Luminescent $Ru(phen)_n(bps)_{3-n}^{2n-4}$ Complexes ($n = 0-3$) as Probes of Electrostatic and Hydrophobic Interactions with Micellar Media

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The $Ru(phen)_n(bps)_{3-n}^{2n-4}$ ($n = 0-3$) complexes (phen = 1,10-phenanthroline, bps = disulfonated 4,7-diphenyl-1,10-phenanthroline) were prepared to probe the hydrophobic and electrostatic interactions with cationic DTAB (*n*-dodecyltrimethylammonium bromide), anionic SDS (sodium dodecyl sulfate), and neutral C12E8 (*n*-dodecyl octaoxyethylene glycol monoether) surfactants. The measured emission maxima and lifetimes are consistent with the population of the Ru → phen MLCT (metal-to-ligand charge transfer) excited state in $Ru(phen)_3^{2+}$ and the lower-lying Ru → bps MLCT excited state in $Ru(phen)_n(bps)_{3-n}^{2n-4}$ ($n = 0-2$). Premicellar aggregates with oppositely charged surfactants lead to decreased overall emission intensity for all complexes. In particular, aggregates formed by $Ru(bps)_3^{4-}$ with DTAB exhibit a 22-fold decrease in emission intensity and marked changes in the electronic absorption spectrum, with a concomitant appearance of a shorter lifetime component. The photophysical characteristics of the premicellar adduct can be explained by changes in the relative energies of the emissive ^{3}MLCT state and the $^3\pi\pi^*$ state of the bps ligands, such that more effective deactivation of the ^{3}MLCT through the $^3\pi\pi^*$ state is possible. The results show that complexes possessing at least one bps ligand do not exhibit significant changes in their spectral properties upon addition of DTAB, C12E8, and SDS micelles, compared to those observed for $Ru(phen)_3^{2+}$, interpreted as reduced interaction between bps-containing complexes and the micellized surfactants. The interactions (inferred from changes in spectral properties) between $Ru(phen)_3^{2+}$ and the cationic DTAB system are greater than those of $Ru(bps)_2(phen)^{2-}$ with the anionic SDS surfactant, although both complexes possess overall charge of equal magnitude. These observations can be explained in terms of the differences in the hydrophilicity of the complexes.

Introduction

Electrostatic and/or hydrophobic interactions arising from amino acid residues often control the structure and function of biological systems.[1] These forces not only dictate the secondary and tertiary structure of proteins and enzymes but also direct the binding among proteins, enzymes, and nucleic acids.[2−4] In addition, these interactions play an important role in enzymatic reactions, driven by the binding of substrates and release of product to and from the active site.[5,6] Electrostatic forces from charged residues within the protein membrane are believed to play a significant role in the transfer of electrons and translocation of protons in biological energy storage and conversion systems, such as the photosynthetic reaction center and bacteriorhodopsin.[7−10]

Much effort has been devoted to the fundamental understanding of these noncovalent interactions in model systems at a molecular level. The noncovalent binding of photoreactive components to the interior and surface of microheterogeneous systems, such as vesicles,[11−16] micelles,[17−21] polymers,[22−24] and

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starburst dendrimers,[25] has been widely utilized in energy conversion and storage relays that mimic those found in biological assemblies.[26−29] The binding of photoactive metal complexes to proteins and DNA has also been the focus of much recent research.[30,31] The utilization of highly emissive probes whose photophysical properties vary with those of their surrounding has proven a very useful tool in studies aimed at probing the environment of supramolecular hosts at the probe's binding site.[32,33] Systematic changes in the hydrophobicity of the probes can be attained through variation of the ligation sphere about a metal center, while keeping the overall charge of the probe molecules constant. One example is the series of Ru(II) complexes possessing substituted 1,10-phenanthroline (phen) ligands to form the homoleptic $Ru(L)_3^{2+}$ series, with L = phen, 5-Mephen, 4,7-Me_2phen, 5,6-Me_2phen, Me_4phen, and 4,7-Ph_2phen.[34] It was shown that the differences in hydrophobicity of the various complexes has a significant effect on the binding to anionic micelles, although it is believed that the electrostatic interactions have a greater effect on the association.[34] However, the changes in the probe's absorption and emission spectral profile and intensity upon systematic variation of its charge in the presence of both ionic and neutral micelles has not been thoroughly addressed.

Owing to the vast current knowledge of the photophysical properties of Ru(II) complexes,[35,36] as well as on the composition, size, and shape of micelles,[37] systematic studies involving the complexes as emissive probes of hydrophobic and electrostatic interactions can be undertaken. To this end, we have prepared a series of Ru(II) complexes with varying overall charge and monitored the changes in the absorption and emission characteristics of the complexes to obtain information on the association of the probes to the various micellar systems. The highly emissive series $Ru(phen)_n(bps)_{3-n}^{2n-4}$ ($n = 0-3$; bps = disulfonated 4,7-diphenyl-1,10-phenanthroline), possessing overall charges of +2, 0, −2, and −4, was chosen to probe the interactions of the various complexes with anionic SDS (sodium dodecyl sulfate), cationic DTAB (*n*-dodecyltrimethylammonium bromide), and neutral C12E8 (*n*-dodecyl octaoxyethylene glycol monoether) surfactants. The complexes and micelle-forming agents have been chosen such that their electrostatic properties can be systematically varied and monitored utilizing the optical properties typical of Ru(II) complexes.

Experimental Methods

Materials. The ligands 1,10-phenanthroline (phen) and disulfonated 4,7-diphenyl-1,10-phenanthroline (bps), as well as $RuCl_3$ and the chloride salt of $Ru(phen)_3^{2+}$, were purchased from Aldrich. SDS, DTAB, and C12E8 were purchased from Sigma and were used without further purification.

