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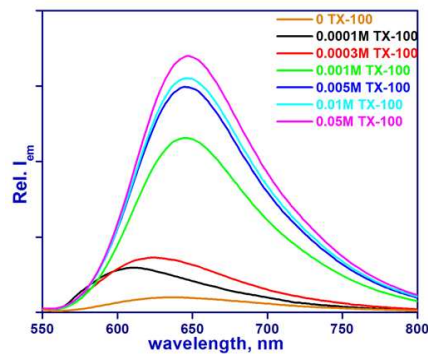
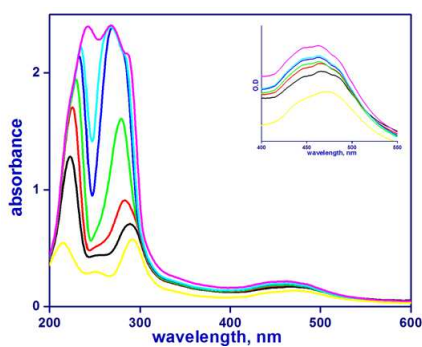
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Graphical abstract

Photophysical Properties of Amphiphilic Ruthenium(II)-Complexes in Micelles

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Photophysical properties of [Ru(dnbpy)₃]²⁺ in the presence of different concentrations of Triton X-100.

Photophysical Properties of Amphiphilic Ruthenium(II)-Complexes in Micelles

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Amphiphilic ruthenium(II)-complexes **II-IV** were synthesized and their photophysical properties investigated in the presence of anionic (SDS), cationic (CTAB) and neutral (Triton X-100) micelles. The absorption and emission spectral data in the presence of micelles show that these Ru(II)-complexes are incorporated in the micelles. There are two type of interactions between complexes **I-IV** and micelle: hydrophobic and electrostatic. In the presence of cationic micelle (CTAB), the hydrophobic interaction is predominant over electrostatic repulsion for binding of cationic complexes **II-IV**, with CTAB. In the presence of anionic micelles (SDS), electrostatic interactions seem to be important in the binding of **II-IV** to SDS. The hydrophobic interaction plays a dominant role in the binding of **II-IV** to the neutral micelle, Triton X-100. Based on the steady state and luminescence experiments, the enhancement of luminescence intensity and longer lifetime in the presence of micelle, which is due to the protection of complexes against exposure to water in this environment.

Introduction

The wide range of functions performed by the biological membranes and membrane proteins has motivated researchers to look for simple model systems¹⁻³. A typical example of such membrane biomimetic model is a micelle, which is an organized assembly of surfactants in aqueous media. Micelles can mimic biosystems and also find extensive applications in solar energy conversion, storage and drug delivery⁴⁻¹³. The structure of micelles (i.e., shape, size, aggregation number (N), hydration, etc.) depends on the architecture of the surfactant molecule, concentration, additives and the solution temperature¹⁴⁻²⁰. Molecules accommodated in molecular assemblies such as micelles, microemulsions, vesicles often achieve a greater degree of organization when compared to their geometries in homogeneous solution.¹⁴⁻²⁰ The optical properties of luminescent probes are strongly affected by the change of polarity and rigidity of their environments. Below the critical micellar concentration (cmc), probes will exist mainly in an aqueous medium, whereas above the cmc they are incorporated into a micelle. The structure, dynamics and reactivity of a probe molecule in micelles are different from bulk media, since the polarity and viscosity at interface differ markedly from the bulk media¹⁸.

The photophysics and photochemistry of ruthenium(II)-polypyridine complexes [Ru(NN)₃]²⁺ (NN= 2,2'-bipyridine and its derivatives) are highly influenced by the change of solvent and the change in medium from homogeneous to heterogeneous²¹⁻²⁸. The [Ru(NN)₃]²⁺ complexes have been extensively used as probes in micellar media and their photophysical properties like wavelength of emission maximum, emission intensity, excited state lifetime and emission quantum yield vary enormously with the nature of the surfactant and concentration²⁸⁻³⁵. Many researchers³⁰⁻⁴¹ reported the binding, partitioning and photosensitization of [Ru(NN)₃]²⁺ complexes in both ionic and nonionic surfactant media. Demas and coworkers³⁸⁻⁴³ have studied the interaction of [Ru(NN)₃]²⁺ complexes with ionic (CTAB and SDS) and neutral micelles (Triton X-100) and the emission spectra, lifetime and quantum yield change

dramatically on micellization. They proposed a model to understand the binding site and local environment for the photosensitizers. The presence of hydrophobic groups like alkyl and aryl in the ligands of [Ru(NN)₃]²⁺ leads to strong binding of [Ru(NN)₃]²⁺ with micelles through hydrophobic interaction. The strength of binding depends on the combination of electrostatic attractions or repulsions and hydrophobic effects⁴³.

