

Photoinduced Electron Transfer Reactions of Ruthenium(II) Phenanthroline Complexes with Dimethylaniline in Aqueous and Micellar Media

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Abstract Four $[\text{Ru}(\text{NN})_3]^{2+}$ complexes (NN=polypyridine) with ligands of varying hydrophobicity with different charges +2, 0 and -4 were synthesized. The photophysics and photo-induced electron transfer reactions of these Ru(II)-complexes with dimethylaniline (DMA) as the quencher have been studied in aqueous medium and ionic and non-ionic micellar medium. The extent of binding of the complexes with the surfactant interface is evident from the calculated binding constant values (K). Dimethylaniline (DMA) being a neutral quencher, the hydrophobic and electrostatic interactions competing with one another and their combined effect with the surfactants were reported by observing the quenching rate constant (k_q) values. The formation of anilinium cation radical in transient absorption spectrum confirms the excited state electron transfer reactions of ruthenium(II) complexes with dimethylaniline. The calculated rate constant values (k_q) are in good agreement with the experimental k_q values giving quantitative evidence for the bimolecular reductive quenching rate constant for the complexes with DMA. Pseudophase ion exchange model is successfully applied to analyse the quenching data.

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Introduction

Electron transfer (ET) is one of the most fundamental processes occurring in chemistry and biology [1–5]. In most chemical systems, transfer of an electron from a ground-state donor to a ground-state acceptor is energetically unfavorable. However, photoexcitation of either the acceptor or the donor often makes the ET reaction energetically favorable and thus the reaction occurs with a reasonable rate. The key factor is to use the photon energy to achieve efficient charge separation over long distances, thereby establishing a potential gradient that, in turn, can be converted into chemical energy, in the case of photosynthetic organisms, or into electric energy, in the case of photovoltaic cells. It is thus interesting to investigate ET processes in organized media to understand how the confined geometry controls the mechanism and dynamics of such reactions. The photophysics and photochemistry of ruthenium(II)-polypyridyl complexes are highly influenced by the change of solvent as well as the change of medium from homogenous to microheterogeneous [6–12].

Ruthenium(II)-polypyridyl complexes of different charges can be designed by introducing CO_2^- and SO_3^- functionalities in the polypyridine ligands to provide an opportunity to bind the crucial interface regions in microheterogeneous medium. Aqueous micelle-bound catalytic systems of this type are attractive alternatives to toxic, expensive organic solvents and are precursors to future designs of surfactant assemblies which may mimic the reactions in biological membranes [13]. The organized media like micelles are well documented as novel environments for photochemical conversion because the micellar systems can promote the ET from electron donor to acceptor by concentrating them [14]. In addition to the above advantages, micelles affect the lifetimes of the

photoexcited states and efficiency of reverse ET by their appropriate microenvironments composed of a hydrophobic core, an aqueous phase and a charged interface [15, 16].

The presence of hydrophobic groups like alkyl and aryl in the ligands of $[\text{Ru}(\text{NN})_3]^{2+}$ leads to strong binding of $[\text{Ru}(\text{NN})_3]^{2+}$ with micelles through hydrophobic interaction. The strength of binding depends on the combination of electrostatic attractions or repulsions and hydrophobic effects [17–22]. Davies et al. studied the effects of micellar solution on the electron transfer reaction between $[\text{Co}(\text{terpyr})]^{2+}$ and a series of Co(III)-complexes in varying ligand structure and ionic charge redox reactions of amphiphilic cobalt complexes [23]. Gutiérrez et al. investigated the generation of singlet oxygen and quenching process in microheterogeneous media and reported that the nature of the ligands and the size and charge of the Ru(II) complexes are important factors affecting their effective location and singlet oxygen production in these media [11]. Though a few reports on photoinduced intermolecular electron transfer in micelles are available the systematic study with varying charge and hydrophobicity is relatively limited. In the present study four $[\text{Ru}(\text{NN})_3]^{2+}$ complexes (**I–IV**) with ligands of varying hydrophobicity and with different charges +2, 0, –4 have been chosen. The nature of the charge and the hydrophobicity of the probe and the environment (anionic, SDS, cationic CTAB and neutral surfactant, Triton X-100) decide the forces that assist in binding. Amines are excellent electron donors because of their low ionization potentials. The lone pair electrons on the nitrogen atom leads to facile electron-transfer (ET) reactions of amines in a number of chemical, electrochemical, photochemical, and biochemical redox processes [24–29]. The neutral quencher *N,N'*-dimethylaniline (DMA), chosen in the present study does not experience any coulombic interaction from the charged surfactants. DMA, being insoluble in water, it is made soluble in water containing 1 % acetonitrile. The observed interesting results on the photoinduced ET reactions of four Ru(II)-complexes with DMA in the presence of different micelles are presented and the data were analyzed using pseudophase ion exchange model.

