Interactions of Ruthenium(II) Photosensitizers with Surfactant Media[1]

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Luminescent tris(α-diimine)ruthenium(II) photosensitizers exhibit complex emission intensity and lifetime curves when titrated with surfactants. The curve shapes depend on the charges and hydrophobicities of the complexes and surfactant. A simple model has been developed that accurately describes the interactions with anionic sodium dodecyl sulfate, nonionic Triton X-100, and cationic cetyltrimethylammonium bromide. The model includes binding of the sensitizer to micelles and may also require formation of small premicellar aggregates. The strength of binding can be attributed to a combination of electrostatic attractions or repulsions and hydrophobic effects. Electrostatic attraction of oppositely charged species always yields tight binding. However, complexes with sufficiently hydrophobic ligands (i.e., 4,7-diphenyl-1,10-phenanthroline) can overcome electrostatic repulsions and bind to like-charged micelles. Binding of metal complexes to premicellar surfactant aggregates is normally stabilized by electrostatic interactions, and optimum aggregate size is close to the number required for charge neutralization. Results of this study can be used in the design of luminescent probes for specific microheterogeneous environments. Ruthenium(II) complexes with cyano ligands are especially sensitive probes of local environment and show potential as luminescent probes for the rapid determination of critical micelle concentrations for anionic surfactants.

Introduction

The interactions of tris(α-diimine)ruthenium(II) photosensitizers with micellar media have been an area of active research.[3] The original goal of studying micelle–Ru(II) interactions was to design photocatalytic systems, including solar energy conversion.[4] Much effort was directed toward the control of excited-state quenching and subsequent thermal processes by the micelle environment.[5]

More recently, emphasis has shifted to utilizing Ru(II) photosensitizers as probes of various heterogeneous and microheterogenous environments. Ionic Ru(II)–α-diimine complexes can be designed that incorporate hydrophobic ligands and, thus, bind to crucial interface regions in microheterogeneous systems. If the polarity and hydrophobicity of a series of complexes are specifically tailored, partitioning of these probes between the bulk and microheterogeneous media can be investigated,[6] thus making valuable local environmental probes for areas that cannot be monitored with bulk measurements.

In our laboratory, we have undertaken a systematic characterization of transition-metal complex–micelle interactions.[7] We have developed a D_2O method of measuring solvent accessibility, which is the degree of bulk solvent exposure of a bound probe.[8] We have studied the binding interactions with a variety of nonionic surfactants. We have employed sensitizer counterion effects[9] and perturbations of quenching properties[10] to investigate sensitizer–micelle binding.

We correlate here binding studies in a variety of surfactant media. Our systems include cationic, neutral, zwitterionic, and anionic Ru(II) complexes with anionic sodium dodecyl sulfate (SDS), nonionic Triton X-100 (TX-100), and cationic cetyltrimethylammonium bromide (CTAB) micelles. We develop a binding model that accounts for behavior in both air- and N_2-saturated solutions. We analyze the effect of ionic strength on the binding interaction. Where biphasic titrations are observed, we develop a model that accounts for premicellar interactions.

Experimental Section

The ligands and their abbreviations are as follows: 2,2′-bipyridine, bpy; 1,10-phenanthroline, phen; 5-methyl-1,10-phenanthroline, Me-phen; 5-chloro-1,10-phenanthroline, 5-Cl-phen; 5,6-dimethyl-1,10-phenanthroline, 5,6-Me_2phen; 4,7-dimethyl-1,10-phenanthroline, 4,7-Me_2phen; 3,4,7,8-tetramethyl-1,10-phenanthroline, Me_4phen; 5-phenyl-1,10-phenanthroline, Ph-phen; 4,7-diphenyl-1,10-phenanthroline, Ph_2phen; 4,7-diphenyl-1,10-phenanthrolinedisulfonic acid, $((Ph\text{-}SO_3)_2phen)^{2-}$; and CN^-. $RuCl_3$ and all ligands were purchased from GFS Chemical Co. The syntheses of the complexes are described elsewhere.[7a,11] Mixed-ligand complexes of the form $[RuL_2L']^{2+}$ were synthesized in a two-step procedure via a RuL_2Cl_2 intermediate.[7a] All cationic complexes were used as perchlorate or chloride salts, and all anionic complexes were used as potassium salts. Probe concentrations were kept in the range of 5–10 μM to minimize micelle multiple occupancy and self-quenching.