$Ru(phen)_2(bps)$ was prepared by refluxing 0.1 g $Ru(phen)_2Cl_2$ with 0.2 g bps ligand in 60 mL of a 3:1 ethanol/water mixture, followed by solvent removal in a rotary evaporator. The orange complex was separated from the water soluble bps ligand using a Sephadex G-15 column in water. $Ru(phen)_2Cl_2$ was synthesized from the reaction of 0.2 g of $RuCl_3$ with a 2-fold excess of phen in 25 mL of anhydrous DMF in the presence of 0.3 g LiCl. Water was added following removal of the DMF and the insoluble $Ru(phen)_2Cl_2$ was collected through filtration. The solid was dissolved in CH_2Cl_2 and was extracted with water to remove $Ru(phen)_3^{2+}$ until the aqueous phase was colorless. $Ru(bps)_2Cl_2^{4-}$ and $Ru(bps)_3^{4-}$ were prepared by refluxing 0.056 g of $RuCl_3$ and 0.29 g of bps (2-fold molar excess) in 30 mL of a 3:1 ethanol/water mixture with 1.0 g LiCl. Since both complexes are water soluble, they were separated using a Sephadex G-15 column. The orange $Ru(bps)_3^{4-}$ eluted first and was collected, whereas unreacted ligand and $RuCl_3$ eluted very slowly. The second component was the broad band of the purple $Ru(bps)_2Cl_2^{4-}$ with remaining $Ru(bps)_3^{4-}$; the mixture was passed through a second Sephadex G-15 column for further separation. $Ru(bps)_2(phen)^{2-}$ was prepared by refluxing $Ru(bps)_2Cl_2^{4-}$ with excess phen in a 3:1 ethanol/water mixture $Ru(bps)_2(phen)^{2-}$ overnight. The reaction mixture was dried, and $Ru(bps)_2(phen)^{2-}$ was precipitated from acetone with ether.

The NMR spectra of all the complexes possessed peaks in the aromatic region.[38] In the mixed-ligand complexes, the overlap of the resonances for phen and bps protons made it difficult to obtain independent integrated areas, although the ratio between the phen 4,7-H (8.75−8.85 ppm) and those in the 8.34−8.43 ppm region, corresponding to overlapped phen 5,6-H and bps 2,9-H, were consistent with the expected integrated values for $Ru(phen)_2(bps)$ and $Ru(bps)_2(phen)^{2-}$. The identity of the complexes containing bps ligands was ascertained by mass spectrometry. The parent ion peaks of the neutral complex $Ru(phen)_2(bps)$ were detected using FAB MS with positive ion detection (m/z = 953, $Ru(phen)_2(bps)\cdot H^+$; 975, $Ru(phen)_2(bps)\cdot Na^+$), and electrospray with negative ion detection for $Ru(bps)_2(phen)^{2-}$ (m/z, z: 630.6, −2; 1263.8, −1) and $Ru(bps)_3^{4-}$ (m/z, z: 392.8, −4; 524.2, −3; 785, −2). In addition the expected ligand-centered $\pi\pi^*$ and MLCT transitions in the electronic absorption spectra were observed, as well as the strong emission in the 600−650 nm spectral region.

Instrumentation. Absorption measurements were performed in a Hewlett-Packard diode array spectrometer (HP 8453) with HP8453Win System software installed in an HP Vectra XM 5/120 desktop computer. Emission spectra were collected on a SPEX FluoroMax-2 spectrometer equipped with a 150 W xenon source, a red-sensitive R928P photomultiplier tube, and DataMax-Std software on a Pentium microprocessor. The decay of the emission was measured following sample excitation with the 532 nm output from a frequency-doubled Spectra-Physics GCR-150-10 Nd:YAG laser (fwhm ∼ 10 ns, 3 mJ/pulse). The emission was collected through a 570 nm cutoff filter (Oriel OG-570), collimated and focused with two fused silica plano-convex lenses (f/4,

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Table 1. Absorption (λ_{abs}) and Emission (λ_{em}) Maxima and Luminescence Lifetimes (τ) of the $Ru(phen)_n(bps)_{3-n}^{2n-4}$ ($n = 1-3$) Series of Complexes in Water

complex	λ_{abs}/nm ($\epsilon/\times 10^3$ M^{-1} cm^{-1})	λ_{em}/nm[a]	$\tau/\mu s$[b]
$Ru(phen)_3^{2+}$	262 (116.), 420 (18.6), 447 (19.4)	603	1.1
$Ru(phen)_2(bps)$	265 (62.9), 277 (sh), 423 (10.1), 430 (10.5)	626	4.6
$Ru(bps)_2(phen)^{2-}$	265 (sh), 276 (82.7), 435 (17.9), 458 (17.7)	627	4.7
$Ru(bps)_3^{4-}$	277 (72.6), 438 (16.1), 465 (16.2)	629	4.6

[a] Emission corrected for instrument and detector response. [b] Monitored at emission maximum (λ_{exc} = 532 nm; 3 mJ/pulse; fwhm ~ 10 ns).

1 in. diameter) into the entrance slit of a Spex H-20 single monochromator (1200 gr/mm grating blazed at 500 nm). The emission was detected utilizing a Hamamatsu R928 photomultiplier tube powered by a Stanford Research PS325 power supply; the signal was digitized on a Tektronics 400 MHz oscilloscope (TDS 380) equipped with a floppy drive. The ASCII data were transferred to a PowerMac 7600/132 (Apple), and the fits were performed utilizing KaleidaGraph plotting software. Attenuated scattered laser light yielded an overall instrument response function with fwhm = 12.5 ns.

Results and Discussion

Photophysical Properties in Water. The absorption maxima and extinction coefficients for the $Ru(phen)_n(bps)_{3-n}^{2n-4}$ ($n = 0-3$) series of complexes are listed in Table 1. The spectral differences in the 250−300 nm region are indicative of the variations in the ligation sphere of the complexes. The LC $\pi\pi^*$ transition of phen appears at 262 nm in $Ru(phen)_3^{2+}$, and that of bps appears at 277 nm in $Ru(bps)_3^{4-}$; the relative intensities of each of these peaks in $Ru(phen)_2(bps)$ and $Ru(bps)_2(phen)^{2-}$ are consistent with the number of phen and bps ligands in each complex. The broad absorption in the 400−500 nm region observed in all complexes is due to $d\pi^*$ (Ru-phen and/or Ru-bps) metal-to-ligand charge transfer (MLCT) transitions.