Experimental Section

Materials

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 1,10-phenanthroline, bathophenanthroline (dpphen) and bathophenanthroline disulphonic acid (dpsphen), and surfactant like CTAB, SDS, Triton X-100 obtained from Aldrich and Merck were used as such. The tris-chelated complexes $[\text{Ru}(\text{phen})_3]^{2+}$ (**I**), $[\text{Ru}(\text{dpphen})_3]^{2+}$ (**II**), $[\text{Ru}(\text{phen})_2(\text{dpsphen})]$ (**III**), and $[\text{Ru}(\text{dpsphen})_3]^{4+}$ (**IV**) were prepared by a published procedures [30–33].

Absorption and Emission Spectral Measurements

Sample solutions of the metal complexes and the surfactants have been freshly prepared for each measurement. The absorption spectral measurements were carried out using a SPECORD S100 diode-array spectrophotometer. Emission intensity measurements were carried out using FP-6300 spectrofluorometer. All the sample solutions used for emission measurements were deaerated for about 30 min by dry nitrogen gas purging by keeping solutions in cold water to ensure that there is no change in the volume of the solution.

Excited State Lifetime Measurements

The excited state lifetime of all the complexes at 298 K are measured using a laser flash photolysis set up with the third harmonic ($\lambda=355$ nm) of a Nd:YAG laser (Quanta-Ray). The transient absorption changes are monitored perpendicular to the laser beam by a 150 W pulsed xenon arc lamp. The transient signals are detected by Hamamatsu R-928 PMT. The PMT output was digitized with 500 MHz storage oscilloscope (Agilent Infiniium) interfaced to a computer. All measurements are taken after purging the solution with dry argon gas for about 30 min. All reported lifetime measurements are averages of at least three measurements which typically agreed to ± 3 %.

Luminescence Quenching Measurements

The reductive quenching of Ru(II)-complexes with DMA has been studied by the luminescence quenching technique in both homogeneous and in heterogeneous medium. The sample solutions were purged carefully with dry nitrogen for 30 min. The luminescence measurements were performed at different quencher concentration and [micelle] is kept constant (in the case of heterogeneous medium) and the quenching rate constant, k_q , values were determined from the Stern–Volmer plot using the equations given below.

$$I_0/I = 1 + K_{sv}[Q]$$

$$K_{sv} = k_q\tau^0$$

where I_0 and I are the luminescence intensity of Ru(II)-complex in the absence and in the presence of [quencher]. τ^0 is the luminescence lifetime of Ru(II)-complex in the absence of quencher. K_{sv} is the Stern–Volmer constant and k_q is the quenching rate constant.

Electrochemical Measurements

The redox potentials of Ru(II)-complexes and the oxidation potential of DMA were determined by cyclic voltammetric technique using EG & G Princeton Applied Research

Potentiostat/Galvanostat Model 273A. Samples of 1 mM solutions of the complexes for the electrochemical studies were prepared in aqueous solution containing 1 % acetonitrile. Potassium chloride was used as the supporting electrolyte. A glassy carbon electrode (working electrode) and a standard calomel reference electrode were used in the electrochemical measurements. Cyclic voltammograms were recorded after purging the solution with dry nitrogen gas for 30 min. The redox potential values of Ru(II)-complexes and DMA used in the study are collected in Table S1 and redox potentials are close to the literature values [34]. The redox potentials of the excited state couples are calculated from the potentials of the ground state couples and the zero-zero energy, E_{0-0} (found to be 2.1 eV).

$$E_{(\text{Ru}2+*/+)} = E_{(\text{Ru}2+/+)} + E_{0-0}$$

Transient Absorption Measurements

Transient absorption measurements were made with a laser flash photolysis technique using an Applied Photophysics SP-Quanta Ray GCR-2(10) Nd:YAG laser as the excitation source [35, 36]. The time dependence of the luminescence decay is 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 light of wavelength 355 nm was measured by monitoring (pulsed xenon lamp of 250 W) absorbance change. The change in the absorbance of the sample on laser irradiation was used to calculate the rate constant as well as to record the time-resolved absorption transient spectrum. The change in the absorbance on flash photolysis was calculated using the expression

$$\Delta A = \log I_0 / (I_0 - \Delta I)$$

$$\Delta I = (I - I_t)$$

where ΔA is the change in the absorbance at time t , I_0 , I and I_t are the voltage after flash, the pre trigger voltage and the voltage at particular time respectively. A plot of $\ln(\Delta A_t - \Delta A_\infty)$ vs time gives a straight line. The slope of the straight line gave the rate constant for the decay and the reciprocal of rate constant gave the lifetime of the triplet. The time-resolved transient absorption spectrum was recorded by plotting the change in absorbance at a particular time vs wavelength.

Results and Discussion

The structures of the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes used in the present study are shown in Chart 1. The electronic absorption

and emission spectral data, emission quantum yield and excited-state lifetime for the complexes in aqueous and different micellar media are summarized in Table 1. The complexes display an intense broad absorption band in the region 400–500 nm (Fig. 1) and luminescence maxima in the region 601–623 nm at room temperature (Fig. 2).