The use of [Ru(NN)₃]²⁺ complexes carrying surfactants as ligands is of interest because of their potential applications in thin film devices, sensors and heterogeneous catalysis⁴⁴⁻⁵⁰. Bowers et al³⁴⁻³⁷ have extensively studied the surface and aggregation behavior of aqueous solutions containing Ru(II)-metallo-surfactants. Castro et al⁴⁹ successfully designed a sensor for hydrocarbon, based on ruthenium(II)-complex, [Ru(NN)₃]²⁺, where (NN = 4,4'-dinonyl-2,2'-bipyridine) which is able to detect reversibly and quantify both aromatic and aliphatic hydrocarbons in aqueous samples.

Even though, few reports are available for the use of amphiphilic ruthenium(II)-complexes, the interaction between amphiphilic ruthenium(II)-complexes and micelles (anionic, cationic and neutral) are limited. Therefore, herein we study the photophysical properties of amphiphilic ruthenium(II)-complexes in the presence of micelles (anionic (SDS), cationic (CTAB) and neutral (Triton X 100)).

Experimental

Materials

The ligands 2,2'-bipyridine, 4,4'-dinonyl-2,2'-bipyridine and RuCl₃·3H₂O were purchased from Aldrich. All of the surfactants, namely SDS, CTAB and Triton X-100 were procured from Aldrich/Fluka and used as received. Triply distilled water was used throughout the experiment. The micellar solutions were freshly prepared to avoid aging. The three complexes, [Ru(bpy)₂(dnpbpy)]²⁺, (**II**), [Ru(bpy)(dnpbpy)₂]²⁺, (**III**), and [Ru(dnpbpy)₃]²⁺, (**IV**) were prepared by reacting RuCl₃·3H₂O with the equivalent amount

of ligands by known procedures^{33,34,50-51}. (The details were given in the supporting information)

Absorption and emission spectral measurements

Sample solutions of the metal complexes and the micelles have been freshly prepared for each measurement. The absorption spectral measurements were carried out using SPECORD S100 diode-array spectrophotometer. Steady state emission measurements were recorded with JASCO FP-6300 spectrofluorometer. All the sample solutions used for emission measurements were deaerated for about 20 min by dry nitrogen gas purging and keeping the solutions in cold water to ensure that there is no change in volume of the solution. Excitation wavelength used for the luminescence titration and quantum yield with micelles for complexes **II**, **III** and **IV** at 456, 460 and 466 nm respectively.

Lifetime measurements

Time resolved luminescence measurements were carried out using a diode laser- based time correlated single photon counting (TCSPC) spectrometer from IBH, U.K. In the present, 452 nm diode laser (40kHz) was used as the excitation source and Hamamatsu photomultiplier tube was used for the luminescence detection. The instrument response function for this system is ≈ 1.2 ns and the luminescence decay was analyzed by using the software provided by IBH (DAS-6) and PTI global analysis software.

Estimation of binding constant (K)

A quantitative estimation of the binding of complexes **II-IV** with the micelles was obtained from the luminescence intensity data. Because the luminescence intensity of the probe molecule in aqueous and micellar environment differ significantly. Almgren et al^{52,53} used the following equation for the estimation of binding constant (K). According to this

$$(I_{\infty} - I_0) / (I_t - I_0) = 1 + (K[M])^{-1} \quad (1)$$

where I_{∞} , I_0 and I_t are the relative intensities under complete micellization, in the absence of surfactant and in the presence of intermediate amounts of surfactants respectively. $[M]$ represents the concentration of micelle which is given by the following equation 2.

$$[M] = ([Surf] - cmc) / N \quad (2)$$

$[Surf]$ represents the surfactant concentration and N is the aggregation number of the micelle. The N values used in the calculation of $[M]$ are 62 for SDS, 60 for CTAB and 143 for Triton X-100.