SDS was purchased from Biorad and recrystallized from methanol. For low ionic strength measurements, an aggregation number of 62 was used.[12] CTAB was purchased from Sigma and recrystallized from methanol. An aggregation number of 61 was used.[12] TX-100 was purchased from Sigma and used as received. An aggregation number of 140 was used.[13] Analytical

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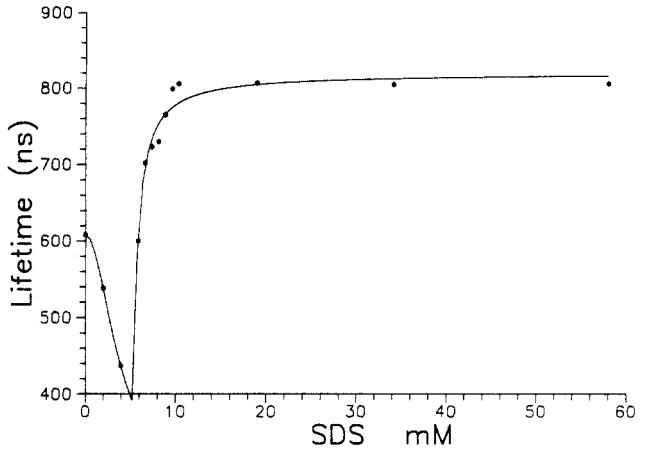

Figure 1. $Ru(bpy)_3^{2+}$ in SDS, N_2 saturated; see Table I for fit parameters.

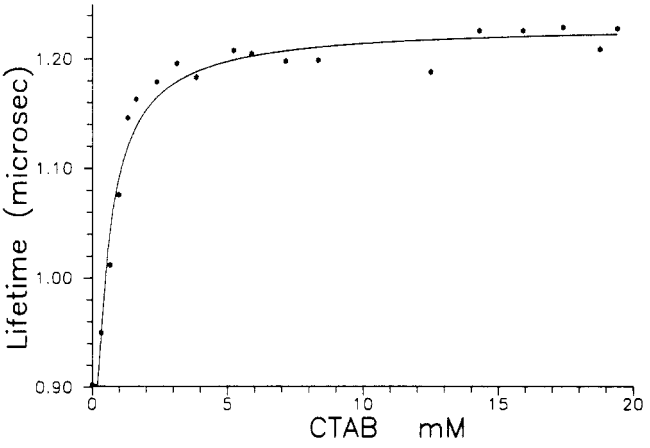

Figure 2. $Ru(phen)_2((Ph\text{-}SO_3)_2phen)$ in CTAB, air saturated; see Table I for fit parameters.

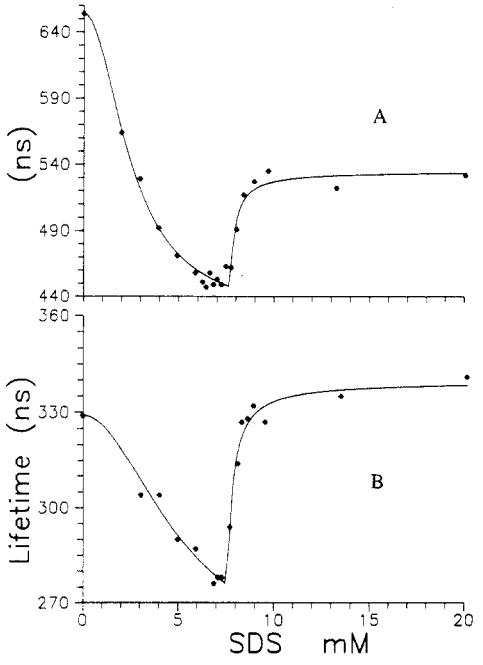

Figure 3. $Ru(phen)_2(CN)_2$ in SDS, (A) N_2 saturated and (B) air saturated; see Table I for fit parameters.

reagent-grade $NaNO_3$ and NaCl were used as received. Water was doubly distilled from alkaline permanganate.