The emission spectra of the four $Ru(phen)_n(bps)_{3-n}^{2n-4}$ ($n = 0-3$) complexes was collected in deoxygenated aqueous solutions with 440 nm excitation, with maxima, λ_{em}, and lifetimes listed in Table 1. The spectra of the bps-containing complexes exhibit emission maxima in the 626−629 nm range, shifted to lower energies from that of $Ru(phen)_3^{2+}$ at 603 nm. In addition, the emission lifetimes of all the complexes possessing bps ligands are in the 4.6−4.7 μs range (Table 1), which are approximately four times greater than that of $Ru(phen)_3^{2+}$ (1.1 μs). These observations are consistent with emission from the Ru(II) → phen MLCT state in $Ru(phen)_3^{2+}$, and from the lower-lying Ru(II) → bps MLCT state in the mixed-ligand complexes and in $Ru(bps)_3^{4-}$. Such behavior is typical of emissive MLCT states of mixed-ligand Ru(II) complexes, where the emission arises from the lowest-lying state.[34,35]

Spectroscopic Changes upon Addition of Surfactant. Electronic Absorption. The relative changes in the absorption of the MLCT transition of all four complexes as a function of added cationic, neutral, and anionic micelle-forming agents are shown in Figure 1. Since in all cases the Ru(II) complex concentration was kept constant, the observed changes are indicative of variations in the extinction coefficient in the premicellar and micellar environments. Changes in the absorption interpreted as premicellar interactions with the complexes

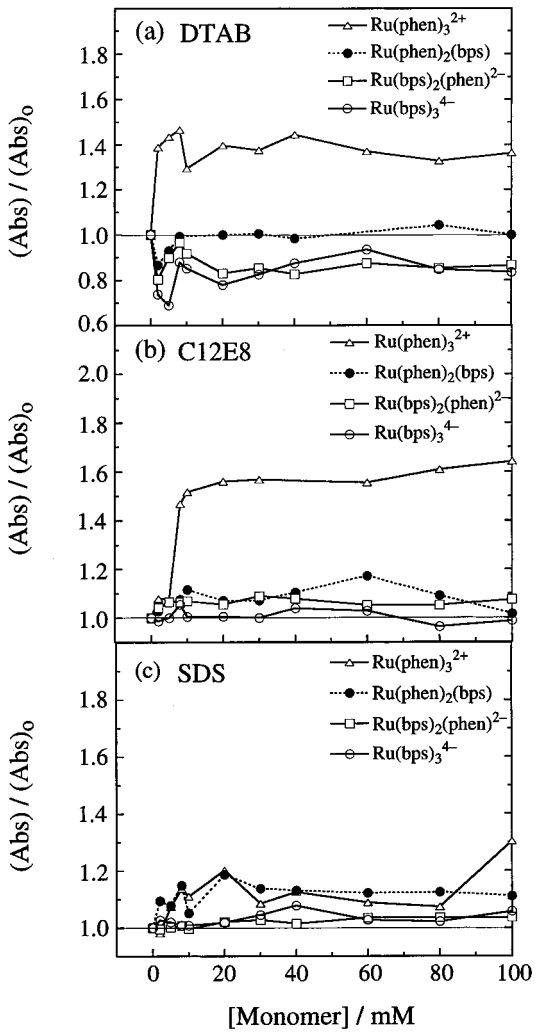

Figure 1. Changes in the maximum of the MLCT absorption, (Abs), of each complex (Table 1) as a function of (a) DTAB, (b) C12E8, and (c) SDS concentration relative to that in the absence of surfactant, $(Abs)_o$.

take place below the critical micelle concentration (cmc) of each surfactant, where the reported cmc values for SDS, C12E8, and DTAB are 8.0, 0.1, and 16 mM, respectively.[39−42] Although the plots in Figure 1 are for a single wavelength in the broad MLCT absorption band, the use of other wavelengths in the 400−500 nm region leads to similar results with the exception of $Ru(bps)_3^{4-}$ and $Ru(bps)_2(phen)^{2-}$ with DTAB. Similar trends are also observed in the 250−350 nm range for each system.

The changes in the absorption spectra as a function of monomer concentration for the $Ru(phen)_3^{2+}$/SDS system are small. Such small changes were observed for all systems with the exception of $Ru(bps)_3^{4-}$ and $Ru(bps)_2(phen)^{2-}$ upon addition of DTAB. Although the molar extinction coefficient of both the $\pi\pi^*$ and MLCT bands of $Ru(phen)_3^{2+}$ change upon addition of SDS, the peak positions and bandwidth remain relatively unchanged. It should also be noted that the largest changes in the absorption spectra in SDS are observed above the cmc, indicating that premicellar aggregates are either not formed or the association does not to cause changes in the absorption

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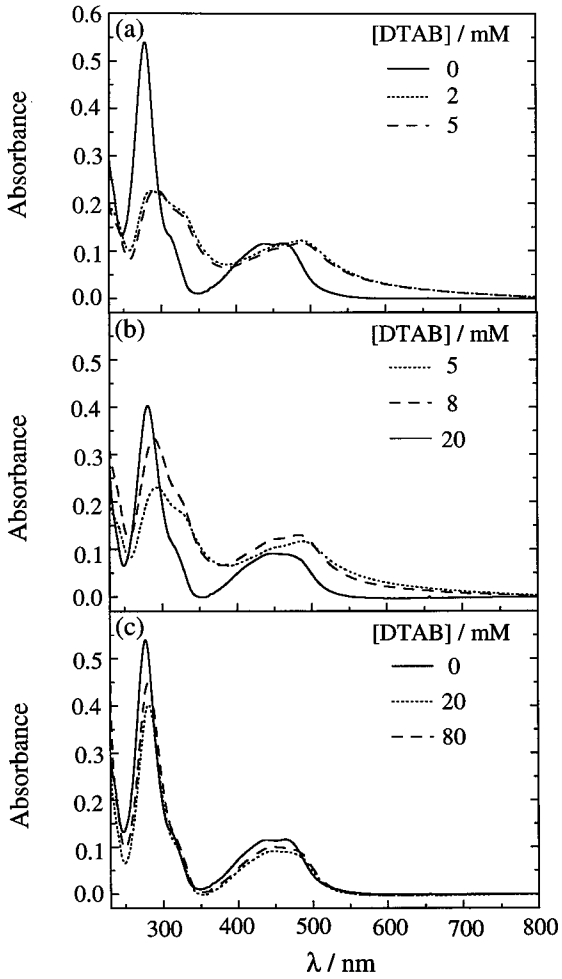

Figure 2. Spectral profile of $Ru(bps)_3^{4-}$ as a function of increasing DTAB at premicellar (top), micellar (bottom), and intermediate (middle) concentrations.

spectra. Similar changes in the spectra were observed for all the complexes with SDS and C12E8 and for $Ru(phen)_3^{2+}$ and $Ru(phen)_2(bps)$ with DTAB, where there was an increase in absorption without significant spectral shifts.