Results

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

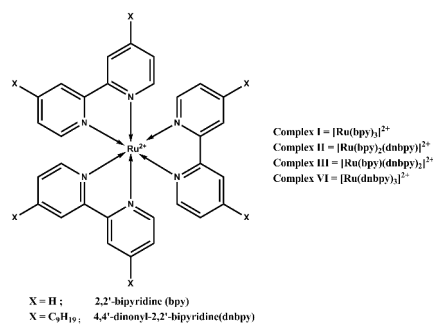


Chart 1: The structures of the $[Ru(NN)_3]^{2+}$ complexes used in the present study.

Photophysical properties in homogenous media

Complexes **I** and **II** are freely soluble in water but complexes **III** and **IV** are water-insoluble, a feature attributed to the strong hydrophobic character of these complexes imposed by the long alkyl chains of the modified 2,2'-bipyridine ligands. Figures 1 and 2 show the normalized absorption and emission spectra of amphiphilic ruthenium(II)-complexes, **II-IV**. The photophysical properties of complexes **I-IV** are collected in aqueous and micellar media and given in Table 1. The absorption spectra of **II-IV**, exhibit the characteristic bands found in the parent ruthenium(II)-complex, $[Ru(bpy)_3]^{2+}$ and its derivatives^{54,56}. The intense absorption band in the 285-300 nm region is assigned to ligand centered transitions ($\pi-\pi^*$) and the band in the visible region (453 - 466 nm) to the metal-to-ligand charge transfer transition ($d\pi(Ru) \rightarrow \pi^*(ligand)$). All the complexes are highly luminescent and show emission maxima in the range of 618 - 632 nm due to 3MLCT ($d\pi(Ru) \rightarrow \pi^*(ligand)$) excited state. These absorption and emission spectral data show that though a red shift to the tune of 13 nm (453 nm to 466 nm) is observed in the absorption spectrum the emission maximum is red shifted to the tune of 36 nm (596 to 632 nm). The energy difference between ground state level of metal and ligand orbitals is lowered, when a long alkyl chain is introduced in the 4,4'-position of 2,2'-bipyridine in aqueous methanol. Complexes **III** and **IV** are weakly luminescent compared to complex **II**.

Complexes **III** and **IV** exhibited weakly luminescent and lower luminescence quantum yield when compared to complex **II** in aqueous methanol solution. This may be due to increased nonradiative decay processes. To have a better understanding of the excited state properties of these complexes, we have carried out nanosecond time resolved luminescence analysis in different media. Table 2 summarizes the luminescence lifetimes of **II-IV**, in the absence and presence of micelles. Complex, **II**, shows a single exponential decay in 1% methanol-99% water(v/v) ($\tau = 324$ ns, Table 2). This observation is due to the freely soluble nature of **II** in water. Since the complexes **III** and **IV** are sparingly soluble in water, they show a biexponential decay profile in 1% methanol-99% water. The major species of the complexes **III** and **IV**, exhibit longer lifetime 210 ns (94.50%) and 118 ns (91.85%), while the minor species has a shorter lifetime of 21 (5.50%) and 17ns (8.15%) respectively. We assume the biexponential decay nature of the complexes **III** and **IV** are due to two spectroscopically different species in the excited state in 1% methanol-99% water.

Photophysical properties in microheterogeneous media

The study of stability and photophysical properties of a sensitizer under physiological conditions is important to evaluate its potential for various biological applications.

Table 1: Absorption (λ_{\max} , nm) and emission maxima (λ_{\max} , nm) quantum yield (Φ_{em}) of $[\text{Ru}(\text{NN})_3]^{2+}$ and complexes **II-IV**, 1% methanol-99% water and in the presence of micelles.

