



## PHOTOEMISSION CHARACTERISTICS OF RUTHENIUM(II) PHENANTHROLINE COMPLEXES IN AOT REVERSE MICELLE

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**ABSTRACT:** The intention of this research is to explore the impact of the microheterogeneous environment on the photophysical properties of environmental probes, ruthenium(II)-polypyridyl complexes ( $[\text{Ru}(\text{NN})_3]^{2+}$ ) with respect to the ligand 1,10-phenanthroline (phen) and its derivatives. This work reports here the photophysical properties of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes in an anionic surfactant, bis(2-ethylhexyl)sulphosuccinate (AOT /aerosol-OT,) media as well. The water content in the reverse micelle was varied by using different values of  $W_0 = [\text{H}_2\text{O}] / [\text{AOT}]$  at fixed AOT (0.1 M) concentration. Absorption and emission characteristics were also employed for the synthesised complexes. The emission spectrum is more sensitive to the change of  $W_0$  value that is to the change of polarity of the microenvironment compared to the original absorption spectra. It was found that the hydrophobicity of  $[\text{Ru}(\text{phen})_3]^{2+}$  can be enormously improved by introducing alkyl and aryl groups in the 4<sup>th</sup> and 7<sup>th</sup> positions of 1,10-phenanthroline. All the three Ru(II) phenanthroline molecules remain solubilized near the water-micelle interface and are not displaced toward the central water pool upon saturating the reverse micelle with water in anionic micelle. The use of  $[\text{Ru}(\text{dpphen})_3]^{2+}$  as a polarity sensitive hydrophobic fluorescent probe will throw more light on the study of biopolymers to understand the environment in detail.

**KEYWORDS:** Microheterogeneous System, Ruthenium(II) Polypyridyl; 1,10-Phenanthroline; AOT Reverse Micelle; Hydrophobic Environment

### INTRODUCTION:

Nowadays emphasis has shifted to the utilization of ruthenium(II) polypyridyl complexes  $[\text{Ru}(\text{NN})_3]^{2+}$  as probes of various heterogeneous and microheterogeneous environments.<sup>i-iii</sup> Ionic Ru(II)- $\alpha$ -diimine complexes can be designed by incorporating hydrophobic ligands and, thus, bind to crucial interface regions in microheterogeneous systems with selectivity. If the charge and hydrophobicity of a series of complexes are specifically tailored, partitioning of these probes between the bulk and interfacial regions can be investigated<sup>iv</sup>, thus making valuable local environmental probes for areas that cannot be monitored with bulk measurements. The photophysics of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy = 2,2'-bipyridine) has been closely scrutinized in micelles and reverse micelles because of its importance in solar energy conversion<sup>v-vii</sup> and extensive use

as molecular probe.<sup>viii-xii</sup> Both luminescence lifetime and emission energy of  $[\text{Ru}(\text{bpy})_3]^{2+}$  are highly sensitive to the environment making this an ideal probe molecule for intracellular environment. Though a considerable amount of experimental and theoretical work on the photophysical properties of  $[\text{Ru}(\text{bpy})_3]^{2+}$  is available in the literature, still it seems to be necessary to accumulate more basic data on the photophysical properties of some more ruthenium (II) polypyridyl complexes in reverse micelle especially in Aerosol-OT which can form a versatile reverse micelle. Though many group of workers have reported the results on the photophysics of  $[\text{Ru}(\text{bpy})_3]^{2+}$  in reverse micelles<sup>xiii-xv</sup> as far as we know no report is available on the photophysics of ruthenium(II) complex carrying the ligand 1,10-phenanthroline (phen) and its derivatives in AOT/isooctane/water reverse micelle.

The objective of this present work is to vary the charge and hydrophobicity of the luminophore and to study the photophysics of these Ru(II)-polypyridyl complexes in reverse micelles and micelles by changing the phenanthroline ligand system systematically. To understand the influence of reverse micelles on the photophysics of ruthenium(II)-polypyridyl complexes and its derivatives, the absorption and emission spectra were recorded, their emission lifetimes were measured and the observed results are compared analysed in terms of an energy level diagram.