Reactions in Homogeneous Medium

N,N'-Dimethyl aniline (DMA) is known to quench the luminescence of $[\text{Ru}(\text{NN})_3]^{2+}$ by the mechanism involving electron transfer from DMA to photoexcited $[\text{Ru}(\text{NN})_3]^{2+}$ complexes [37]. In the present study on the addition of quencher DMA, the luminescence of all the complexes is efficiently quenched in homogeneous medium. The observation of linear Stern-Volmer plots and the k_q values obtained from luminescence quenching measurements suggest that the quenching of the Ru(II)-complexes, with DMA is dynamic in nature and the contribution from the static quenching is negligible. The observed quenching rate constant, k_q , in homogeneous (Fig. 3 and Table S1), ionic (SDS and CTAB) and nonionic (Triton X-100) micelle are collected in Tables 2, 3 and 4. The k_q data given in Table 2 show that the value of k_q is sensitive to the hydrophobicity and charge of the Ru(II)-complexes. The electron transfer nature of the quenching of $[\text{Ru}(\text{NN})_3]^{2+}$ with amines has been reported using laser flash photolysis technique [38] and it can be explained by Scheme 1.

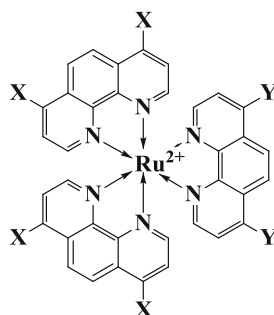
Reductive Quenching of $[\text{Ru}(\text{NN})_3]^{2+}$ Complexes with DMA in Homogeneous Medium

After establishing electron transfer nature of the reaction from the transient absorption spectral study (vide infra), it is appropriate to compare the experimental values with the values that can be calculated from the theories of electron transfer. To meet this end we have calculated the rate constants for the ET reaction of DMA to the excited state Ru(II)-complexes using semiclassical theory of ET [39, 40]. The semiclassical expression of ET (Eq. 1) popularized by Closs and Miller [41] has been applied to this photoinduced ET reaction.

$$k_{\text{et}}(r) = 2\pi/\hbar [1/\lambda_0 k_B T]^{1/2} |H_{\text{DA}}|^2 \sum_{m=0}^{\infty} e^{-s} s^m / m! \exp\left[-(\lambda_0 + \Delta G^0 + mh\nu)^2 / (4 \lambda_0 k_B T)\right] \quad (1)$$

In Eq. 1 H_{DA} is the electronic coupling matrix element, the reorganization energy λ is composed of solvational, λ_0 and vibrational λ_i contributions with $s = \lambda_i / h\nu$, ν is the high energy

Chart 1 The structures of the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes used in the present study



- I** = $[\text{Ru}(\text{phen})_3]^{2+}$; X, Y = H
II = $[\text{Ru}(\text{dpphen})_3]^{2+}$; X, Y = C_6H_5
III = $[\text{Ru}(\text{phen})_2(\text{dpsphen})]^{0+}$; X = H, Y = $\text{C}_6\text{H}_4\text{SO}_3^-$
IV = $[\text{Ru}(\text{dpsphen})_3]^{4+}$; X, Y = $\text{C}_6\text{H}_4\text{SO}_3^-$

vibrational frequency associated with the acceptor and m is the density of product vibrational levels. As all the ET reactions in the present study fall in the normal region ($-\Delta G^0 < \lambda$) the above equation is simplified to Eq. 2.

$$k_{\text{et}}(r) = 2\pi/\hbar [1/\lambda_0 k_B T]^{1/2} |H_{\text{DA}}|^2 \exp[-(\lambda_0 + \Delta G^0)^2 / (4 \lambda_0 k_B T)] \quad (2)$$

The total driving force ΔG^0 , includes electrostatic corrections for the work required to bring the products and reactants together ($\Delta G^0 = \Delta G^{\circ} - w_p - w_r$) as described below. The solvational reorganization energy, λ_0 , can be estimated from the classical dielectric continuum model (Eq. 3).

$$\lambda_0 = (\Delta e)^2 [1/2 r_A + 1/2 r_B - 1/r] [1/D_{\text{op}} - 1/D_s] \quad (3)$$

where D_{op} and D_s are the optical and static dielectric constants of the solvent respectively and r_A and r_B are the reactants radii and r is the sum of r_A and r_B . The values of solvent parameters have been collected from the literature [18, 42–48], and radii of the Ru(II)-complexes (**I–IV**) were calculated from MM3 model. The value of λ_0 calculated using Eq. (3) is 0.90 eV. The value of λ_i is found to be 0.2 eV and is employed in the calculation of the rate constant for ET reaction. Thus the value of the reorganization energy (λ) for this redox system is found to be 1.72 eV.