Lifetime measurements were carried out on a nitrogen laser system described elsewhere.[14] Deoxygenation was accomplished

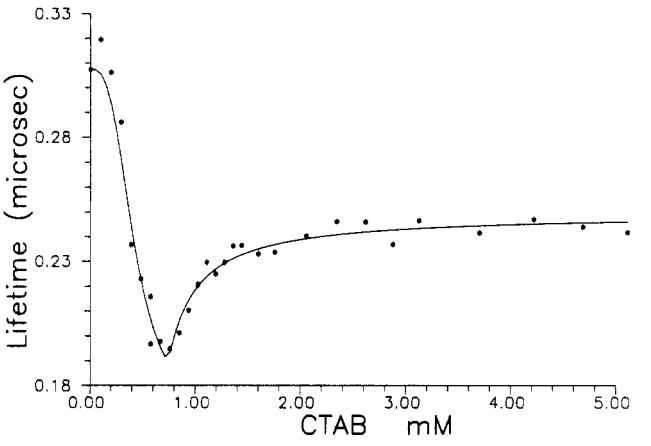

Figure 4. $Ru(phen)(CN)_4^{2-}$ in CTAB, air saturated; see Table I for fit parameters.

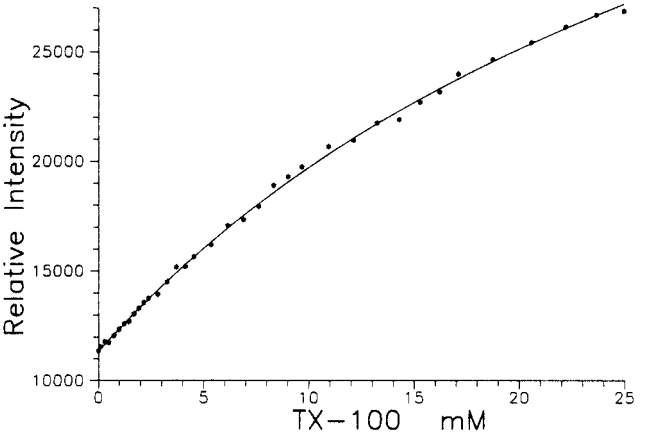

Figure 5. $Ru(phen)_2(CN)_2$ in TX-100, air saturated; intensity monitored; see Table I for fit parameters.

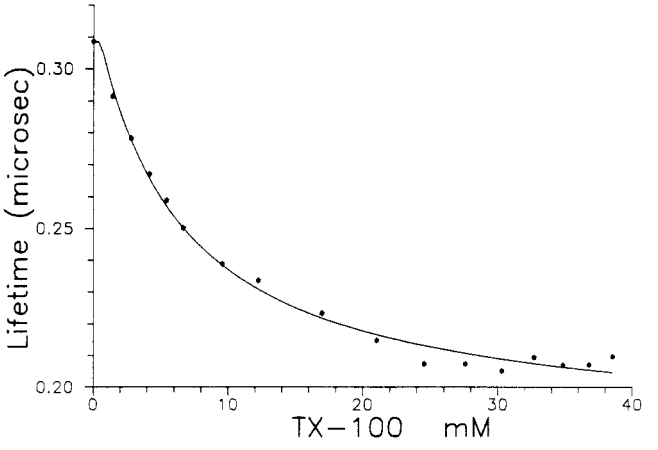

Figure 6. $Ru(phen)(CN)_4^{2-}$ in TX-100, air saturated; see Table I for fit parameters.

by bubbling with solvent-saturated N_2,[15] and all measurements were made at 25 °C.[16] Steady-state emission measurements were carried out on an SLM 8000 spectrofluorimeter.

Most luminescent decays were single exponential and were fit by a linear least-squares analysis of the semilogarithmic plot of intensity vs time.[15] Double-exponential decays were fit by a Marquardt nonlinear least-squares method.[17]

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The binding titrations were fit to the models by a simplex error minimization technique.[17c,18] Several sets of initial guesses were tried in order to avoid trapping in local minima. At least five data points per floating parameter are required for reliable calculations. Fits were performed on an AT&T 6300 with an 8087 in Turbo Pascal.