Additive	$[\text{Ru}(\text{bpy})_3]^{2+}$ ^a		$[\text{Ru}(\text{bpy})_2(\text{dnbpy})]^{2+}$		Φ_{em}	$[\text{Ru}(\text{bpy})(\text{dnbpy})_2]^{2+}$			$[\text{Ru}(\text{dnbpy})_3]^{2+}$		
	abs	Em	abs	Em		Abs	em	Φ_{em}	Abs	Em	Φ_{em}
1% MeOH-H ₂ O	453	596	456	618	0.020	460	630	0.006	466	632	0.003
SDS	454	628	452	620	0.042	461	632	0.018	463	636	0.016
CTAB	455	611	457	626	0.034	458	634	0.017	462	640	0.015
Triton X-100	454	610	458	630	0.049	462	636	0.020	461	646	0.021

^a from ref. 39,40 For parent and complex **II**, the concentration of micelles are 100mM, 50mM, 50mM for SDS, CTAB and Triton X-100 respectively. For complex **III** and **IV** concentration of micelles are 50mM, 10mM, 10mM for SDS, CTAB and Triton X-100 respectively.

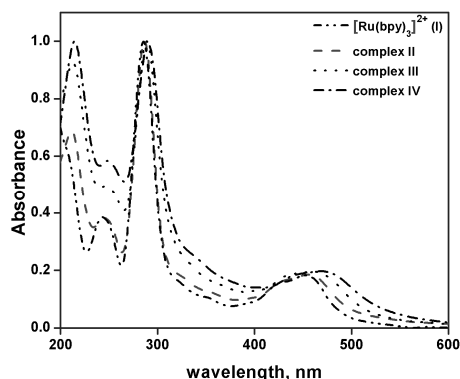


Figure 1: Absorption spectra of and $[\text{Ru}(\text{bpy})_3]^{2+}$ (**I**) $[\text{Ru}(\text{bpy})_2(\text{dnbpy})]^{2+}$ (**II**), $[\text{Ru}(\text{bpy})(\text{dnbpy})_2]^{2+}$ (**III**) and $[\text{Ru}(\text{dnbpy})_3]^{2+}$ (**IV**) 1% methanol-water.

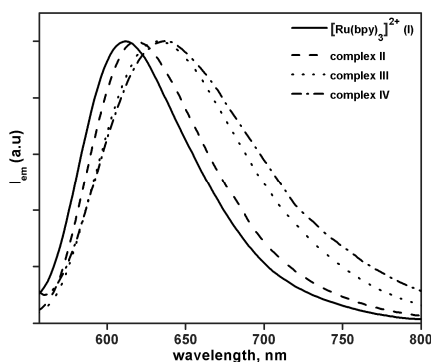


Figure 2: Normalized emission spectra of and $[\text{Ru}(\text{bpy})_3]^{2+}$ (**I**) $[\text{Ru}(\text{bpy})_2(\text{dnbpy})]^{2+}$ (**II**), $[\text{Ru}(\text{bpy})(\text{dnbpy})_2]^{2+}$ (**III**) and $[\text{Ru}(\text{dnbpy})_3]^{2+}$ (**IV**) 1% methanol-water.

In order to mimic the biological membranes, we have employed anionic, cationic and neutral surfactants that can form micellar structures at and above critical micellar concentration (CMC)⁶⁰.

The effect of adding surfactants on the photophysical properties of amphiphilic ruthenium(II)-complexes **II-IV**, in different micelles were investigated. For the sake of comparison we have included the data available for the parent complex, $[\text{Ru}(\text{bpy})_3]^{2+}$.

Effect of anionic micelles, SDS

In order to understand the ground state interaction between amphiphilic ruthenium(II)-complexes **II-IV**, and SDS we have recorded the absorption spectrum in the absence and in the presence of different concentrations of SDS and the spectra are shown in supporting information (Figures S1-S2). The increase in the concentration of anionic micelle (SDS) resulted in a slight change in the absorption intensity of **III** with a slight blue shift of about 3 nm. Similar observations were made with **I** and **II** in the presence of SDS. Complex **III** shows a shift in emission maximum 632 nm to 636 nm along with an increase in intensity (Figure 3). Such a bathochromic shift in the emission maximum of $[\text{Ru}(\text{bpy})_3]^{2+}$ with the change of the medium from aqueous to SDS micelle is a well-documented phenomenon³⁸⁻⁴⁰. The complex **II** shows an emission maximum at 618 nm in aqueous medium. The initial addition of SDS causes a red shift in the emission maximum from 618 nm to 628 nm with decrease in emission intensity. A similar decrease in the luminescence intensity is quite common at the lower concentrations of various surfactants which is ascribed to the formation of pre-micellar aggregates^{43,57-64}. A further increase in the concentration of SDS brings back the emission maximum close to the value in aqueous medium (630 to 620 nm) along with enhancement in its luminescence intensity. Complexes **I** and **II** exhibit a single exponential decay in SDS micelle, whereas complex **III** and **IV** shows a biexponential decay. Major component exhibit longer lifetime in the SDS micelle and minor component have negligible contribution to the decay. In the presence of SDS micelles, **II-IV** show all three complexes relatively longer lifetime (Table 2). For example the lifetime of **IV** in the presence of anionic micelle is almost three times of that in the aqueous medium.