The free energy change (ΔG^0) of ET reaction can be calculated by using the expression (4).

$$\Delta G^0 = E_{(\text{DMA}/\text{DMA}^+)} - E_{\text{Ru}^{2+/+}} + w_p - w_r \quad (4)$$

Where w_p and w_r are electrostatic correction terms for product and reactant. By using Eq. (2) the rate constants for electron transfer, k_{et} , have been calculated and then used to get k_q values from Eq. (5).

$$k_q = k_{\text{et}} k_d / (k_{\text{et}} + k_d) \quad (5)$$

where k_d is the diffusion rate constant given by Eq. (6)

$$k_d = 4\pi N D / 1000 \left[\int_r^\infty e^{-U(r)/k_B T} r^{-2} dr \right]^{-1} \quad (6)$$

where D is the sum of the diffusion coefficients of the reactants given by the Stokes-Einstein relationship. The calculated rate constants for ET from DMA to $[\text{Ru}(\text{NN})_3]^{2+}$ by applying semiclassical expression of ET along with experimentally observed values for the above ET reaction are given in Tables S2–S4. The k_q data in Tables S2–S4 show that the values calculated from semiclassical theory are in fair agreement with experimental values (i.e., the difference between them is in the range 2–10 times). Considering the assumptions involved in

Table 1 Absorption and emission maxima, quantum yield and lifetime of complexes **I–IV**, water and in the presence of micelles

Complex	H_2O				CTAB				SDS				Triton X-100			
	λ_{abs}	λ_{em}	Φ_{em}	τ , μs	λ_{abs}	λ_{em}	Φ_{em}	τ , μs	λ_{abs}	λ_{em}	Φ_{em}	τ , μs	λ_{abs}	λ_{em}	Φ_{em}	τ , μs
I	447	601	0.064	0.8	452	599	0.131	0.9	455	611	0.218	0.9	450	601	0.123	0.9
II	464	623	0.201	3.2	488	637	0.473	4.6	475	630	0.591	4.2	472	633	0.671	3.8
III	460	620	0.254	3.3	480	631	0.290	3.8	460	611	0.307	2.3	460	620	0.431	3.8
IV	467	617	0.323	3.7	488	627	0.658	5.0	469	611	0.715	3.8	464	623	0.768	4.2

[CTAB]=0.01 M; [SDS]=0.02 M; [Triton X-100]=0.01 M

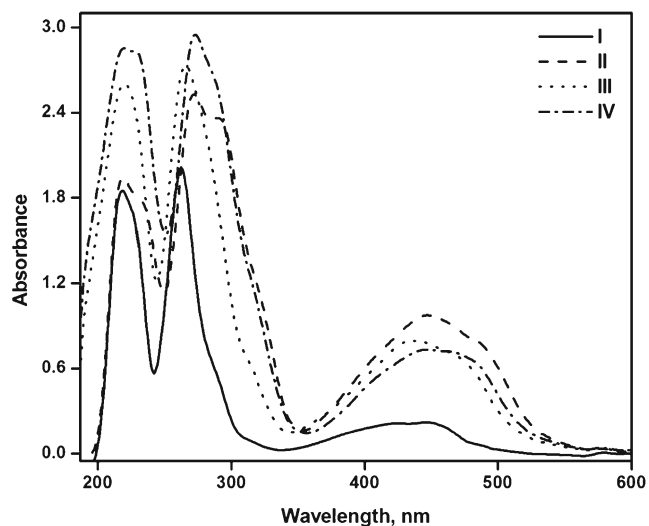


Fig. 1 Absorption spectra of Complexes **I–IV** in the presence of CTAB (0.01 M) at 298 K

the application of Eq. (2) to the titled reaction this agreement can be taken as the success of the Marcus theory to this reaction.

Reductive Quenching of $[\text{Ru}(\text{NN})_3]^{2+}$ Complexes with DMA in Microheterogeneous Medium

The luminescence quenching of $^*[\text{Ru}(\text{bpy})_3]^{2+}$ with DMA has been extensively studied in homogeneous and in mixed solvent systems [49–52]. Some recent reports concentrate on the luminescence quenching of Ru(II) complexes with 1,1'-diheptyl-4,4'-viologen [52] and oxygen [11] and dyes with DMA [53] in microheterogeneous medium. These studies indicate the role of the nature of the ligand and the size and the charge of the Ru(II)-complexes as important factors

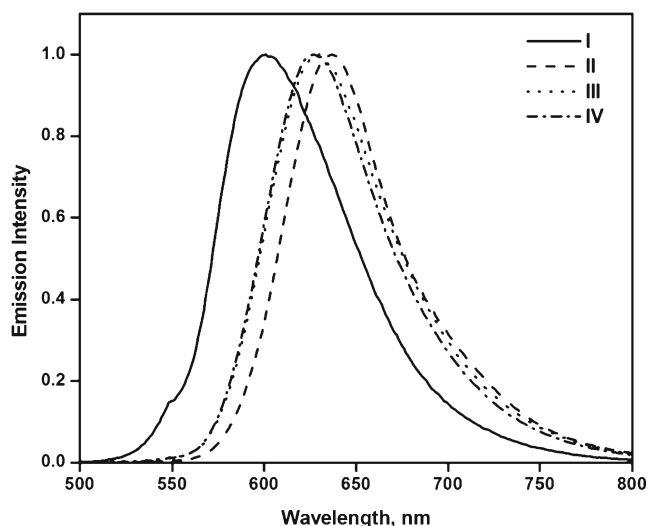


Fig. 2 Normalized emission spectra of complexes **I–IV** in the presence of CTAB (0.01 M) at 298 K