Results

Luminescence Titrations. Upon addition of surfactant, the excited-state lifetime and luminescent intensity of many Ru(II) complexes are altered. Figures 1–6 show the wide range of possible luminescent behavior observed. Titrations with a single curved region (monophasic) and two curved regions (biphasic) can occur depending upon the surfactant and probe; compare Figures 1 and 2. In addition, both increasing and decreasing trends in the luminescent intensity or lifetime can occur, even in the identical surfactant-probe system, by varying the oxygen concentration.

As we will show, the shapes of these curves are controlled by a combination of electrostatic and hydrophobic interactions. Oppositely charged donor–micelle combinations show tight binding while like-charged donor–micelle combinations bind with greater difficulty. In general, increasing hydrophobicity of the ligands increases probe binding to all types of surfactants.[7]

We have developed a binding model that accounts for all of these types of behavior. The model is general enough to be applied to cationic, anionic, and nonionic surfactants. We have used the model to successfully explain the titrations of numerous Ru(II) probes under a variety of conditions.[6]

Model

A complete binding model begins with interactions between the surfactant molecules (S) to form aggregates (S_n) or micelles (M) of aggregation number N

$$S_n + S \leftrightarrows S_{n+1} \longleftrightarrows S_{N-1} + S \leftrightarrows M \tag{1}$$

where the micelle concentration is given by

$$[M] = \frac{[S]_{formal} - cmc}{N} \qquad [S]_{formal} \geq cmc \tag{2}$$

where $[S]_{formal}$ designates the formal surfactant concentration and cmc is the critical micelle concentration.

Our model includes interactions between the photosensitizer (D) and either micelles or free surfactant molecules

$$D + nS \leftrightarrows DS_n \tag{3a}$$

$$D + S_n \leftrightarrows DS_n \tag{3b}$$

where DS_n is an aggregate of n surfactant molecules and a donor. Potentially, a variety of paths can lead to aggregate formation, and these equations represent two extremes. For simplicity, we choose the limiting situation of eq 3a. However, both models give identical data fits; only the significance of the fitting equilibrium constants varies.

Our model also includes donor–micelle association

$$D + M \leftrightarrows DM \text{ or } D + NS \leftrightarrows DM \tag{4a}$$

$$DS_n + M \leftrightarrows DMS_n \tag{4b}$$

where DM depicts a micelle-bound donor. The alternate form of eq 4a suggests the induced formation of micelles by the presence of the donor. We use only the first of these equations in our modeling and treat induced micelle formation by making the cmc an adjustable parameter, the icmc.

We assume that the micelles interact similarly with free probes and small probe–surfactant aggregates. A micelle of aggregation number N approximates the average solution species, but the free surfactant species are in rapid equilibrium and enter and leave the micelle on a microsecond time scale.[12] Since micelle size is distributed around N, there is little difference between DM and DMS_n. Thus, the binding constants for eq 4a and 4b should be similar.

The free-donor binding constant, K_{DM}, is given by

$$K_{DM} = \frac{[DM]}{[D][M]} \tag{5}$$

Since the donor is relatively large with respect to the micelle size, it can act as a nucleating site, and an induced cmc (icmc) must be employed.[19]

$$[M] = \frac{[S] - icmc}{N} \tag{6}$$

In the presence of premicellar aggregation, the binding constant K_{DS_n} is given by

$$K_{DS_n} = \frac{[DS_n]}{[D][S]^n} \tag{7}$$

The fractions of free donor, f_D, of donor–surfactant aggregate DS_n, f_{DS_n}, and micelle-bound probe, f_{DM}, are given by simple equilibrium expressions summarized in the supplementary material. The equilibrium concentration [S] is equal to the $[S]_{formal}$ below the icmc and is equal to the icmc when $[S]_{formal}$ is above it.

These fractions can be related to our spectroscopic measurements. With our lifetime instrumentation, it is difficult to detect double-exponential behavior. The observed rate constant, k_{obs}, for excited-state decay is given by a concentration-weighted average of the rate constants for the separate emitting components. Therefore, the observed lifetime, τ_{obs}, is related to a weighted fraction of the bound and unbound rate constants

$$\frac{1}{\tau_{obs}} = f_D\tau_D^{-1} + f_{DS_n}\tau_{DS_n}^{-1} + f_{DM}\tau_{DM}^{-1} \tag{8}$$

where the subscript on each τ indicates the lifetime that would be measured for that species in the absence of exchange. Substituting in f's, we obtain

$$\frac{1}{\tau_{obs}} = \frac{\tau_D^{-1} + K_{DS_n}[S]^n\tau_{DS_n}^{-1} + K_{DM}[M](1 + K_{DS_n}[S]^n)\tau_{DM}^{-1}}{1 + K_{DS_n}[S]^n + K_{DM}[M](1 + K_{DS_n}[S]^n)} \tag{9}$$

