonitrile at 298K Figure 3b.
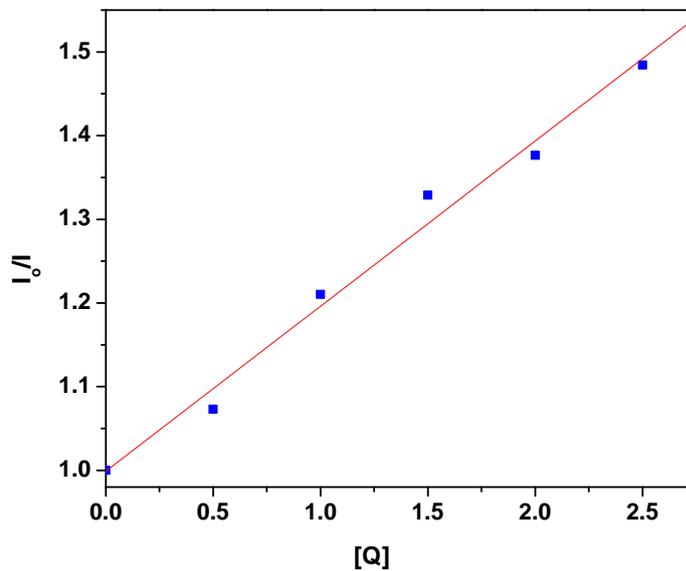

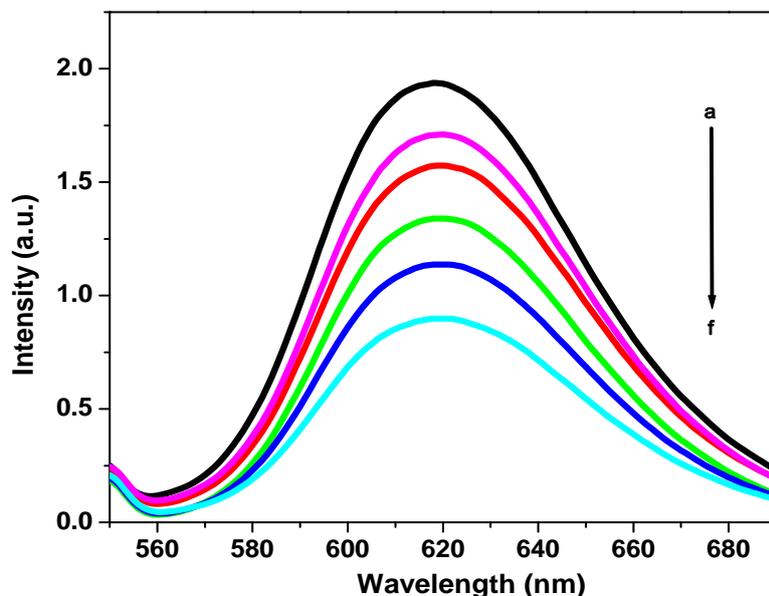Fig. 3 (b) S-V plot of **I** (2 x 10^{-5} M) with different concentration of Aniline in aerated acetonitrile at 298K

Fig. 4 (a) Overlay emission spectrum of **II** (2×10^{-5} M) with different concentration of Aniline in aerated acetonitrile at 298K
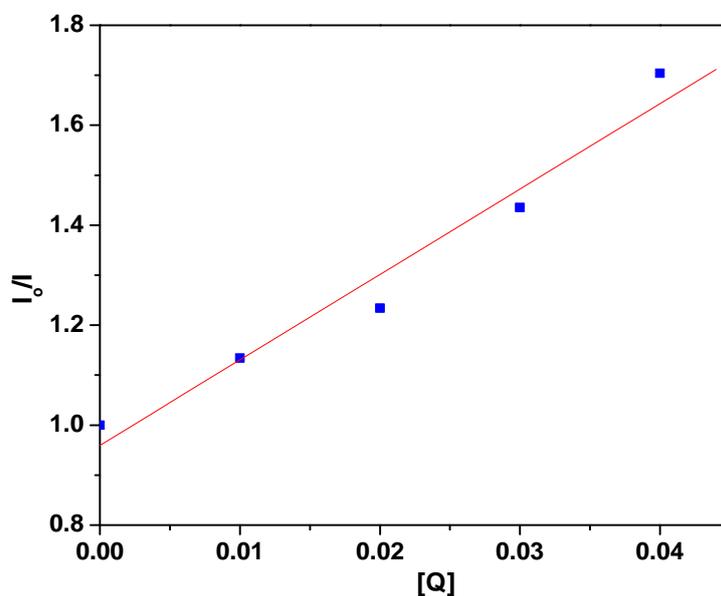

Fig. 4 (b) S-V plot of **II** (2×10^{-5} M) with different concentration of Aniline in aerated acetonitrile at 298K

The corresponding Stern− Volmer quenching rate constants, k_q values have been given in Table 2. All the Stern−Volmer plots exibit a good linear relationship (Figure 3b and 4b).