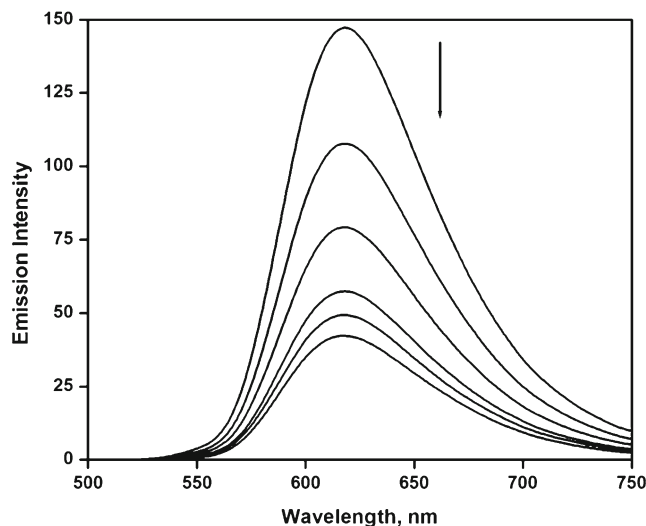


Fig. 3 Change of luminescence intensity of Complex **IV** with increasing concentration aqueous solution of DMA containing 1 % acetonitrile at 298 K. $[\text{DMA}] = 0.000, 0.001, 0.002, 0.003, 0.004$ and 0.005 M

affecting the rate of luminescence quenching by electron transfer in microheterogeneous medium.

Reductive Quenching in Cationic Micelle, CTAB

DMA is a very good electron donor, neutral in nature and sparingly soluble in aqueous solution [38, 54–60]. However, in the presence of CTAB micelles, the solubility of DMA has drastically increased. The absorption spectra of the Ru(II)-complexes (**I–IV**) remain unchanged even in the presence of highest $[\text{DMA}]$. From the steady-state spectra it is seen that the luminescence of complexes **I–IV** is quenched efficiently with the gradual addition of aromatic amine. The quenching rate constant, k_q values observed at different $[\text{CTAB}]$ for the quenching of **I–IV** with DMA along with excited state life time, τ , values are given in Table 2. If we analyze the quenching rate constant (k_q), the trend depends on the nature of the ligand as well as the charge of the $[\text{Ru}(\text{NN})_3]^{2+}$ complexes. In all cases the increase in $[\text{CTAB}]$ leads to different results and may be generalized in the form of following trends. (i) the k_q value remains almost constant with increase in $[\text{CTAB}]$, (ii) the increase in $[\text{CTAB}]$ increases the k_q value, attains saturation and then decreases (iii) the k_q value goes on increasing with increase in $[\text{CTAB}]$. These observations may be explained by considering the operation of the electrostatic (charge) as well as the hydrophobic interactions present in the system.

For complex **I**, the observed quenching rate constant, k_q , is slightly less in CTAB than in homogeneous medium. The decrease in k_q value is attributed to the electrostatic repulsion between the complex **I** and the cationic surfactant, CTAB. Complex **I** is probably present in the aqueous phase whereas

Table 2 Rate constant, k_q ($M^{-1} s^{-1}$) values for the reductive quenching of phenanthroline complexes by DMA, at different [CTAB] in RT along with lifetime data, τ in μs

[CTAB], M	Complex I		Complex II		Complex III		Complex IV	
	τ , μs	$k_q \times 10^9$	τ , μs	$k_q \times 10^9$	τ , μs	$k_q \times 10^9$	τ , μs	$k_q \times 10^9$
0	0.90	0.27	3.44	1.4	3.13	0.74	2.79	2.1
0.0004	0.89	0.25	3.20	1.4	2.75	1.1	3.50	1.8
0.002	0.88	0.26	3.93	1.5	3.02	1.2	4.21	4.4
0.004	0.85	0.22	3.98	1.9	3.13	1.6	4.50	6.8
0.006	0.87	0.20	4.23	3.5	3.50	1.8	4.98	6.6
0.008	0.86	0.25	4.61	2.8	3.38	2.0	5.02	5.2
0.010	0.85	0.21	3.99	2.2	3.51	2.2	5.03	4.1

cmc value of CTAB is 9.2×10^{-4} M

the quencher DMA being insoluble in water is concentrated in the Guoy-Chapman and Stern layer. Hence, micellar inhibition is observed which is confirmed by the slight decrease in k_q value (Table 1). The lifetime of the complex in CTAB is the same as that in homogeneous medium which also supports our conclusion that the complex **I** is present in the aqueous phase (Table 1). For complex **II**, it has strong hydrophobic character, due to the presence of phenyl moiety in the 4, 7- position of the phenanthroline ligand. The k_q value increases steadily from 0 to 0.006 M [CTAB]. But further increase in [CTAB] decreases the k_q value, at high [CTAB] the local concentration of the probe in the micellar phase is very high compared to the stoichiometric concentration in the aqueous phase leading to self quenching. Here the hydrophobic character of the complex **II**, offsets the electrostatic repulsion thereby bringing more reactant molecules close to each other at the micellar interface. The longer lifetime of the complex **II** in micellar medium supports the location of complex **II** in the micellar phase i.e., in a confined environment. In general the lifetime of the complexes in the confined environment is reported to be higher in the microheterogeneous medium [61]. Micellar catalysis is observed with the neutral complex, **III**. With increasing

[CTAB], the k_q value increases and this trend indicates that the neutral complex binds with the cationic micelle because of the negative charge of the dpsphen ligand.