#### **EXPERIMENTAL METHODS:**

##### **Synthesis of Tris(1,10-Phenanthroline)Ruthenium (II) Chloride ( $[\text{Ru}(\text{phen})_3]^{2+}$ )**

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (0.6 g, 3 mmol) was dissolved in 50 mL of ethanol containing one drop of 6 N HCl and a stoichiometric amount (1.6 g, 9 mmol) of phenanthroline was added slowly with stirring. The mixture was refluxed for 40 h. Then the mixture was filtered, and 10 mL of 6 N HCl was added drop wise with stirring to the hot filtered solution. If no solid had formed at this point, the volume of the solution was reduced by evaporation until crystals formed. The crude product was recrystallized from hot water. The absorption and emission maxima values are  $\lambda_{\text{max}}^{\text{ab}} = 446 \text{ nm}$  and  $\lambda_{\text{max}}^{\text{em}} = 600 \text{ nm}$  respectively.

##### **Synthesis of Tris(4,7-Dimethyl-1,10-Phenanthroline)Ruthenium(II) Chloride ( $[\text{Ru}(\text{dmphen})_3]^{2+}$ )**

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (0.45 g, 1.5 mmol) and 4,7-dimethylphenanthroline (1.4 g, 4.5 mmol) were treated with 25 mL of ethyl alcohol and refluxed. After 5 minutes two drops of 6 N HCl was added and continued the reflux until the greenish dark solution turned reddish. Then the solution was condensed and 2 mL of 6 N HCl was added. Further required little amount of HCl was added and the precipitate was filtered and dried. The absorption ( $\lambda_{\text{max}}^{\text{ab}} = 446 \text{ nm}$ ) and emission ( $\lambda_{\text{max}}^{\text{em}} = 608 \text{ nm}$ ), maxima were observed.

##### **Synthesis of Tris(4,7-Diphenyl-1,10-Phenanthroline)Ruthenium(II) Chloride ( $[\text{Ru}(\text{dpphen})_3]^{2+}$ )**

The similar procedure was adopted as before using 4,7-diphenyl-1,10-phenanthroline in the place of 1,10-phenanthroline as ligand but the heating was continued for 72 h and the crude product was chromatographed using silica gel. The solution on evaporation yielded orange red crystals. The absorption maximum was found to be  $\lambda_{\text{max}}^{\text{ab}} = 465 \text{ nm}$  and emission maximum was  $\lambda_{\text{max}}^{\text{em}} = 625 \text{ nm}$  (in 2 percent ethanol solution).

##### **Formation of Microemulsions**

Microemulsions were prepared by mixing the requisite volume (a few microlitre) of the stock solution of the complex in water (except  $[\text{Ru}(\text{dpphen})_3]\text{Cl}_2$  which was dissolved in 1% ethanol) with the calculated amount of double distilled water to yield a required  $W_0$  and calculated quantity (0.5 mL) of 1 M AOT in isooctane solution. The final volume was adjusted with isooctane to yield a final concentration of 0.1 M AOT surfactant in isooctane. Then the mixture was stirred at room temperature until water was solubilized to form optically transparent uniform solution. All experiments were performed at room temperature (298 K) with the

solutions at 0.1 M (in the cell) surfactant concentrations [AOT in isooctane]. The water content of the microemulsion is expressed as the molar concentration ratio  $W_0 = [H_2O]/[AOT]$ . Studies were performed at seven different  $W_0$  values ranging from 6 to 50.

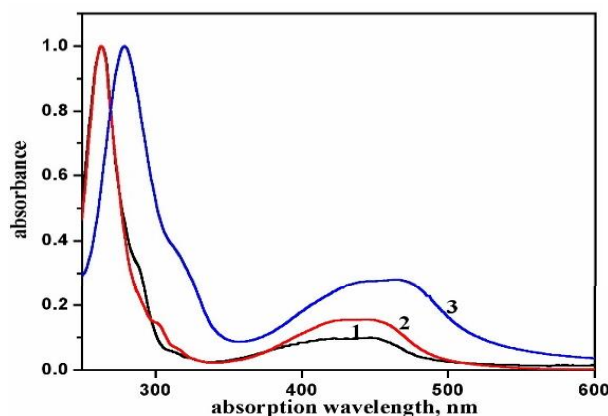
### Absorption and Emission Spectral Measurements

Sample solutions of the metal complexes and the quenchers were freshly prepared for each measurement. All experiments were performed with freshly prepared solutions. UV-visible absorption spectra were obtained on a HewlettPackard 8453A diode array spectrophotometer using 1 cm path length cuvette. The emission spectra were recorded with Jasco FP- 6300 spectrofluorometer using 1 cm path length quartz cuvette. Excitation and emission slits with a band-pass of 2.5 nm were used for all measurements. 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. Care had been taken to minimize solvent and/or water evaporation that could modify the water to surfactant molar ratio. The nitrogen gas is purified by passing through Fieser's solution to remove the oxygen present in the solution.