In contrast, large spectral changes were observed for the anionic $Ru(bps)_3^{4-}$ and $Ru(bps)_2(phen)^{2-}$ complexes upon addition of the cationic DTAB, especially at premicellar concentrations. The observed spectral changes upon addition of DTAB were more pronounced for $Ru(bps)_3^{4-}$ (Figure 2) than for the less negative $Ru(bps)_2(phen)^{2-}$. The greatest spectral changes shown in Figure 2 take place at premicellar concentrations of DTAB (cmc = 16 mM); further addition of DTAB leads to progressive changes that ultimately result in a spectrum similar to that observed in water. These data point to a strong premicellar $Ru(bps)_3^{4-}$/DTAB aggregate, with a complex−micelle adduct that is either weaker or that does not lead to spectral changes. In the premicellar aggregate, a large hypochromic shift is observed for the bps $\pi\pi^*$ peak, which shifts from 277 nm in water to 298 nm in the presence of 2.0 mM DTAB, with a smaller red-shift of the broad MLCT peaks from 465 to 475 nm (Figure 2). As shown in Figure 3, the relative changes in absorption in the $\pi\pi^*$ and MLCT regions are similar, both in the decrease of the initial spectrum and in the increase at the new red-shifted maxima at 326 and 492 nm. In both cases it is apparent that the largest changes take place at [DTAB] < 20 mM.

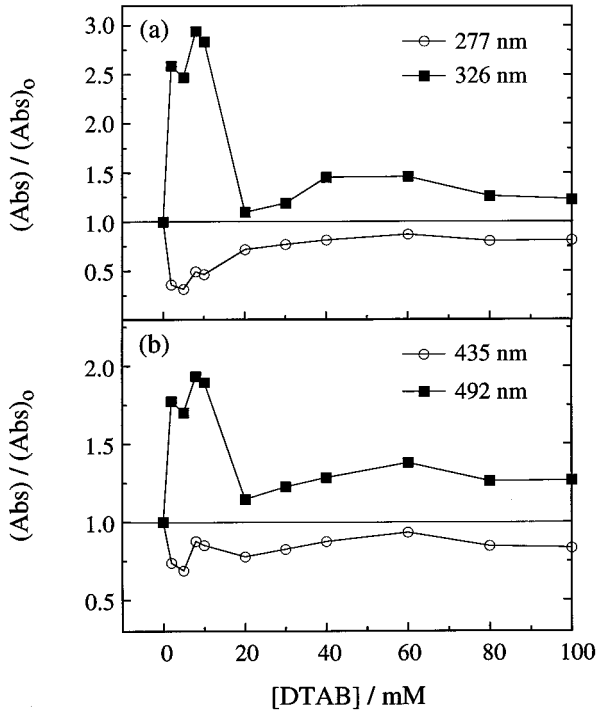

Figure 3. Relative changes in the absorption of $Ru(bps)_3^{4-}$ in the (a) LC $\pi\pi^*$ transition of the ligand and (b) MLCT region, showing both the decrease in free complex and the formation of premicellar and micellar adducts.

These shifts can be correlated with hydrophobic interactions between the bps ligands and the long alkyl chain of DTAB monomers. Since the same behavior is not observed with the neutral C12E8 system, it is likely that the cationic head group in DTAB plays an important role in the association. However, ionic interactions upon addition of various salts, including tetramethylammonium chloride and tetrabutylammonium chloride, do not appear to affect the absorption characteristics. It is known that $Ru(phen)_3^{2+}$ binds electrostatically to the surface of the anionic SDS micelles, however, as discussed above the spectral changes in the electronic absorption observed in this system are small.[27,28]

Emission Intensity. SDS and C12E8. The changes in the integrated emission intensity (I), relative to the intensity in water (I_o), are shown in Figure 4 for all four $Ru(phen)_n(bps)_{3-n}^{2n-4}$ ($n = 0-3$) complexes in the presence of SDS and C12E8. The small relative emission intensity changes measured ($1.0 \leq I/I_o \leq 1.6$) as a function C12E8 concentration for all Ru(II) complexes (Figure 4b) result from the observed changes in the extinction coefficient at the excitation wavelength (Figure 1b). Similar results were obtained for all the complexes with SDS, with the exception of $Ru(phen)_3^{2+}$ (Figure 4a). Although the relative changes in absorbance of $Ru(phen)_3^{2+}$ in the MLCT region were in the 1.0−1.2 range for [SDS] ≤ 80 mM, a slight decrease in emission at premicellar SDS concentrations was observed followed by a 5−6-fold increase at [SDS] ≥ 10 mM. Therefore, the increase in emission intensity in the $Ru(phen)_3^{2+}$/SDS system is not derived from the changes in the probe's extinction coefficient, and cannot be attributed to a salt effect, since the emission of $Ru(phen)_3^{2+}$ does not increase significantly upon addition of similar concentrations of NaCl or Na_2SO_4 in deoxygenated solutions. As determined by other groups, shielding from solvent upon surface micelle binding leads to the increased emission owing to a decrease in the rate of nonradiative excited-state deactivation, believed to operate through coupling to the OH vibrations of water molecules in

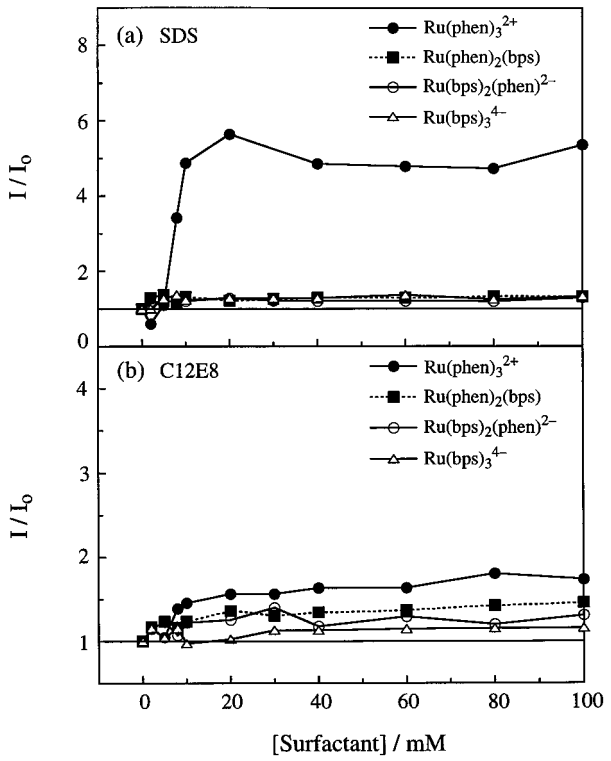

Figure 4. Integrated emission intensity (I) as a function of (a) SDS and (b) C12E8 concentration relative to the free complex (I_o).