In the case of the negatively charged complex **IV**, the quenching rate constant, k_q value is highest in CTAB medium. Thus a maximum of more than 3 fold increase in k_q value is observed when compared with neat solvent (Table 2). Similar trend is observed for complex **II** and complex **IV**. In both cases micellar catalysis is observed but at high [CTAB] and then the k_q values start to decrease. The luminescence quenching data were analyzed in terms of pseudophase ion exchange model and binding constants of reactants, of Ru(II)-ion and DMA with micelles. As both reactants bind with CTAB, we can use the Scheme 1 for the analysis of k_q data with the change of [surfactant] i.e., for the micellar catalysis (vide infra).

Reductive Quenching in Anionic Micelle, SDS

The quenching rate constant, k_q values observed for the quenching of four Ru(II)-complexes (**I-IV**) with DMA at

Table 3 Rate constant, k_q ($M^{-1} s^{-1}$) values for the reductive quenching of phenanthroline complexes by DMA, at different [SDS] in room temperature along with lifetime data, τ in μs

[SDS]	Complex I		Complex II		Complex III		Complex IV	
	τ , μs	$k_q \times 10^9$	τ , μs	$k_q \times 10^9$	τ , μs	$k_q \times 10^9$	τ , μs	$k_q \times 10^9$
0	0.90	0.3	3.44	1.4	3.13	0.7	2.79	2.1
0.002	0.97	0.3	3.76	1.0	3.18	1.0	2.74	2.3
0.004	1.12	2.0	3.98	1.0	3.44	1.0	2.31	3.3
0.006	1.30	1.8	4.05	1.4	3.40	1.1	2.85	4.6
0.008	1.32	1.9	4.17	3.9	3.18	1.2	2.84	4.8
0.010	1.30	1.7	4.20	3.4	2.28	1.7	2.84	4.6
0.020	1.28	1.6	3.90	3.1	2.25	1.6	2.40	4.3

cmc value of SDS is 8×10^{-3} M

Table 4 Rate constant, k_q ($M^{-1} s^{-1}$) values for the reductive quenching of phenanthroline complexes by DMA, at different [Triton X-100] in RT along with lifetime data, τ in μs

[Triton X-100]	Complex I		Complex II		Complex III		Complex IV	
	τ , μs	$k_q \times 10^9$	τ , μs	$k_q \times 10^9$	τ , μs	$k_q \times 10^9$	τ , μs	$k_q \times 10^9$
0	0.90	0.27	3.44	1.4	3.1	0.7	2.8	2.1
0.0001	0.88	0.28	3.58	1.5	2.7	0.9	3.0	2.3
0.002	0.87	0.25	4.13	3.1	2.0	1.3	3.3	2.5
0.004	0.92	0.24	4.62	4.0	2.2	1.3	3.7	3.1
0.006	0.95	0.22	4.75	4.2	2.3	1.0	4.1	2.5
0.008	0.90	0.26	3.82	4.8	2.2	1.3	4.2	2.8
0.010	0.95	0.24	3.44	5.1	2.0	1.3	3.9	2.5

cmc value of Triton X-100 is 2.6×10^{-4} M

different [SDS] of varying hydrophobicity and charge of the complex with DMA are collected in Table 3. All the complexes exhibit increase in the k_q value relative to that of aqueous medium. This increase in k_q value may be attributed to the electrostatic attraction of positively charged Ru(II)-ion with anionic micelle SDS and hydrophobic interaction between ligand and SDS micelles. Complex I, exhibits micellar catalysis in the presence of SDS. The observed micellar catalysis could be attributed to the predominant electrostatic interaction between the probe and the micelle. The lifetime (τ) of the complex I is found to be higher in the SDS micellar phase (1.32 μs) than homogeneous phase (0.90 μs). This observation is also interesting when we compare with the lifetime of the same complex observed in CTAB. For complex II, which contains a strong hydrophobic ligand and it is expected that both the electrostatic attraction and the hydrophobic effect will enhance the rate to a large extent. However the k_q value increases by 3 fold. The moderate micellar catalysis may be due to the operation of steric effect because of the bulkiness of the ligand.

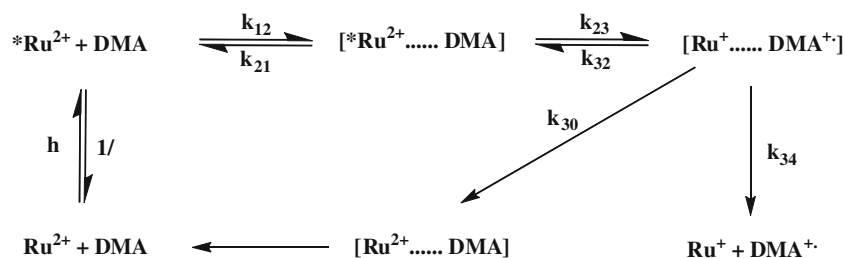
For the neutral complex, III moderate micellar catalysis is observed which shows the effect of small order of hydrophobic interaction. The observed quenching rates (k_q) in micellar solution is found to be 2 times higher than homogeneous medium (Table 3). It is likely that major portion of the complex is distributed in the aqueous phase and the rest in the micellar interface. This is also supported by the

lifetime of the complex which is slightly altered in the presence of micellar phase.