The quenching rate constant values, k_q for the excited state electron transfer reactions of the $[Ru(bpy)_3]^{2+}$ and that of $[Ru(phen)_3]^{2+}$ with various aromatic amines have been tabulated in Tables 2 in the presence and absence of dissolved oxygen. From table 2 we can infer that all the aromatic amines quench the excited triplet state of $[Ru(bpy)_3]^{2+}$ efficiently even in the presence of dissolved oxygen. The k_q value varies from 3.1×10^5 $M^{-1}s^{-1}$ to 3.1×10^9 $M^{-1}s^{-1}$ for aniline and benzidine respectively. The gradation in the quenching rate can be explained in terms of the variation in the oxidation potential of the aromatic amines. These results show that both electronic and steric effects play important role

in the reductive quenching of the excited state of $[Ru(bpy)_3]^{2+}$. A similar trend was observed with $[Ru(phen)_3]^{2+}$ also. The k_q values gradually vary from 1.0×10^5 to $2.8 \times 10^9 \, M^{-1}s^{-1}$. This can be explained in line with Tazuke et al as follows [23]. The quenching was shown to depend on the nature of the aromatic amine; the quenching by tertiary amines was always faster than that by primary and secondary amines when k_q are compared at the same free energy change. The results are explained by the variation of outer-sphere reorganization energy and with the nature of a quencher. For the quenching by tertiary and primary/secondary amines, the radii of the quencher (r_Q^{ex}) were estimated to be 3 and 2.4 Å, respectively [23]. A close scrutiny of the Table 2 reveals the fact that the k_q values for the excited state electron transfer reaction between $[Ru(bpy)_3]^{2+}$ and aromatic amines in the absence of dissolved oxygen exhibits an enormous enhancement to the tune of four orders in same cases e.g. Aniline. Except Benzedrine the k_q values shows a difference of two to four orders which is remarkable one. These results prove the efficient interacting mechanism of oxygen with the excited state of $[Ru(bpy)_3]^{2+}$.
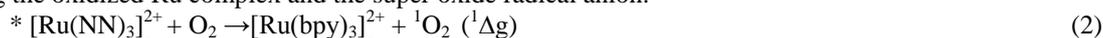
TABLE II
Rate constants for the reductive quenching of *$[Ru(bpy)_3]^{2+}$ and *$[Ru(phen)_3]^{2+}$ in aerated and deaerated acetonitrile at 298K.

S.No	Quencher (E (D$^+$/D) *vs* SCE) [a]	k_q M^{-1} s^{-1}			
		$[Ru(bpy)_3]^{2+}$		$[Ru(phen)_3]^{2+}$	
		Aerated	Deaerated	Aerated	Deaerated
1	*o*-Anisidine (0.76)	1.1×10^6	3.0×10^8	1.1×10^6	3.4×10^9
2	N-Methylaniline (0.77)	3.9×10^6	1.3×10^9	1.0×10^5	3.0×10^9
3	N,N-Dimethylaniline (0.81)	1.9×10^7	2.7×10^9	5.1×10^7	3.9×10^9
4	Diphenylamine (0.83)	3.5×10^5	9.4×10^8	2.2×10^6	3.1×10^8
5	*o*-Toludine (0.85)	7.2×10^5	3.8×10^8	9.0×10^5	5.0×10^8
6	Aniline (0.98)	2.3×10^5	1.9×10^9	9.6×10^5	3.4×10^9
7	Benzidine (1.03)	3.1×10^9	3.7×10^{10}	2.8×10^9	2.8×10^6

[a]Oxidation potential of D in acetonitrile (Volt *vs* SCE).