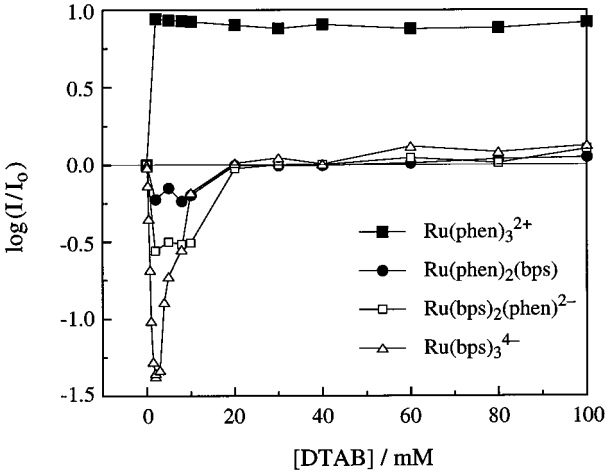

Figure 5. Changes in the relative emission intensity as a function of DTAB concentration of all the complexes plotted as $\log(I/I_o)$ vs [DTAB].

the second and third coordination spheres.[33] Our data are consistent with this explanation.

DTAB. The changes in the relative emission intensity as a function of increasing DTAB concentration for all four complexes is shown in Figure 5, where owing to the magnitude of the observed changes the data were plotted as $\log(I_o/I)$ vs [DTAB]. For the neutral $Ru(phen)_2(bps)$ complex, the changes in the overall emission are not significant for [DTAB] $\geq$ 20 mM, although a slight decrease in intensity is observed at premicellar concentrations. Similar but more pronounced results were obtained for $Ru(bps)_2(phen)^{2-}$ and $Ru(bps)_3^{4-}$, where at premicellar DTAB concentrations the MLCT emission markedly decreases. In fact, for $Ru(bps)_3^{4-}$ the emission decreases by a factor of 22 at [DTAB] = 2.0 mM. Although these two complexes possess an overall negative charge, their emission intensity increases slightly and their spectral profile does not change significantly in the presence of cationic DTAB micelles ([DTAB] $\geq$ 20 mM).

In the case of the cationic $Ru(phen)_3^{2+}$ complex, its emission intensity increases significantly with increasing DTAB concentration. The increase is relatively constant for all DTAB concentrations investigated, whether premicellar or above the cmc, and it is greater than the increase in the extinction coefficient at the excitation wavelength. Increased emission of $Ru(phen)_3^{2+}$ was also observed upon addition of tetramethylammonium chloride and tetrabutylammonium chloride, but the emission intensity remained constant in deoxygenated solutions when NaCl or Na_2SO_4 were added.

Effect of Noncovalent Interactions on Spectroscopic Properties. $Ru(phen)_3^{2+}$. The spectral and intensity changes of the emission observed upon addition of anionic SDS to deoxygenated solutions of $Ru(phen)_3^{2+}$ are indicative of aggregates at premicellar concentrations and those above the cmc. Owing to the opposite charges on the probe and SDS, the interactions can be interpreted as being mostly electrostatic. However, comparison of the spectral profiles upon addition of SDS and a nonmicellizing agent such as Na_2SO_4 suggest that other interactions must be present in the micellar aggregates. Furthermore, the overall increase in relative emission intensity in the micellar SDS system by a factor of 5 is much greater than that observed with similar Na_2SO_4 concentrations, where $I/I_0 \sim 1.2$. Therefore, it can be concluded that although driven by electrostatic interactions, the binding in the $Ru(phen)_3^{2+}$/SDS systems is partly hydrophobic in nature.[27,28]

The importance of hydrophobic interactions associated with the binding of $Ru(phen)_3^{2+}$ to micellar media is also apparent in the increase in absorption cross section and emission intensity observed in the presence of the neutral C12E8 and cationic DTAB. In C12E8, the emission intensity changes follow the variations of the extinction coefficient at the excitation wavelength. Although no electrostatic forces are present in the $Ru(phen)_3^{2+}$/C12E8 system, the probe is sufficiently hydrophobic to interact with the micelles. A similar effect was observed for the cationic complex with DTAB, although in this case there was an additional increase in the emission quantum yield that was not related to the increase in the absorption at the excitation wavelength. Since a similar but less pronounced effect was observed upon addition of tetramethylammonium chloride and tetrabutylammonium chloride, it can be concluded that the enhanced emission is partly related to the presence of the quaternary ammonium salts in addition to hydrophobic probe/surfactant interactions.

$Ru(phen)_2(bps)$. No changes in the absorption or emission spectral profile were observed for $Ru(phen)_2(bps)$ above the cmc for ionic and neutral micelles, or at premicellar concentrations of C12E8 and SDS. By comparison to the related $Ru(phen)_3^{2+}$, it may be concluded that the sulfonated bps ligand provides greater water solubility or hydrophilicity to the complex. These properties provide the probe with added stability in the aqueous phase in the presence of micelles and premicellar aggregates, and therefore optical changes attributed to hydrophobic interactions between the complex and micelles are not observed. Small changes in the absorption and emission intensity were recorded for premicellar aggregates of $Ru(phen)_2(bps)$ and DTAB, where the long hydrophobic chain of the surfactant may interact with the aromatic ligation sphere while the cationic head groups experience electrostatic attraction to the anionic part of the bps ligand.

$Ru(bps)_3^{4-}$ and $Ru(bps)_2(phen)^{2-}$. There were no changes in the electronic absorption and emission spectra of the anionic