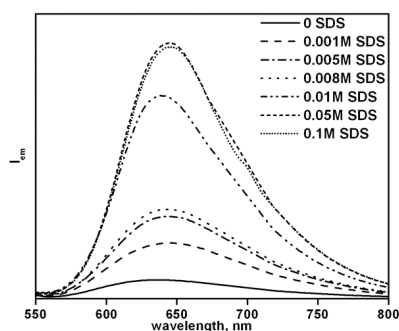


Figure 3: Emission spectra of $[\text{Ru}(\text{dnbpy})_3]^{2+}$ (**IV**) in the presence of anionic micelle, SDS, at different concentrations.

Effect of cationic micelle, (CTAB)

The absorption spectrum of complexes **I-IV** very slightly altered in the presence of CTAB (Figure not shown). For example addition of CTAB to the complex **IV**, resulted in a small increase in the molar extinction coefficient (ϵ) with a shift of about 3 nm at the absorption maximum. Figure 4 shows the changes in the luminescence spectrum of complex **II**, with a change in [CTAB]. The luminescence intensity of the complexes **II-IV** showed a significant enhancement with the increase in the concentration of CTAB with a red shift of 4-8 nm at the highest concentration of CTAB studied (supporting information Figure S3 and S4). These changes in the emission maximum and intensity confirm that the hydrophobic interactions between the ligands and the cationic surfactants overcome the electrostatic repulsive forces to bring them closer thereby stabilizing emitting $^3\text{MLCT}$ state of $[\text{Ru}(\text{NN})_3]^{2+}$. These spectral changes show the strong binding of ruthenium(II)-complex with micelle and that $^3\text{MLCT}$ state, a charge separated state, is stabilized in the presence of micelle compared with that of d-d state and similar observations were reported in other media^{64,65}.

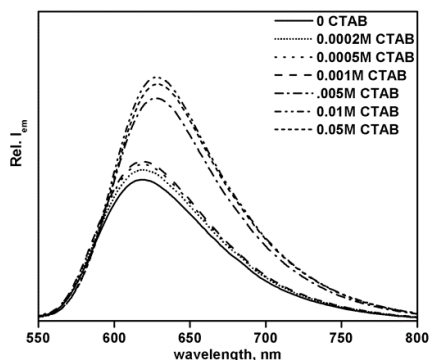


Figure 4: Emission spectra of $[\text{Ru}(\text{bpy})_2(\text{dnbpy})]^{2+}$ (**II**) in the presence of cationic micelle, CTAB, at different concentrations.

Though the increase of [CTAB] leads to an increase in the emission intensity, at high [CTAB] the emission intensity begins to decrease. Similar behavior observed for $[\text{Ru}(\text{dpphen})_3]^{2+}$ complex at different concentration of CTAC⁶⁵⁻⁶⁷. At high [CTAB] the local concentration of the probe in the micellar phase may be very high compared to the stoichiometric concentration in the aqueous phase. A similar explanation put forward in earlier studies for the decrease in the emission intensity or lifetime at higher concentration of microheterogeneous systems^{22,23,65-67}. These interesting

experimental observations substantiate the importance of hydrophobic interactions. These interesting experimental observations substantiate the importance of hydrophobic interactions. Complexes **II-IV** show a longer excited state lifetime (~ 1.5 to 3 fold increase in τ value) in the presence of CTAB as observed in the presence of SDS. The inference from this observation is that the coulombic repulsion between the like charges of the Ru(II) complexes and micellar surface is offset by the strong hydrophobic interaction between the alkyl chain and micelle^{22,23,65-67}.