## RESULTS AND DISCUSSION:

### Absorption and Emission Spectrum of Ruthenium (II) Phenanthroline Complexes in Water

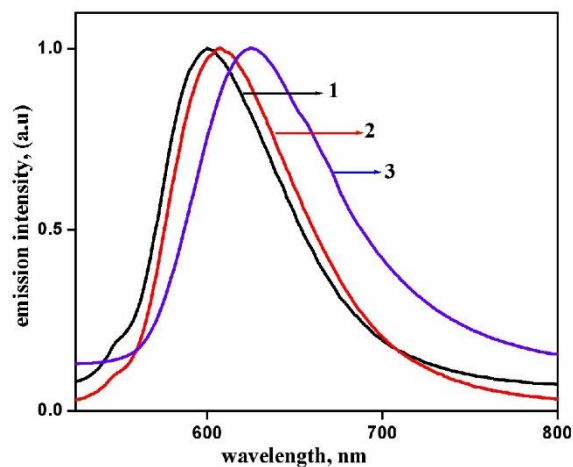
The absorption and emission spectrum of all the three ruthenium (II) phenanthroline complexes,  $[Ru(phen)_3]^{2+}$ ,  $[Ru(dmphen)_3]^{2+}$  and  $[Ru(dpphen)_3]^{2+}$  in water are shown in Figs. 1 and 2; and the values of  $\lambda_{max}^{abs}$  and  $\lambda_{max}^{em}$  are given in Tables 1 - 3. They show a strong ligand centered  $\pi \rightarrow \pi^*$  transition in the region 260 to 270 nm and introduction of phenyl group red shifts the  $\pi \rightarrow \pi^*$  transition from 263 nm to 278 nm. The spectra in the visible region are dominated by the metal  $d \rightarrow$  ligand  $\pi^*$  transitions. The absorption maxima of the lowest energy  $^1MLCT$  bands of the three complexes  $[Ru(phen)_3]^{2+}$ ,  $[Ru(dmphen)_3]^{2+}$  and  $[Ru(dpphen)_3]^{2+}$  occur at 445, 446 and 465 nm respectively. The absorption maxima of the lowest energy  $^1MLCT$  band are red shifted by the introduction of alkyl and aryl groups as shown in Fig. 1.



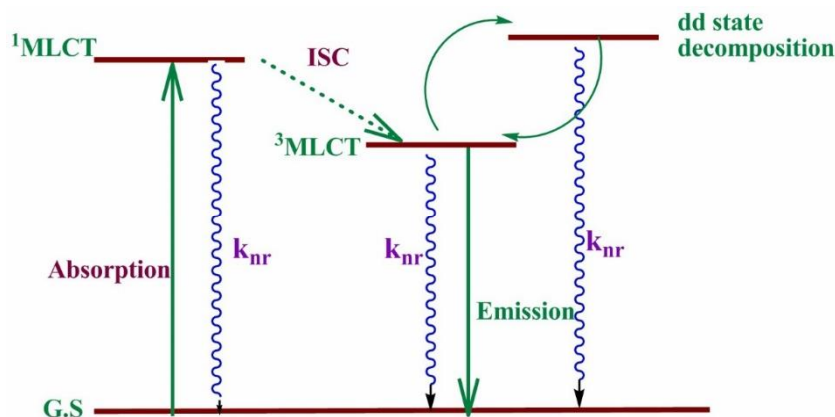
**Fig. 1** Normalized absorption spectra of  $[Ru(phen)_3]^{2+}$  (1),  $[Ru(4,7dmphen)_3]^{2+}$  (2) and  $[Ru(4,7-dpphen)_3]^{2+}$  (3) in aqueous medium at room temperature