Scheme 1

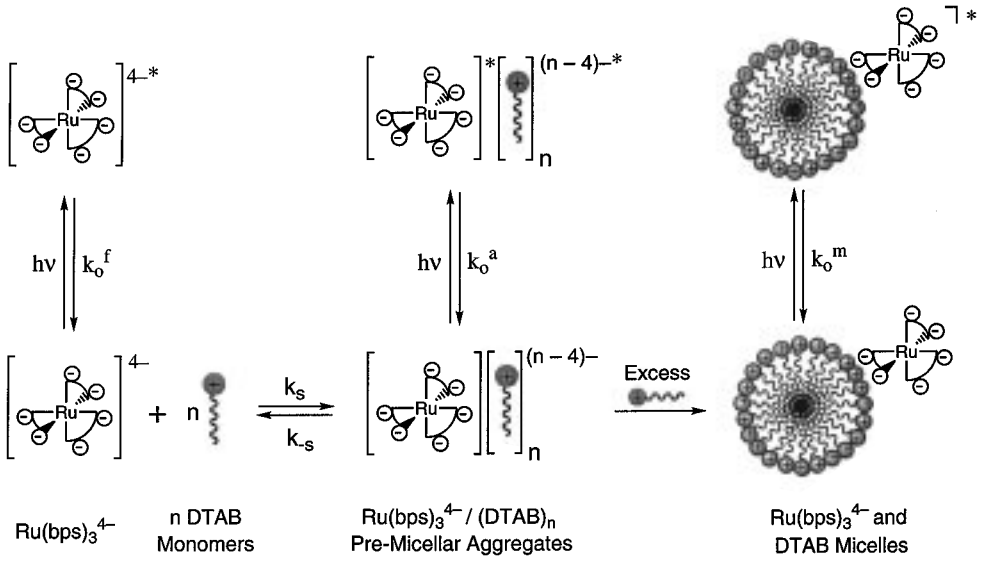

Table 2. Emission Decay Parameters[a] for Ru(bps)$_3^{4-}$ upon Addition of DTAB

[DTAB]/mM	%(τ_a)	τ_a/ns	%(τ_f)	τ_f/μs
0.10			100	4.6
0.25			100	4.8
0.50[b]	23.2	180	76.8	4.4
0.75	42.3	181	57.7	4.2
1.0	50.0	176	50.0	4.2
1.5	62.0	165	38.0	4.1
2.0	61.8	151	38.2	4.2
3.0	62.6	166	37.4	4.2
4.0	43.8	190	56.2	4.3

[a] Fit to biexponential decay of the form $A \exp(-t/\tau_a) + B \exp(-t/\tau_f)$, where $\%(\tau_a) = 100A/(A + B)$ and $\%(\tau_f) = 100B/(A + B)$. [b] Fit by setting $\tau_a = 180$ ns.

complexes in the presence of C12E8 and SDS. As discussed above for Ru(phen)$_2$(bps), the sulfonated ligands appear to make the complexes highly water soluble, and therefore hydrophobic interactions that give rise to changes in the absorption and/or emission spectra with neutral and anionic micelles and their premicellar aggregates are not observed. Even in the presence of DTAB micelles ([DTAB] ≥ 16 mM), the interactions measured by optical methods between the anionic complexes and the cationic micelles do no appear to be large (see Figure 4).

However, the premicellar DTAB aggregates lead to a large decrease in the emission intensity for these complexes. The emission intensity of the Ru(bps)$_3^{4-}$/DTAB system was reduced up to a factor of 22 at DTAB concentrations below the cmc ([DTAB] < 16 mM), and although there is a slight decrease in the extinction coefficient at the excitation wavelength, these changes do not account for the observed decrease in emission. This system will be discussed in detail below.

Ru(bps)$_3^{4-}$/DTAB System. Scheme 1 shows the premicellar aggregation of DTAB monomers to the anionic complex leading to the formation of stable species in the ground state, which possesses photophysical properties different from the free Ru(bps)$_3^{4-}$ complex in water. At small concentrations of DTAB, the emission decay is biexponential, with lifetimes of 4.1−4.8 μs and 150−190 ns (Table 2). The long lifetime component can be attributed to free Ru(bps)$_3^{4-}$ in water ($\tau_f = 1/k_o^f$), whereas the short lifetime corresponds to premicellar aggregates shown in Scheme 1 ($\tau_a = 1/k_o^a$), Ru(bps)$_3^{4-}$/(DTAB)$_n$. The changes in the relative amplitude of each component as a function of added DTAB in the premicellar concentration range are consistent with this explanation (Table 2). Similar results were reported for Ru(bps)$_3^{4-}$ bound to CTAB (cetyltrimethylammonium bromide), where the measured lifetime was 8.1 μs in the presence of micelles and 19.7 ns at premicellar concentrations.[43] However, in addition to the differences in the micellar systems employed, the reported lifetimes were deduced from fits of the decays to a more complex kinetic model, with variables that included the two lifetimes, the micellar and premicellar binding constants, and surfactant aggregation number, and therefore cannot be directly correlated to those obtained in the present work. Above [DTAB] = 4.0 mM the overall emission intensity and absorption spectra begin to resemble that observed for the free complex, indicating that if there are interactions between the probe and the micelles or DTAB aggregates present (Scheme 1), these interactions do not lead to significant spectral changes. The lifetime decay is monoexponential at DTAB concentrations well above the cmc. A lifetime of 5.8 μs was measured at [DTAB] = 100 mM, therefore $k_o^m = 1.7 \times 10^5$ s^{-1} (Scheme 1).

The biexponential decay with lifetimes relatively independent of surfactant concentration is indicative of slow binding kinetics with respect to the decay of the excited states in the free and aggregated Ru(II) complex, k_o^f and k_o^a, respectively, with k_s[S], $k_{-s} \ll k_o^f$, k_o^a (Scheme 1). The binding constant for up to two surfactant molecules with Ru(bps)$_3^{4-}$, K_s, was be determined to be 2.5×10^3 M^{-1} from changes in the absorption spectrum of 10 μM Ru(II) complex as a function of DTAB concentration up to 2.0 mM.[44] Above 2.0 mM DTAB the absorbance began to increase, probably due to the formation of higher surfactant aggregates, perhaps including micelles (Scheme 1). Fits to the absorption data utilizing the binding of one surfactant molecule per complex did not yield satisfactory fits. Another method of obtaining binding constants that does not rely on the knowledge of the extinction coefficient of the Ru−surfactant aggregates

(43) Snyder, S. W.; Buell, S. L.; Demas, J. N.; DeGraff, B. A. *J. Phys. Chem.* **1989**, *93*, 5265.

(44) The equation $[\text{DTAB}]_o/(\epsilon_a - \epsilon_f) = [\text{DTAB}]_o/(\epsilon_b - \epsilon_f) + 1/(K_b(\epsilon_b - \epsilon_f)$ can be utilized to obtain K_b, where $\epsilon_a = [(A_{obs}/[\text{Ru}]_o) - \epsilon_f]$ and the ratio of the slope and intercept from the plot of $[\text{DTAB}]_o/(\epsilon_a - \epsilon_f)$ vs $[\text{DTAB}]_o$ equals K_b (Wolfe, A.; Shimer, G. H. Meehan, T. *Biochemistry* **1987**, *26*, 6392). Data and fits to the various models are shown in Supporting Information.