Photochemical Oxidation of [Ru(NN)3]2+ using molecular oxygen
Molecular oxygen is among several molecules which exhibit high efficiency towards quenching of excited state of the complex, *[Ru(bpy)3]2+ in aqueous solution (kq = 3.3x109 M-1s-1) [24]. The quenching of *[Ru(bpy)3]2+ by molecular oxygen can in principle occur mostly via two mechanisms. One is energy transfer quenching (eq. 2) generating the ground state sensitizer and singlet oxygen. The other mechanism is electron transfer (ET) quenching (eq. 3) generating the oxidized Ru complex and the super oxide radical anion.

$$* [Ru(NN)_3]^{2+} + O_2 \rightarrow [Ru(bpy)_3]^{2+} + {}^1O_2 \ ({}^1\Delta g) \tag{2}$$

$$* [Ru(NN)_3]^{2+} + O_2 \rightarrow [Ru(bpy)_3]^{3+} + O^{\bullet}_2 \ ({}^1\Delta g) \tag{3}$$

Much of the work on this system has focused on the issue of charge transfer *vs.* energy transfer. Both processes are energetically possible ($\Delta G^o_{CT} = -0.72$ eV, $\Delta G^o_{ET} = -1.17$ eV in H_2O at pH 7.0). These thermodynamic data indicate that energy transfer is thermodynamically the preferred pathway at pH 7.0. Lin and Sutin [25] were the first to suggest that quenching occurs *via* the electron transfer pathway. Moreover, reaction of *$[Ru(bpy)_3]^{2+}$ with O_2 and Fe(II) in acid solutions leads to the formation of Fe(III) which presumably involves an electron transfer pathway. A similar trend is observed with our case also. We come to a conclusion that either of the mechanisms or both the mechanisms, may be operating in our case also. The variation of the k_q values shows a gradation from 2 to 3 orders except benzidine which shows only one order difference. These vast variations in the quenching rate constants again prove the effective role of oxygen in the quenching pathway. The interesting thing is that we have not purged molecular oxygen as molecular nitrogen in all our experiments. The dissolved oxygen itself was sufficient to quench the excited triplet states of the

ruthenium polypyridyl complexes. The gradation in the quenching rates can be explained in terms of the oxidation potential of aromatic amines and the reduction potential of ruthenium polypyridyl complexs.

IV. CONCLUSION

Two ruthenium(ii) polypyridyl complexes, i.e., *$[ru(bpy)_3]^{2+}$ and *$[ru(phen)_3]^{2+}$ have been prepared by a novel one-pot, ecofriendly solvothermal method. They were characterized by both uv-vis and fluorescence techniques. The excited stated behaviors of these complexes were studied using various aromatic amines both in presence and absence of molecular oxygen. The efficient quenching of these excited states were further enhanced by the presence of molecular oxygen. The effective role of oxygen in these quenching mechanisms may be *via* tow pathways producing either singlet oxygen or super oxide radical anion.