Emission maxima of  $[Ru(phen)_3]^{2+}$ ,  $[Ru(dmphen)_3]^{2+}$  and  $[Ru(dpphen)_3]^{2+}$  complexes in aqueous solution occur at 600, 608 and 625 nm respectively (Fig. 2). As the hydrophobicity increases the emission maximum shifts towards a longer wavelength with the replacement of (phen) ligand by (dmphen) and (dpphen) ligands. This suggests stabilization of the  $^3MLCT$  state with the increase in hydrophobicity of the ligand and is consistent with the observed trend in the absorption spectra of these compounds. The stabilization of  $^3MLCT$  state of  $[Ru(dpphen)_3]^{2+}$  compared to  $[Ru(phen)_3]^{2+}$  may be attributed to better delocalization of

electron in the case of (dpphen) than that in (phen) which leads to stabilization of the charge density at the metal centre as depicted in Fig. 3.



**Fig. 2** Normalized emission spectra of  $[\text{Ru}(\text{phen})_3]^{2+}$  (1),  $[\text{Ru}(\text{dmphen})_3]^{2+}$  (2) and  $[\text{Ru}(\text{dpphen})_3]^{2+}$  (3) complexes in aqueous medium



**Fig. 3** Energy level diagram showing various deactivation pathways of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes

**Table 1** Photophysical properties of  $[\text{Ru}(\text{phen})_3]^{2+}$  in  $\text{H}_2\text{O}$  and 0.1 M AOT/isooctane/water reverse micelle at 298 K

| Complex                                   | $[\text{Ru}(\text{phen})_3]^{2+}$  |                                  |                    |
|---|--|----------------------------------|--------------------|
| $W_0 = [\text{H}_2\text{O}]/[\text{AOT}]$ | $\lambda_{\text{abs}}, \text{nm}, (\epsilon, \text{M}^{-1}\text{cm}^{-1})$ | $\lambda_{\text{em}}, \text{nm}$ | $\Phi_{\text{em}}$ |
| Water                                     | 445(18793)   | 600                              | 0.049              |
| 6   | 447 (19547)  | 618                              | 0.156              |
| 10  | 429 (18313)  | 622                              | 0.142              |
| 16  | 429 (18413)  | 622                              | 0.130              |
| 20  | 430 (18200)  | 622                              | 0.117              |
| 30  | 430(18006)   | 620                              | 0.109              |
| 40  | 430(17106)   | 620                              | 0.108              |
| 50  | 430(16587)   | 620                              | 0.082              |

**Table 2** Photophysical properties of [Ru(dmphen)<sub>3</sub>]<sup>2+</sup> in H<sub>2</sub>O and 0.1M AOT/isooctane/water reverse micelle at 298K

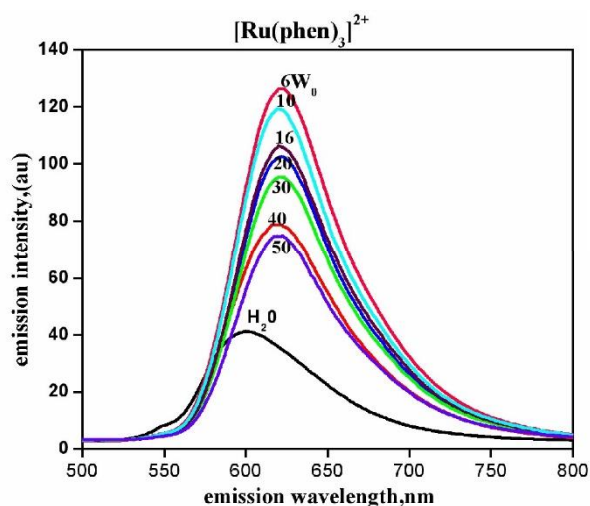
| Complex                                  | [Ru(phen) <sub>3</sub> ] <sup>2+</sup>                        |                      |                 |
|--|---|----------------------|-----------------|
| W <sub>0</sub> =[H <sub>2</sub> O]/[AOT] | λ <sub>abs</sub> , nm, (ε, M <sup>-1</sup> cm <sup>-1</sup> ) | λ <sub>em</sub> , nm | Φ <sub>em</sub> |
| Water                                    | 446 (25127)   | 612                  | 0.057           |
| 6  | 448 (26700)   | 624                  | 0.266           |
| 10                                       | 438 (23806)   | 626                  | 0.257           |
| 16                                       | 438 (24111)   | 628                  | 0.249           |
| 20                                       | 436 (24566)   | 629                  | 0.247           |
| 30                                       | 436(24567)  | 629                  | 0.240           |
| 40                                       | 436(24003)  | 628                  | 0.236           |
| 50                                       | 436(24000)  | 628                  | 0.199           |