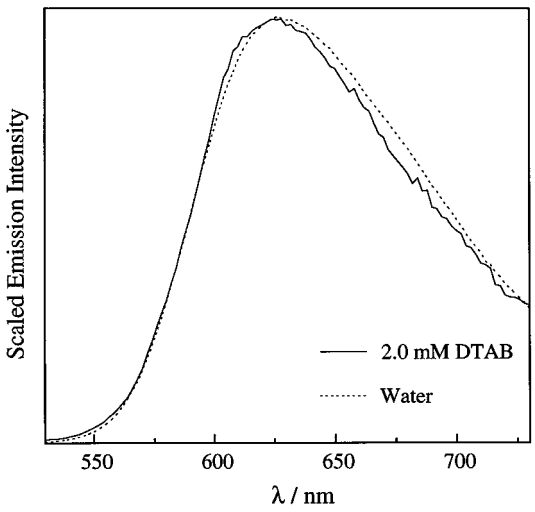

Figure 6. Scaled emission spectra of $Ru(bps)_3^{4-}$ (λ_{exc} = 440 nm) in water and in the presence of 2.0 mM DTAB (multiplied by a factor of 22).

yielded $K_s = 1.9 \times 10^4$ M^{-1}, which appears too high for the interaction between two molecules in a high dielectric medium.[44]

Since the addition of water to premicellar samples of DTAB containing $Ru(bps)_3^{4-}$ results in the regeneration of the emission, irreversible sample decomposition can be ruled out. Furthermore, addition of NaCl or pentanol to $Ru(bps)_3^{4-}$ samples in the presence of 2 mM DTAB leads to the recovery of the emission, pointing to the dissociation of the premicellar aggregates. Quenching of the excited state of the complex by DTAB via electron or energy transfer can be excluded, since a decrease in the emission intensity was not observed upon addition of tetramethylammonium chloride and tetrabutylammonium chloride, which possess similar redox and electronic properties to DTAB.

As depicted in Scheme 1, it appears that as the DTAB concentration is increased the formation of micelles is more favorable than the premicellar $Ru(bps)_3^{4-}/(DTAB)_n$ aggregates, since the photophysical properties resemble those of the free complex. As described above, at [DTAB] = 100 mM the decay of the $Ru(bps)_3^{4-}$ emission is monoexponential, therefore it can be concluded that above the cmc $Ru(bps)_3^{4-}$ exhibits only surface electrostatic interactions with the micelles that do not result in significant spectral or photophysical changes.

Changes in the relative energies of the nonemissive bps-centered $^3\pi\pi^*$ and luminescent Ru → bps MLCT excited states can be utilized to explain the observed spectral changes, lower emission intensity, and shorter lifetime in the $Ru(bps)_3^{4-}/(DTAB)_n$ premicellar aggregates. The MLCT absorption maximum of $Ru(bps)_3^{4-}$ at 465 nm is shifted to lower energies by ~1200 cm^{-1} in the presence of 2.0 mM DTAB. The measured emission spectrum of $Ru(bps)_3^{4-}$ in 2.0 mM DTAB has been multiplied by a factor of 21.5 for comparison with that obtained in water, and both are plotted in Figure 6. The emission spectrum in the presence of 2.0 mM DTAB shown Figure 6 is slightly blue-shifted with respect to that measured in water. This behavior is indicative of a displacement of the MLCT potential energy surface relative to the ground state along the nuclear coordinate rather than a shift in energy of the state, consistent less polar surroundings of a charge transfer state. Since in the presence of DTAB micelles (Scheme 1) the lifetime and spectral profile of $Ru(bps)_3^{4-}$ are not significantly altered, it is likely that it is not the electrostatic interactions between the complex and the DTAB headgroups but the solvation of the ligands by the long hydrophobic alkyl chains ($-C_{12}H_{25}$) that gives rise to the observed spectral shifts. It can be concluded from these observations that the overall energy of the emissive ^{3}MLCT state does not change significantly in the premicellar aggregates, and remains at ~17 000 cm^{-1}.[45]

The absorption maximum of the bps $^1\pi\pi^*$ transition shifts from 277 nm in water to 298 nm in 2.0 mM DTAB (Δ = 2540 cm^{-1}). For the related Ph_2phen complexes of Rh(III) and in the free ligand (Ph_2phen = 4,7-diphenyl-1,10-phenanthroline) the $^1\pi\pi^*$ and $^3\pi\pi^*$ states lie 27 700 and 20 700 cm^{-1} above the ground state, respectively.[46] A shift of the bps $^3\pi\pi^*$ state by 2540 cm^{-1} in the DTAB premicellar aggregates would lower its energy to ~18 200 cm^{-1}. The MC ^{3}dd states typically lie above 19 000 cm^{-1} in Ru(II) polypyridyl complexes, and it is unlikely that changes in solvation would affect the energy of these states.[47,48]

The interaction of the long alkyl chains with the bps ligands in $Ru(bps)_3^{4-}/(DTAB)_n$ premicellar adducts does not appear to result in a change of the overall energy of the emissive ^{3}MLCT state (~17 000 cm^{-1}); however, the energy of the bps $^3\pi\pi^*$ excited state is lowered from 20 700 cm^{-1} in water to 18 200 cm^{-1} in the adducts. Such a scenario would lead to lower activation energy for deactivation of the ^{3}MLCT through the nonemissive $^3\pi\pi^*$, resulting in higher rate constant for the ^{3}MLCT to $^3\pi\pi^*$ process and therefore shorter emission lifetime and intensity. From the decrease in the lifetime of $Ru(bps)_3^{4-}$ in water (4.6 μs) to that in $Ru(bps)_3^{4-}/(DTAB)_n$ (~160 ns), a rate constant of 6.0×10^6 s^{-1} can be calculated for the ^{3}MLCT to $^3\pi\pi^*$ deactivation (assuming that the nonradiative rate constant of the complex, k_{nr}, is equal in water and premicellar aggregates). From transition state theory, a rate constant, k, is related to the activation energy, E_A, by $k = \nu \exp(-E_A/k_BT)$, with $\nu \sim 10^{12}$ s^{-1} and k_BT = 207 cm^{-1}, a rate constant 6.0×10^6 s^{-1} yields E_A = 2490 cm^{-1}. This value is not unreasonable compared to our estimated 1200 cm^{-1} energy difference between the two states, and it is significantly lower than those measured for the deactivation of MLCT states of Ru(II) complexes through MC dd states.[48] Although the scenario above assumes that the energy of the MLCT excited state is the same in water and in the presence of DTAB, preliminary emission spectra at 77 K show a shift of the MLCT emission of $Ru(bps)_3^{4-}$ to higher energies by ~1500 cm^{-1} in 2 and 40 mM DTAB compared to water.