Equation 9 is the general form of the binding equation in which interactions with surfactant aggregates of size n only have been included. The quality of titration data is inadequate to allow modeling to a distribution of different-sized surfactant aggregates. Equation 9 can be used to model a surfactant titration where τ_{obs} is measured versus $[S]_{formal}$. The unbound lifetime, τ_D, can be independently measured in the absence of surfactant. Simplex methods are used to fit the other six parameters: τ_{DS_n}, τ_{DM}, K_{DS_n}, K_{DM}, n, and icmc. An important limiting case occurs where there is no premicellar aggregation. In that case, we only fit for τ_{DM}, K_{DM}, and icmc. Equation 9 successfully fits all our monophasic and biphasic titrations.

These titration analyses are not unique to lifetime changes. Luminescent intensity titrations, although generally slightly less reliable, can also be fit with eq 9.[20] However, intensity measurements can be useful when lifetime equipment is not available or when an experimental coincidence makes the lifetime changes small as compared to the intensity changes.

Discussion

We will show that all combinations of cationic, anionic, and neutral probes and surfactants are successfully fit by our model. Further, chemically reasonable parameters are obtained, and the results provide insight into the forces driving binding. In addition, we explore the impact of the microheterogeneous environment on

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TABLE I: Binding of Ru(II) Photosensitizers to Various Surfactants[a]

Ru(II) complex	purge gas	surfactant	τ_D, ns	τ_{DS}, ns	τ_{DM}, ns	n^b	K_{DS_n}, mM^{-n}	K_{DM}, mM^{-1}	icmc, mM
$(bpy)_3^{2+}$	N_2	SDS	608	270	821	2	0.029	265	5.40
$(phen)_3^{2+}$[c]	N_2	SDS	890		1930				
$(phen)_3^{2+}$[d]	air	SDS	429	–	756	–	–	1600	0.59
$(phen)_3^{2+}$[d]	air	SDS	429	328	756	1	6×10^{-9}	1600	0.59
$(bpy)_2(CN)_2$	air	SDS	199	–	352	–	–	24.1	7.44
$(bpy)_2(CN)_2$[e]	air	SDS	1	0.944	1.67	2	0.0785	44.7	7.52
$(phen)_2(CN)_2$	N_2	SDS	654	424	534	2	0.105	320	7.71
$(phen)_2(CN)_2$	air	SDS	329	251	340	2	0.0283	289	7.60
$(phen)_2(CN)_2$[f]	N_2	SDS	653	427	548	1	0.359	538	2.62
$((Ph\text{-}SO_3)_2phen)_3^{4-}$	N_2	SDS	3770	–	5270	–	–	31.1	1.54
$(phen)(CN)_4^{2-}$	N_2	SDS	560	–	–				
$(Ph_2phen)_3^{2+}$	air	CTAB	801	–	1230	–	–	252	0.57
$(Me_4phen)_3^{2+}$	air	CTAB	500	458	2350	2	4.00	0.73	0.83
$(5,6\text{-}Me_2phen)_3^{2+}$	N_2	CTAB	1860		–				
$(5\text{-}Cl\text{-}phen)_3^{2+}$	N_2	CTAB	759		–				
$(phen)_2((Ph\text{-}SO_3)_2phen)$	air	CTAB	902	–	1232	–	–	153	0.255
$(phen)_2((Ph\text{-}SO_3)_2phen)$	N_2	CTAB	3403	–	3867	–	–	44.1	0.823
$(phen)_2(CN)_2$[g]	N_2	CTAB	621		2560				
$(phen)_2(CN)_2$	air	CTAB	342	–	1080	–	–	3.66	0.0
$(phen)_2(CN)_2$[e]	air	CTAB	1	–	6.10	–	–	11.8	0.48
$(phen)(CN)_4^{2-}$[c]	N_2	CTAB	548		452				
$(phen)(CN)_4^{2-}$	air	CTAB	307	168	250	3	7.30	295	0.75
$((Ph\text{-}SO_3)_2phen)_3^{4-}$	N_2	CTAB	3769	19.7	8100	3	10.9	345	0.11
$(phen)_2(5\text{-}Ph\text{-}phen)^{2+}$[h]	N_2	TX-100	1100	–	2010	–	–	126	0.46
$(phen)_2(CN)_2$[e]	air	TX-100	1	–	4.43	–	–	17.0	0.008
$(phen)(CN)_4^{2-}$	N_2	TX-100	589	–	288	–	–	18.5	1.31
$(phen)(CN)_4^{2-}$	air	TX-100	309	–	186	–	–	12.5	0.56