**Table 3** Photophysical properties of [Ru(dpphen)<sub>3</sub>]<sup>2+</sup> in H<sub>2</sub>O and 0.1M AOT/isooctane/water reverse micelle at 298 K

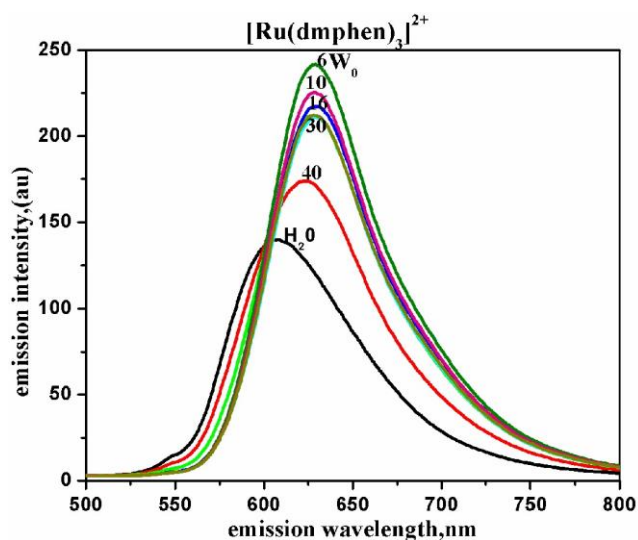
| Complex                                  | [Ru(phen) <sub>3</sub> ] <sup>2+</sup>                        |                      |                 |
|--|---|----------------------|-----------------|
| W <sub>0</sub> =[H <sub>2</sub> O]/[AOT] | λ <sub>abs</sub> , nm, (ε, M <sup>-1</sup> cm <sup>-1</sup> ) | λ <sub>em</sub> , nm | Φ <sub>em</sub> |
| Water                                    | 465 (29120)   | 626                  | 0.063           |
| 6  | 465 (27200)   | 615                  | 0.341           |
| 10                                       | 465 (25580)   | 616                  | 0.284           |
| 16                                       | 467 (25480)   | 619                  | 0.253           |
| 20                                       | 465 (26440)   | 621                  | 0.241           |
| 30                                       | 465(26180)  | 628                  | 0.235           |
| 40                                       | 467(26180)  | 630                  | 0.212           |
| 50                                       | 465(27220)  | 634                  | 0.172           |

### Absorption and Emission Spectrum of Ruthenium (II) Phenanthroline Complexes in AOT/Water/Isooctane Reverse Micelle

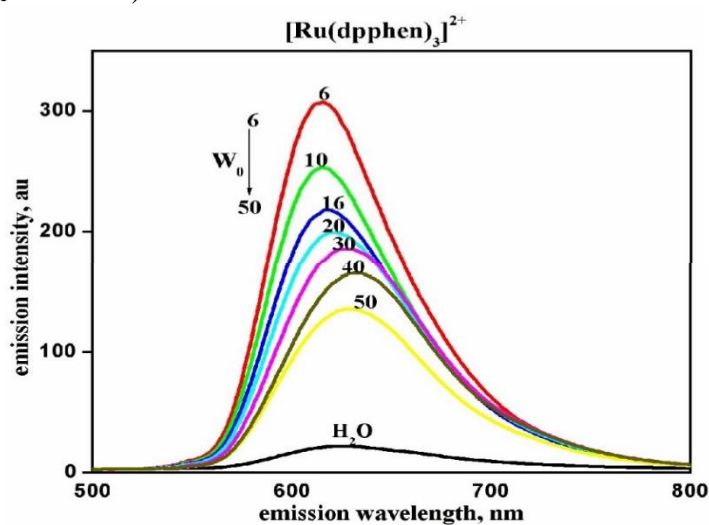
The absorption and emission maxima of three ruthenium(II)phenanthroline complexes, [Ru(phen)<sub>3</sub>]<sup>2+</sup>, [Ru(dmphen)<sub>3</sub>]<sup>2+</sup> and [Ru(dpphen)<sub>3</sub>]<sup>2+</sup> in aqueous (water) and reverse micelles are depicted in Tables 1-3. The absorption maxima of [Ru(phen)<sub>3</sub>]<sup>2+</sup> and [Ru(dmphen)<sub>3</sub>]<sup>2+</sup> are substantially affected by the change of medium from bulk water to reverse micelles (W<sub>0</sub>=10), though there are slight changes in the ε values as shown in Tables 1-3. Contrary to these observations there is slight change in the λ<sub>max</sub> value of [Ru(dpphen)<sub>3</sub>]<sup>2+</sup> with the change of medium. On the other hand, there is a substantial shift in the peak position of the emission spectra and enormous increase in the emission intensity of all the complexes when the medium is changed from bulk water to AOT/isooctane reverse micelle. Representative emission spectra of [Ru(NN)<sub>3</sub>]<sup>2+</sup> complexes in bulk water and in AOT/isooctane/water reverse micelle as a function of W<sub>0</sub> are shown in Figs. 4 - 6.