In the anionic complex, IV the hydrophilic nature of the dpsphen ligand makes the complex more soluble in the aqueous phase. This is evident from lifetime value which is slightly affected by the change of [SDS]. Interestingly moderate micellar catalysis is observed for the quenching of complex IV with DMA in the presence of anionic surfactant. Thus the hydrophobic character of the ligand overcomes the electrostatic repulsion between the anionic complex and the anionic micelle SDS and makes the complex to reside in the micellar interface. Thus the increased k_q value in SDS shows that the electrostatic repulsion is overcome by the hydrophobic interaction. A similar effect is also observed for the complex, II in CTAB. From these results it is clear that the electron transfer process in the anionic micelle is facile compare to that in homogeneous solutions. The above observations are also substantiated by the binding constant values (Tables S2 and S3).

Reductive Quenching in Neutral Micelle, Triton X-100

The observed quenching rate constants for the complex I, in the presence of neutral micelle show that the electron transfer reaction between the probe and the quencher, DMA is little affected by the neutral micelle (Table 4). This could be attributed to the absence of any effective electrostatic and

**Scheme 1** Mechanism for the reductive quenching of Ru(II)-complexes with DMA

hydrophobic interaction between the probe and micelle. For the complex **II**, the quenching rate constant increases in the presence of neutral micelle by more than 3 fold, when compared with the homogeneous medium (Table 4). This observation clearly confirms the predominant contribution of hydrophobic interaction of the ligand, bathophenanthroline with micelle. In the case of neutral complex **III**, and the anionic complex **IV**, the contribution of hydrophobic character of the ligand is less pronounced.

The data collected in Table 4 show an interesting trend that the quenching rate increases with increasing hydrophobicity of the following order.

i.e., $[\text{Ru}(\text{phen})_3]^{2+} < [\text{Ru}(\text{phen})_2(\text{dpsphen})] < [\text{Ru}(\text{dpsphen})_3]^{4-} < [\text{Ru}(\text{dpphen})_3]^{2+}$

Pseudophase Ion Exchange (PIE) Model

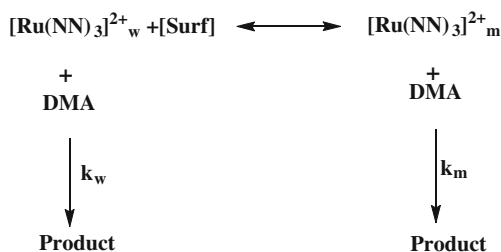
The results on the rate of the electron transfer quenching reaction of the excited state $[\text{Ru}(\text{NN})_3]^{2+}$ complex with DMA can be rationalized by applying pseudophase ion exchange model in micelle [9, 10]

$[\text{Ru}(\text{NN})_3]_w^{2+}$ and $[\text{Ru}(\text{NN})_3]_m^{2+}$ denote the complex in aqueous and micellar phase respectively. N,N-Dimethylaniline will partition between the aqueous phase and the micellar phase (Scheme 2). In the present system two parallel reactions are considered to take place: one in the aqueous phase and the other in the interface (m). Hence the overall quenching rate constant, k_q , for the process will be given by Eq. (7).

$$k_q = (k_w + k_m K [\text{surf}]) / (1 + K [\text{surf}]) \quad (7)$$

In this expression, $[\text{surf}]$ represents the concentration of the micellized surfactant (i.e., the total concentration of surfactant minus cmc), k_w is the rate constant for the reaction in the aqueous bulk medium and k_m is the rate constant in the micellar phase Eqs. (8) and (9).

$$k_m = \frac{\text{moles of DMA in the micellar pseudophase}}{\text{volume of the solution}} \quad (8)$$



Scheme 2 General reaction scheme for the quenching of $[\text{Ru}(\text{NN})_3]^{2+}$ complexes by DMA in micelles

$$k_m = \frac{\text{moles of DMA in the micellar pseudophase}}{\text{volume of the micellar pseudophase}} \quad (9)$$

k_m is related to true rate constant in the micellar phase, k^m , by the Eq. (10).

$$k_m = k^m [\text{DMA}]^m / [\text{DMA}]_T \quad (10)$$

Finally, K , the binding constant in Eq. (7) is given by Eq. (11).

$$K = [\text{Ru}(\text{NN})_3]_m^{2+} / [\text{Ru}(\text{NN})_3]_w^{2+} [\text{surf}] \quad (11)$$

The values of the binding constant for $[\text{Ru}(\text{NN})_3]^{2+}$ in the presence of micelles are determined by using the emission spectral data as a function of different surfactant and the data are collected in Tables S2-S4. The calculated quenching rate constant, k_q by the application of pseudophase ion exchange model and experimentally observed rate constants are also tabulated in Tables S2-S4. The values of the micellar rate constant, k_m is reflecting the experimental result obtained for the reductive quenching of $[\text{Ru}(\text{NN})_3]^{2+}$ with DMA in micelle. The calculated values are in good agreement with the experimental values for the reductive quenching of $[\text{Ru}(\text{NN})_3]^{2+}$ with DMA. From the quenching and lifetime measurement studies helped us to understand the location of the probes and the accessibility of the quencher to the probe in heterogeneous medium. The calculated k_q values are in good agreement with the experimental k_q values giving quantitative evidence for the bimolecular reductive quenching rate constants of the $[\text{Ru}(\text{NN})_3]^{2+}$ with DMA. In conclusion, the pseudophase model can explain the results obtained in the presence of micelle.