[a] All measurements are by the lifetime method, unless otherwise specified. [b] The premicellar aggregate size S_n, used in the fit of eq 9. [c] The solution bleached near the cmc. Therefore, only τ_D and τ_{DM} are reported. [d] For a solution with 100 mM $NaNO_3$ added. At this ionic strength, SDS has been reported to have a cmc of 1.45 mM[12] and an aggregation number of 90.[13] [e] Intensity was monitored for this titration. [f] For a solution with 40 mM NaCl added. [g] These decays were double exponential and were fit by eq 10. The reported lifetimes, τ_D and τ_{DM}, are the averages of the short- and long-lifetime components, respectively, for several decays collected over the 3–6 mM CTAB concentration range. [h] For a solution with 120 mM $NaNO_3$ added.

the photophysical properties of various environmental probes.

A summary of the binding fits with eq 9 by the model either with or without premicellar aggregation is presented in Table I. Each system was modeled under multiple sets of conditions, and the best fits are included in the table.

Interactions with SDS. SDS forms an anionic micelle with $N = 62$[12] and cmc = 8.1 mM.[21] The binding of Ru(II)–polypyridine complexes arises from both hydrophobic interactions of the ligands with the surfactant alkyl chain and electrostatic attractions between the cationic metal center and the anionic head group.[7] Many cationic Ru(II) complexes bind too tightly to SDS to allow determination of binding constants by luminescent titrations. Smaller hydrophilic cationic, anionic, and neutral probes are better suited for modeling.

Ru(bpy)$_3^{2+}$. On the binding of $Ru(bpy)_3^{2+}$ to SDS, we observe the lifetime trend $\tau_{DM} > \tau_D > \tau_{DS}$, in N_2-saturated solutions.[7b] Since O_2 normally quenches the aqueous-borne probes more than the bound form, this lifetime trend is expected in air-saturated solutions. $Ru(bpy)_3^{2+}$ has a reported solvent accessibility of 0.31,[8a] indicating that about one-third of the complex remains accessible to the bulk water. The K_{DM} of 265 000 M^{-1} indicates a strong interaction between the cationic probes and SDS. The icmc of 5.4 mM^{-1} is lower than expected for a salt-free solution and suggests that $Ru(bpy)_3^{2+}$ induces SDS micelle formation. We present our best fit in Figure 1. Because of the difficulty of making measurements below or near the cmc, the uncertainties in the parameters are relatively large.

Ru(phen)$_3^{2+}$. $Ru(phen)_3^{2+}$ is very similar to $Ru(bpy)_3^{2+}$ in size and aqueous solubility, and we expected it to behave similarly in SDS. $Ru(phen)_3^{2+}$ follows the same lifetime trend with $\tau_{DM} > \tau_D > \tau_{DS}$. The complex is approximately two-thirds shielded by the SDS micelle ($F = 0.36$).[8a] Unfortunately, when solutions in the premicellar region were bubbled with N_2, the sample was bleached irreversibly, and the experiment had to be discontinued. Titrations were attempted in both concentration directions without success, and only the end points τ_D and τ_{DM} are reported for N_2-saturated solutions.

We were able to carry out a full SDS titration for $Ru(phen)_3^{2+}$ (0.1 M $NaNO_3$) in air-saturated solutions, since unbubbled solutions did not bleach. At this ionic strength, SDS has a reported cmc of 1.45 mM[21] and an aggregation number of 90.[22] We calculated a K_{DM} of 1 600 000 M^{-1} and an icmc of 0.59 mM. Clearly, $Ru(phen)_3^{2+}$ induces SDS micelle formation similar to $Ru(bpy)_3^{2+}$.