**Fig. 4** Emission spectra of  $[\text{Ru}(\text{phen})_3]^{2+}$  in AOT/isooctane/water reverse micelle as a function of  $W_0$  ( $\lambda_{\text{exc}} = 445 \text{ nm}$ )

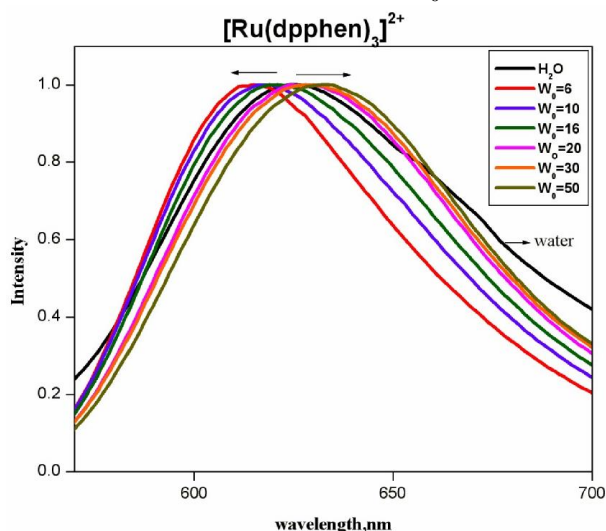


**Fig. 5** Emission spectra of  $[\text{Ru}(\text{dmphen})_3]^{2+}$  in AOT /isooctane/water reverse micelle as a function of  $w_0$  ( $\lambda_{\text{exc}} = 446 \text{ nm}$ )



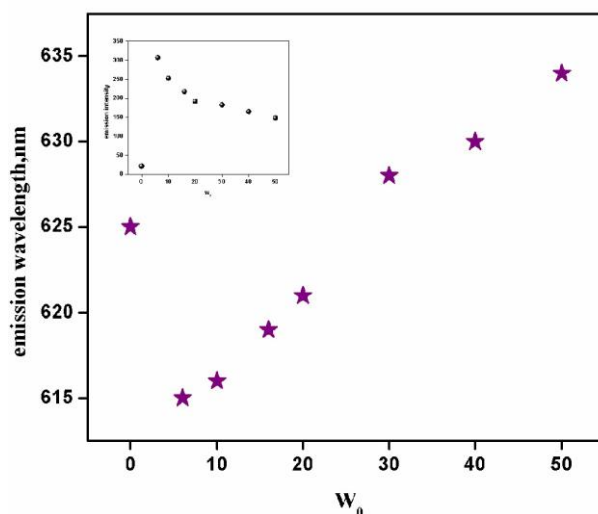
**Fig. 6** Emission spectra of  $[\text{Ru}(\text{dpphen})_3]^{2+}$  in AOT/ isooctane /water reverse micelle as a function of  $W_0$  ( $\lambda_{\text{exc}} = 465 \text{ nm}$ )