Effect of neutral micelle, (Triton X-100)

In addition to the anionic and cationic micelles, we have investigated the effect of adding nonionic micelle Triton X-100 on the photophysical properties of **II-IV**. Absorption spectrum of amphiphilic ruthenium(II) complexes were slightly altered in the presence of different concentrations of neutral micelle. For example, the addition of neutral surfactant to complex **IV**, resulted in a small increase in the ϵ value with a blue shift of about 5 nm at the absorption maximum (*vide infra*). Figure 5 show the effect of adding of Triton X-100 on the emission spectra of the complex **IV**. All the amphiphilic ruthenium(II)-complexes **II-IV**, showed red shift in the range of 6–14 nm in the emission maximum along with enhancement in luminescence intensity with increase in [TX-100] (supporting information Figures S5 and S6).

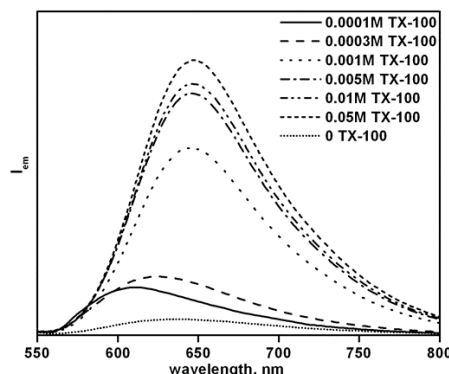


Figure 5: Emission spectra of $[\text{Ru}(\text{dnbpy})_3]^{2+}$ (**IV**) in the presence of neutral micelle, Triton X-100, at different concentrations.

Discussion

In the presence of micelles, all the three ruthenium(II)-complexes, **II-IV**, showed luminescence enhancement when compared to that in aqueous medium. This is attributed to the microencapsulation of the ruthenium(II)-complexes into the micellar medium, resulting in the change in the microenvironment experienced by the ruthenium(II) complexes. These microenvironmental changes include higher viscosity, lower dielectric constant and polarity⁵⁹⁻⁶¹. Micelles are characterized by three distinct regions: a nonpolar core region formed by the hydrocarbon chains of the surfactant, a compact Stern layer having the head groups and relatively wider Gouy-Chapman layer containing the counter ions. Depending upon the nature of the probe and micelle, a probe molecule can bind either to head group region or to the nonpolar core region of the micelle.

The two microenvironments (the Stern layer and the core region) of the micelles have quite different properties. The core

region is usually characterized by a highly viscous hydrocarbon like environment with a very low degree of water penetration. The Stern layer mainly consists of polar head groups, bound counter ions and largely structured water molecules. Since, the nature of micelles depends on nature of head group and core region, the probe is located in different region in accordance with their nature^{38-40,61-64}.

The excited state lifetime of $[\text{Ru}(\text{bpy})_3]^{2+}$ in SDS micellar solution ($\tau = 712$ ns) is longer than those in aqueous solution ($\tau =$

600ns). Since the cationic complex must bind to the surface of the anionic micelle, the excited state complex will be shielded to some extent from attack by the solvent water molecules. The parent complex $[\text{Ru}(\text{bpy})_3]^{2+}$ does not undergo primary electrostatic interaction with cationic or non-ionic micelles. Miesel et al⁵⁷ reported a red shift in emission maximum for this complex in SDS micellar solutions and ascribed this shift to a static interaction of $[\text{Ru}(\text{bpy})_3]^{2+}$ with hydrocarbon chain rather than with the polar head group.

Table 2: Lifetime data (τ , ns (relative amplitude)) of $[\text{Ru}(\text{NN})_3]^{2+}$ and complexes, **II-IV**, in homogenous and heterogeneous media.

Additive	$[\text{Ru}(\text{bpy})_3]^{2+}$	Complexes				
		II	III	IV		
1% MeOH-H ₂ O	600	324	210 (94.50%)	21 (5.50%)	118 (91.85%)	17 (8.15%)
SDS	712	534	428 (98.85%)	14 (1.15%)	334 (97.66%)	18 (2.34%)
CTAB	567	587	446 (98.79%)	15 (1.21%)	328 (96.51%)	15 (3.49%)
Triton X-100	585	630	465 (98.55%)	17 (1.45%)	415 (98.88%)	16 (1.12%)

^afrom ref^{39,40} For parent and complex **II**, the concentration of micelles are 100mM, 50mM, 50mM for SDS, CTAB and Triton X-100 respectively. For complex **III** and **IV** concentration of micelles are 50mM, 10mM, 10mM for SDS, CTAB and Triton X-100 respectively.