It has recently been found that the ^{3}MLCT excited state of Ru(II) complexes possessing ligands with low-lying $^3\pi\pi^*$ states can be effectively deactivated through this nonemissive pathway.[49] In $Re(bpy)(CO)_3N(CH_2)_n-CH_3^+$ (n = 0−17) complexes it has been shown that the longer alkyl chains interact more strongly with the bpy ligand, resulting in a shift of the Re → bpy MLCT excited state to higher energies, thus placing the ^{3}MLCT state near the ligand-centered bpy $^3\pi\pi^*$ state through

(45) The energy of the ^{3}MLCT was taken as that for the related complex $Ru(Ph_2phen)_3^{2+}$ (Ph_2phen = 4,7-diphenyl-1,10-phenanthroline), whose photophysical properties are closely related to those of $Ru(bps)_3^{4-}$ reported in the present work (Lin, C. T.; Boettcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536).
(46) Estimated from absorption, fluorescence, and phosphorescence spectra reported by: Ohno, T.; Kato, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3391.
(47) Lytle, F. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 253.
(48) Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1986**, *25*, 227.
(49) Baba, A. I.; Ensley, H. E.; Schmehl, R. H. *Inorg. Chem.* **1995**, *34*, 1198.
(50) Reitz, G. A.; Demas, J. N.; DeGraff, B. A.; Stephens, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 5051.
(51) Turro, C.; Bossmann, S. H.; Leroi, G. E.; Barton, J. K.; Turro, N. J. *Inorg. Chem.* **1994**, *33*, 1344.

which the emissive state was deactivated.[50] In addition, the reversal of the lowest MLCT state of $Ru(bpy)_2(4,7\text{-}Ph_2phen)^{2+}$ in the presence of SDS has been previously attributed to hydrophobic interactions between the 4,7-Ph_2phen ligand and the micelles' interior, thus raising the Ru → 4,7-Ph_2phen MLCT state above that for the more hydrophilic bpy ligand.[51] At the present time, the possibility that some of our observed spectral changes in the presence of premicellar aggregates are due to the formation of microprecipitants cannot be ruled out.

$Ru(phen)_3^{2+}$/DTAB and $Ru(bps)_2(phen)^{2-}$/SDS. The interactions between $Ru(phen)_3^{2+}$ and $Ru(bps)_2(phen)^{2-}$ with like-charge micellar media can be directly compared owing to the opposite overall charge of equal magnitude of the two complexes. It is evident from the changes in the absorption (Figure 1) and the emission (Figure 5) that there are significant interactions between $Ru(phen)_3^{2+}$ and the cationic DTAB surfactant, where the extinction coefficient increases by a factor of ~1.4 and there is a ~10-fold increase in emission intensity. However, this is not the case for the $Ru(bps)_2(phen)^{2-}$ complex upon addition of the anionic SDS (Figures 1 and 4), where the absorption varies by a factor of ≤1.05 and the changes in the emission intensity parallel the small increase in the extinction coefficient at the excitation wavelength.

The differences observed in the two systems can be ascribed to the charged $-SO_3^-$ groups on the bps ligands in $Ru(bps)_2(phen)^{2-}$, which make the complex more hydrophilic than $Ru(phen)_3^{2+}$. Although both complexes possess an overall charge of equal magnitude, in $Ru(phen)_3^{2+}$ the charge is localized on the central metal and the ligation sphere, which interacts with the solvating water molecules, is hydrophobic. Therefore, the interaction between $Ru(phen)_3^{2+}$ and the hydrophobic alkyl chains of DTAB molecules is more favorable than that of $Ru(bps)_2(phen)^{2-}$ with SDS, since the latter complex possesses two hydrophilic ligands. This conclusion is supported by the greater interaction between $Ru(phen)_3^{2+}$ and the neutral C12E8 micelles that result in a greater spectral change than any of the other complexes (Figures 1 and 4), where only hydrophobic interactions play a role in binding. Furthermore, even the overall neutral $Ru(phen)_2$bps complex interacts to a lesser extent than $Ru(phen)_3^{2+}$ with all of the micellar systems, in agreement with the hypothesis that the presence of bps ligands leads to greater hydrophilicity of the complex and, therefore, less hydrophobic interactions with supramolecular assemblies.

Conclusions

The series $Ru(phen)_n(bps)_{3-n}^{2n-4}$ ($n = 0-3$) of Ru(II) complexes were synthesized to probe the interactions with supramolecular assemblies. The electronic absorption and emission of the Ru(II) complexes with varying overall charge were utilized to investigate the electrostatic and hydrophobic interactions with cationic, anionic, and neutral micelle-forming agents. Premicellar aggregates of the complexes with oppositely charged surfactants leads to decreased overall emission intensity. However, in the $Ru(bps)_3^{4-}$/DTAB system a 22-fold decrease in emission intensity and significant changes in the electronic absorption spectrum were observed, with a concomitant appearance of a shorter lifetime component. The stable premicellar aggregate possesses markedly different photophysical properties to those of the free complex, owing to hydrophobic interactions between the surfactant's alkyl chain and the bps ligands. These interactions lead to a shift of the bps-centered $^3\pi\pi^*$ state to lower energies, providing a deactivation pathway of the emissive ^{3}MLCT state through the nonemissive LC state with a rate constant of 6.0×10^6 s^{-1}.

The results are consistent with a reduced interaction between the complexes that possess at least one bps ligand with DTAB, C12E8, and SDS, compared to $Ru(phen)_3^{2+}$, where the aromatic ligands are neutral and the ionic charge is in the central metal. The interactions between $Ru(phen)_3^{2+}$ and the cationic DTAB system give rise to greater spectral changes than those of $Ru(bps)_2(phen)^{2-}$ with the anionic SDS micelles and premicellar aggregates, although both complexes possess an overall charge of equal magnitude. These observations point to the importance of the hydrophilicity and hydrophilicity of the complexes in binding to supramolecular assemblies, even in cases where charged probe molecules and micellar system would be expected to exhibit strong repulsion.

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Supporting Information Available: Binding constant determination from the changes in the absorption of the anionic complex to DTAB assuming one and two surfactant molecules per complex and fits with relevant discussion are available (4 pages). Ordering information is given on any current masthead page.

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