Transient Absorption Spectral Studies

The transient absorption spectra of the complexes show bleach around 450 nm and a positive absorption with maxima centred at 370, 470 and 555 nm (Figs. 4 and 5). In Fig. 4, the increase in absorption observed at 370 nm and 555 nm is due to the formation of phenanthroline anion radical. The bleach at 440–470 nm shows the decay of ground state complex absorption that is $^1\text{MLCT}$ transition and the developing absorption above 550 nm is due to the excited state absorption of the complex. A negative absorbance change in the region 400–500 nm was caused by the bleaching of the ground state, Ru^{2+} . The positive absorption observed at 470 nm was due to the production of a transient species dimethylaniline cation radical, DMA^+ . The formation of N,N-diethylaniline cation radical, as transient has absorption at 470 nm was also

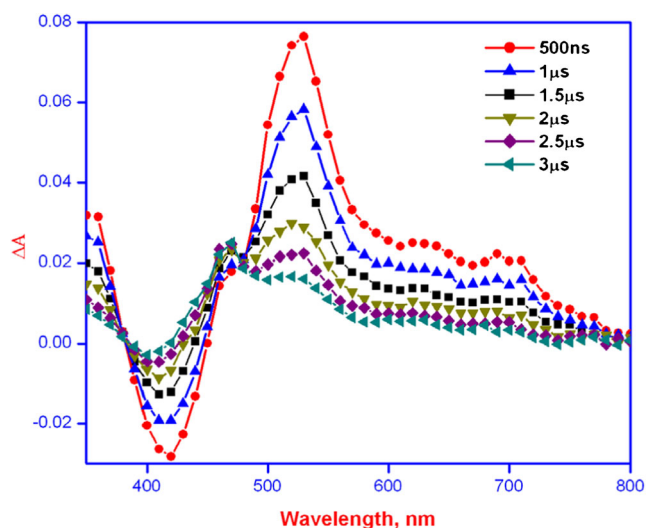


Fig. 4 Transient absorption spectra of Complex II in the presence of DMA in SDS medium at 298 K at different time intervals

reported by Thanesekaran et al. [51] in the ET study of rhenium(I) rectangles with N,N-diethylaniline. Ohno et al. [37] also confirmed the production of the cation radical of the quencher, DMA^+ during the course of the quenching of ruthenium(II)-polypyridine complexes by aromatic amines.

Conclusion

The results observed in the present study establish that the luminescence of $^3\text{MLCT}$ excited state of Ru(II) complexes is efficiently quenched by DMA in homogeneous and micellar solutions at room temperature. Hydrophobic character of the ligand is mainly responsible for micellar catalysis and it offsets the electrostatic repulsion between the micelle and

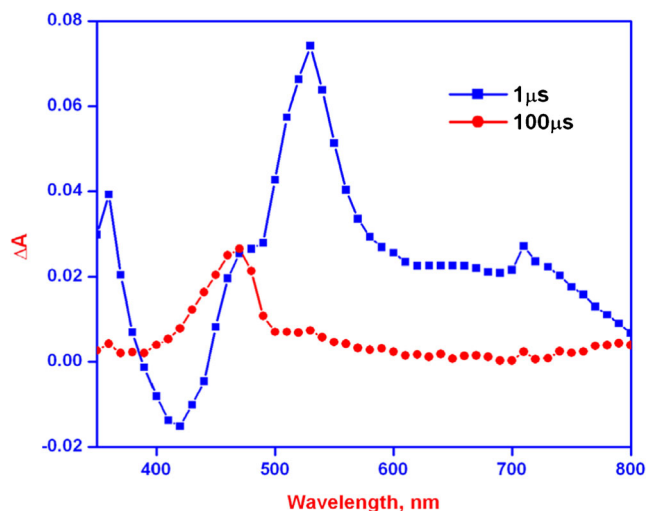


Fig. 5 Transient absorption spectra of Complex IV in the presence and absence of DMA in aqueous solution at 298 K at different time intervals

the probe. In the absence of hydrophobic character, electrostatic attraction between the complex and the probe catalyzed the reaction. Combined effect of both hydrophobic character and electrostatic attraction also involved in the micellar catalysis. The transient absorption spectra and luminescence quenching data clearly show that the excited state of Ru(II)-complexes undergo rapid ET reactions with aromatic amines. The pseudophase ion exchange model is successfully applied for the titled reaction.

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