However, the red shift should be attributed to a dynamic effect; a dipole moment induced within the complex by the MLCT excitation displaces or reorients to the most stable orientation on the anionic surface of SDS micelles during the excited state lifetime. In the case of complexes **II-IV**, the cationic head group is on the ionic surface of the micelle and the alkyl chains penetrate into the hydrocarbon region of the micelles. Interestingly the τ values of **II-IV** in CTAB are almost close to values observed in SDS. The inference from this observation is that the coulombic repulsion between the like charges of the Ru(II) complexes and micellar surface is offset by the strong hydrophobic interaction between the alkyl chain and micelle^{22,23}.

Table 3: Binding constant values for $[\text{Ru}(\text{bpy})_3]^{2+}$ and complexes **II-IV** with micelles

Additive	$[\text{Ru}(\text{bpy})_3]^{2+}$	Complex, II	Complex, III	Complex, IV
	$K_b \text{ M}^{-1}$			
SDS	440	820	760	980
CTAB	320	940	720	1250
Triton X-100	-	1050	790	2130

The excited state properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ are not much affected in the presence of the cationic micelle CTAB and it remains in the aqueous phase because of coulombic repulsion from the cationic micelle. Thus the addition of CTAB has little effect on the excited state properties of $[\text{Ru}(\text{bpy})_3]^{2+}$. However the trend changes when we introduce long alkyl chain in the ligand of Ru(II) complexes. The binding constants of $[\text{Ru}(\text{NN})_3]^{2+}$ as well as complexes **II-IV**, with the micelles are determined from the luminescence intensity data and are given in Table 3. Binding constant of $[\text{Ru}(\text{bpy})_3]^{2+}$ in SDS is 440 M^{-1} , whereas it is 320 M^{-1} in CTAB. This is due to the effect of similar charges on the probe and surfactant interface. However the introduction of long alkyl group in the 4,4'-position of 2,2'-bipyridine ligand facilitates the binding to the cationic micelles and binding constants in the anionic and cationic are almost similar.

After observing a considerable shift in the absorption and emission spectra, we have measured the excited state lifetime of $[\text{Ru}(\text{NN})_3]^{2+}$. As expected a large change is observed in the excited state lifetime in the presence of CTAB. In the case of $[\text{Ru}(\text{dnbpy})_3]^{2+}$, though the lifetime is 118 ns in the micellar-free medium, it increases with the concentration of CTAB, it attains maximum 334 ns at high [CTAB]. As the complex carries long hydrocarbon chains in the 2,2'-bipyridine ligand, it binds with cationic micelle which results in the increase in lifetime. The increase in the lifetime in the presence of micelle can be explained in terms of a model proposed by Demas et al^{38,39} (Figure 6).

The model shown in Figure 6 leads to eqn. 3 for the rate of decay of excited state $[\text{Ru}(\text{NN})_3]^{2+}$ which relates the observed emission lifetime to k_r , k_{nr} and k_{dd} .

$$1 / \tau (T) = k + k_{dd} \quad (3)$$

$$k = k_r + k_{nr} \quad (4)$$

$$k_{dd} = k' \exp(\Delta E / RT) \quad (5)$$

where k_r and k_{nr} are the radiative and nonradiative rate constants for the deactivation of $^3\text{MLCT}$ state and k_{dd} represents the sum of radiative and nonradiative decay rate constants for the depopulation of the corresponding state. These parameters provide the information about the effect of micellization on the excited state energy degradation. Since the value of the excited state lifetime and quantum yield increases on micellization, k_r , k_{nr} and/or k_{dd} are likely to be affected. Within the experimental error, k_r is invariant on micellization.³⁸⁻⁴⁰ Thus, the change in τ arises from changes in the nonradiative decay. Table 1 shows the increase in quantum yield in the presence of micelles. The increase in quantum yield is due to decrease in the rate of nonradiative decay from the excited state. It has already been indicated that the relaxation to the ground state *via* the dd state is also markedly affected by micellization and the k_{dd} are reduced by $\sim 50\%$ ³⁹.