REFERENCES

[1]. P. Guillo, O. Hamelin, P. Batat, G. Jonusauskas, N. D. McClenaghan and S. Ménage, Inorg. Chem., 2012, 51, 2230.
[2]. C. Herrero, A. Quaranta, W. Leibl, A. W. Rutherford and A. Aukauloo, Fuel. Energy Environ. Sci. 2011, 4, 2365.
[3]. (a). K. Kalyanasundaram, In Photochemistry in Microheterogeneous System; Academic Press: New York, 1987;
(b). H. Imahori, H. Yamada, D. M. Guldi, Y. Endo, A. Shimomura, S. Kundu, K. Yamada, T. Okada, Y. Sakata and S. Fukuzumi, Angew. Chem., Int. Ed., 2002, 41, 2344.
(c). S. Dutta Choudhury and S. Basu, J. Phys.Chem. A, 2005, 109, 8113;
(d). P. Lopez-Cornejo, M. Hernandez, P. Perez-Tejeda, F. Perez, R. Prado-Gotor and F. Sanchez, J. Phys. Chem. B, 2005,109, 1703.
[4]. V. Balzani, A. Juris and M. Venturi. Chem. Rev., 1996, 96, 759.
[5]. (a). T. Rajendran, P. Thanasekaran, S. Rajagopal, G. A. Gnanaraj, C. Srinivasan, P. Ramamurthy, B. Venkatachalapathy, B. Manimaran and K-L. Lu, Phys. Chem. Chem. Phys., 2001, 3, 2069;
(b). T. Rajendran, S. Rajagopal, C. Srinivasan and P. Ramamurthy, J. Chem. Soc., Faraday Trans., 1997, 93(17), 3160.
(c). Photophysics and photochemistry of some metal complexes. Ph. D diss., Madurai Kamaraj Univsrity.
[6]. R. A. Marcus and N. Sutin, Biochim. Biophys. Acta., 1985, 811, 265.
[7]. J. R. Bolton, N. Mataga and G. McLendon, Electron Transfer in Inorganic, Organic and Biological Systems, ed. American Chemical Society, Washington DC, 1991.
[8]. H. B. Gray and J. R. Winkler Annu. Rev. Biochem., 1996, 65, 537.
[9]. T. J. Meyer, (1983). Excited-state electron transfer. Prog. Inorg. Chem., 30, 389.
[10]. K. Kalyanasundaram, Photochemistry of Polypyridine and Porphyrin Complexes, Academic Press, London, 1992.
[11]. D. Clark and M. Z. H. Man, Coord. Chem. Rev., 1997 159, 359.
[12]. N. Kitamura, H. B. Kim, V. Okano and S. J. Tazuke, Phys. Chem., 1989, 93, 5750.
[13]. R. Rau, R. Franck and G. J. Greiner, J. Phys. Chem., 1986, 90, 2476.
[14]. H. Sun and M. Z. Ho. Man, J. Phys. Chem., 1994, 98, 11719.
[15]. D. Sandrini, M. Maestri, P. A. Belser, V. Zelewsky and V. Balzani, J. Phys. Chem., 1985, 89, 3675.
[16]. G. McLendon, Acc. Chem. Res., 1988, 21, 160.
[17]. M. R. Wasielewski, Chem. Rev., 1992, 92, 435.
[18]. V. L. Davidson, Acc. Chem. Res., 2000, 33, 87.
[19]. T. J. Meyer, Acc. Chem. Res., 1989, 22, 163.
[20]. M. Gratzel, Heterogeneous Photochemical Electron Transfer, CRC Press, Boca Raton, FL, 1989.
[21]. (a) P. Chen, A. M. Doweyko, D. Norris, H. H. Gu, S. H. Spergel, J. Das, R. V. Moquin, J. Lin, J. Wityak, E. J. Iwanowicz, K. W.McIntyre, D. J. Shuster, K. Behnia, S. Chong, H. de Fex, S. Pang, S. Pitt, D. R. Shen, S. Thrall, P. Stanley, O. R. Kocy, M. R. Witmer, S. B. Kanner, G. L. Schieven and J. C. Barrish, J. Med. Chem., 2004, 47, 4517.
(b) K. Strømgaard and I. Mellor, Med. Res. Rev., 2004, 24, 589.
(c) A. Krezel and W. Bal, Chem. Res. Toxicol., 2004, 17, 392.
(d) R. D. Theys, and G. Sosnovsky, Chem. Rev., 1997, 97, 83;
(e) S. K. Bergstrom, N. Edenwall, M. Laven, I. Velikyan, B. Langstrom and K. E. Markides, Anal. Chem., 2005, 77, 938;
(f) L. J. Mathias, B. S. Shemper, M. Alirol and J. F. Morizur, Macromolecules, 2004, 37, 3231.
[22]. (a) P. Thanasekaran, R.-T. Liao, B. Manimaran, Y.-H. Liu, P.-T. Chou, S. Rajagopal and K.-L. Lu, J. Phys. Chem. A, 2006, 110, 10689;
(b) P. Thanasekaran, J-Y. Wu, B. Manimaran, T. Rajendran,I-J. Chang, S. Rajagopal, G-H. Lee, S.-M. Peng and K.-L. Lu, J. Phys. Chem. A., 2007, 111(43)10960;
(c) T. Rajendran, B. Manimaran, R.-T. Liao, Y.-H. Liu. P. Thansekaran, R.-J. Lin, P.-T. Chang, R. Ramaraj, S. Rajagopal, K.-L. Lu, Dalton Trans., 2010, 39, 2935.
[23]. N. Kitamura, H. B. Kim, V. Okano and S. J. Tazuke, Phys. Chem., 1989, 93, 5750.
[24]. (a) R. S. Lumpkin, E. M. kober, L. A. Worl, Z. Murtaza and T. J. Meyer, J. Phys. Chem., 1990, 94, 239.
(b) T. S. Akasheh and Z. M. El-Ahmed, Chem, Phys. Lett., 1988, 154, 414.
[25]. C. T. Liu, W. Bottcher, M. Chou, C. Crutz and N. Sutin, J. Am. Chem. Soc., 1976, 98, 6536.
(a) P. Thanasekaran, T. Rajendran, S. Rajagopal, C. Srinivasan, R. Ramaraj, P. Ramamurthy and B. Venkatachalapathy, Phys. Chem. A., 1997, 101, 8199.