In all ruthenium(II)-phenanthroline complexes the change of medium from aqueous to reverse micelle leads to enormous increase in the luminescence intensity initially ( $W_0=6$ ) but further increase in the  $W_0$  value decreases the emission intensity. As far as the emission maximum of  $[\text{Ru}(\text{phen})_3]^{2+}$  and  $[\text{Ru}(\text{dmpphen})_3]^{2+}$  are concerned, there is a red shift of 22 nm (600 to 622nm) and 16 nm (612 to 628 nm) respectively (Tables 1 and 2), similar to the results observed with  $[\text{Ru}(\text{bpy})_3]^{2+}$ <sup>xiii</sup>. This red shift in emission maximum may be attributed to the stabilization of emitting <sup>3</sup>MLCT state compared to d-d state in reverse micelles compared to that in aqueous medium. On the other hand, there is an initial blue shift in the emission maximum in the case of  $[\text{Ru}(\text{dpphen})_3]^{2+}$ , when the medium is changed from water to reverse micelle,  $W_0 = 6$ . But with further increase in  $W_0$  value the shift in the emission maximum is in the reverse direction finally leading to red shift (Table 3). The blue shift of the emission maximum at  $W_0 = 6$  is due to the increased rigidity of the surrounding medium<sup>xvi-xvii</sup>. This is because the luminescent excited state of  $[\text{Ru}(\text{dpphen})_3]^{2+}$  complex with a polar MLCT character cannot be completely stabilized within its lifetime when solvent reorientation is prevented in rigid medium<sup>xvi</sup>. At  $W_0 = 6$  the size of the micelle is small and there will be only bound water and the chance for the availability of free water is less. At this situation the probe will experience a more rigid environment and orient near the nonpolar region rather than surfactant/water interface. The normalized emission spectra of  $[\text{Ru}(\text{dpphen})_3]^{2+}$  complex in aqueous medium as well as in AOT/isooctane/water reverse micelle as a function of  $W_0$  are shown in Fig. 7.



**Fig. 7** Normalized emission spectra of  $[\text{Ru}(\text{dpphen})_3]^{2+}$  in AOT/isooctane/water reverse micelle as a function of  $W_0$  ( $\lambda_{\text{exc}}=445$  nm)

Fig. 8 displays the variation of wavelength of emission maximum as a function of  $W_0$  and the inset shows the variation of total luminescence intensity with  $W_0$ . An enormous initial increase in the emission intensity was observed in the low water content ( $W_0 = 6$ ) in the reverse micelle. The emission intensity decreases with increasing water content. The emission maximum of  $[\text{Ru}(\text{dpphen})_3]^{2+}$  is 615 nm in reverse micelle, ( $W_0 = 6$ ) blue shifted approximately by 10 nm from that in water (625nm). Such a dramatic blue shift of emission maximum in reverse micelle indicates that the microenvironment of  $[\text{Ru}(\text{dpphen})_3]^{2+}$  is significantly different from bulk water. However, with the increase of  $W_0$  value the emission maximum shows a progressive red shift and when the  $W_0$  value is 50, the emission maximum is 634 nm. As more and more water added, the water pool swells in size and the polarity of the microenvironment increases<sup>xviii</sup> and so the hydrophobic probe experiences relatively more polar environment resulting in the red shift in the emission maximum. The above shift indicates an important point that the change of polarity experienced by the probe will be dependent on the location of the probe molecule.



**Fig. 8** Variation of wavelength of emission maximum of  $[\text{Ru}(\text{dpphen})_3]^{2+}$  in AOT/isooctane/reverse micelle as a function of  $W_0$ . The inset shows the variation of fluorescence intensity as function of  $W_0$

#### CONCLUSION:

The conclusion from the spectral data observed in the present study is that the properties of Ru(II)– phenanthroline complexes are dramatically altered in the presence of reverse micelle. Specifically reverse micelle encapsulation of metal complexes in restricted environment causes blue shift in the emission spectra as well as have longer radiative lifetime. These effects can be attributed to what was originally termed rigidochromism. The observation of this interesting phenomenon is caused by decreased rotational freedom of the entrapped probe molecule due to its strong electrostatic and hydrophobic interaction with the sulfonate groups and alkyl chain of AOT at the interface and restriction in the dipole reorientation time scales. Thus, it can also be used as a hydrophobic probe for studying biomolecules and molecular probe for chemosensing in the field of medicine. This present study provides support for extending the application of this interesting metal complex as sensor for biosystems.

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