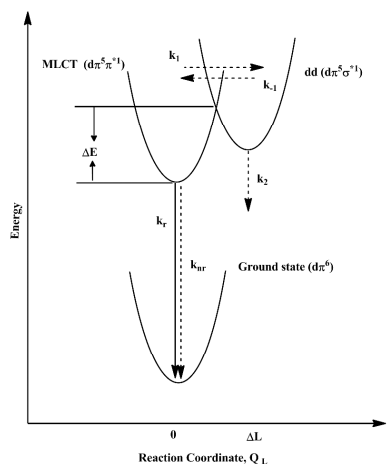


Figure 6: Energy level diagram showing the pathways of energy degradation for $[\text{Ru}(\text{NN})_3]^{2+}$.

The proposal of slow non-radiative decay in the presence of micelle is supported by the red shift observed in the emission spectrum of $[\text{Ru}(\text{NN})_3]^{2+}$ in the presence of CTAB. This red shift in emission indicates stabilization of $^3\text{MLCT}$ state in micelles compared to aqueous medium. This leads to more energy gap between $^3\text{MLCT}$ and dd states thereby suppressing the decay of the excited state via nonradiative dd state. Similar explanation has been provided in other rigid media which inhibited the MLCT-dd interconversion by destabilizing ligand field or dd states, thereby increasing the MLCT-dd energy gap.³⁸⁻⁴³

Demas et al.³⁸⁻⁴³ reported that $[\text{Ru}(\text{bpy})_3]^{2+}$ exhibit large solvent exposures and negligible spectral shifts due to weak interaction with either the Triton X-100 monomer or micelles. Also, the +2 charge of the complex favors solvation by water than Triton X-100. These two factors provide a reasonable explanation for the observed lack of interaction between $[\text{Ru}(\text{bpy})_3]^{2+}$ and Triton X-100. Thus the lifetime of $[\text{Ru}(\text{bpy})_3]^{2+}$ was unaffected by the addition of Triton X-100. Amphiphilic ruthenium(II)-complexes **II-IV** showed red shift in the range of 6–14 nm in the emission maximum along with enhancement in luminescence intensity with increase in [TX-100]. The substantial enhancement of emission intensity and longest excited state lifetime of complexes **II-IV** in the presence of neutral surfactant Triton X-100 indicate the strong binding of the probe with the neutral micelle. This can be explained by a dominant role of hydrophobic interactions due to presence of long hydrocarbon in the 4,4'-position of 2,2'-bipyridine with the alkyl chain of the surfactant.

This could be attributed to the microencapsulation of the $[\text{Ru}(\text{NN})_3]^{2+}$ into the micellar medium, resulting in the change in the microenvironment experienced by the ruthenium(II) complexes. In the presence of cationic micelle hydrophobic interaction is predominant over electrostatic repulsion leading to large binding constants relative to SDS. The substantial enhancement of emission intensity and longest excited state lifetime of complexes **II-IV** in the presence of neutral surfactant Triton X-100 indicate the strong binding of the probe with the neutral micelle. This can be explained by a dominant role of hydrophobic interactions due to presence of long hydrocarbon in the 4,4'-position of 2,2'-bipyridine with the alkyl chain of the surfactant. In Table 1, the emission quantum yield of **II-IV** increased in the presence of micelles, especially more pronounced in the case of neutral micelle. For example, complex **IV** has the quantum yield of 0.002 in homogeneous media, whereas in the presence of neutral micelle it increases to 0.021. This is due to the decrease in the rate of nonradiative decay.

Conclusion

In the presence of micelles, amphiphilic ruthenium(II)-complexes showed moderate changes in the absorption spectrum, whereas enormous increase in their emission intensity and emission lifetimes indicating the binding of these complexes with micelles. The interactions of amphiphilic complexes were more pronounced in neutral micelles when compared to the charged micelles. The hydrophobic interaction plays a dominant role in the binding of **II-IV** to the neutral micelle Triton X-100. The binding of cationic complexes **II-IV**, with CTAB can be attributed to a dominant role of hydrophobic interactions over electrostatic repulsion. Electrostatic interactions seem to be important in the binding of **II-IV** to SDS. These results demonstrate that the introduction of amphiphilic moiety in the fluorescent probe leads to favorable photophysical properties which can lead to their potential applications as sensors for biological systems.

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Notes

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