Due to the low icmc and the premicellar bleaching problems, work near the icmc is difficult and few data are available in this region. The lifetime drops little, and therefore, fits in this region are not very meaningful.

Ru(bpy)$_2$(CN)$_2$. Since $Ru(bpy)_2(CN)_2$ is a small neutral probe, we would not expect it to bind as tightly to SDS as $Ru(bpy)_3^{2+}$ or $Ru(phen)_3^{2+}$. This is particularly true since $Ru(bpy)_2(CN)_2$ is rather polar as shown by its high water solubility (>50 μM) compared to the virtually insoluble $Ru(phen)_2(CN)_2$ or $Ru(Ph_2phen)_2(CN)_2$. Its solvent accessibility of 0.47[8a] shows that it is not as well shielded as the cationic probes.

In Table I, we include entries for $Ru(bpy)_2(CN)_2$ binding titrations monitored by lifetime and intensity methods. Little change was detected below the cmc. Both titrations yielded icmc of $\approx$7.5 mM, which is near the literature values. This indicates little perturbation of micelle formation. In both titrations, similar K_{DM} values were obtained. While there is a suggestion of a premicellar interaction, the changes are too small to allow accurate estimation of a K_{DS_n}. This result suggests that without electrostatic attractions small polar probes will show only weak premicellar interactions and photophysical properties will be minimally perturbed.

Ru(phen)$_2$(CN)$_2$. $Ru(phen)_2(CN)_2$ is a small neutral probe but is much less soluble in water than its bpy analogue (<20 μM). Its solvent accessibility of 0.43[8a] is slightly less than $Ru(bpy)_2(CN)_2$. $Ru(phen)_2(CN)_2$ follows the lifetime trend $\tau_D > \tau_{DM} > \tau_{DS}$ in N_2 and $\tau_{DM} > \tau_D > \tau_{DS}$ in air-saturated solutions. These

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TABLE II: Binding of $Ru(phen)_2(CN)_2$ to SDS

purge gas	n^a	τ_D, ns	τ_{DS}, ns	τ_{DM}, ns	K_{DS_n}, mM^{-n}	K_{DM}, mM^{-1}	icmc, mM	$f_{DS_n}{}^b$ at icmc	*rel* error,[c] %
N_2	1	654	324	535	0.114	334	7.70	0.467	1.59
N_2	2	654	424	534	0.105	320	7.71	0.862	1.29
N_2	3	654	444	535	0.0445	300	7.72	0.953	1.38
N_2	4	654	452	531	0.0178	937	7.96	0.986	1.78
N_2	5	654	455	531	0.00639	914	7.96	0.995	2.20
air	1	329	0.026	340	2.4×10^{-6}	291	7.60	1.8×10^{-5}	0.938
air	2	329	251	340	0.0284	289	7.60	0.621	0.995
air	3	329	269	340	0.0121	282	7.60	0.842	1.06
air	4	329	275	340	0.00387	276	7.61	0.928	1.21
air	5	329	277	340	0.00114	270	7.61	0.966	1.36

[a] Premicellar aggregate size used in the fit to eq 10. [b] Weighted from calculated value with [S] = icmc and [M] = 0 (see supplementary material). [c] Sum of the error residuals, calculated from *rel* error = $\sum_{points}\{(Y_{obs} - Y_{calc})^2/Y_{obs}\}(100\%/points)$.

changes are a consequence of the differential O_2 quenching of bound and unbound donors and demonstrate the usefulness of performing titrations under different atmospheres.

$Ru(phen)_2(CN)_2$ has large binding constants to both SDS micelles and premicellar aggregates under a variety of conditions. Titrations were performed in deoxygenated and air-saturated pure water and in deoxygenated 40 mM NaCl solutions.

The K_{DM}'s of 320 000 and 290 000 M^{-1} for N_2- and air-saturated solutions, respectively, agree well. $Ru(phen)_2(CN)_2$ binds to SDS much tighter than $Ru(bpy)_2(CN)_2$ and on the same order as $Ru(bpy)_3^{2+}$. This larger binding cannot be explained by an electrostatic attraction. Rather, since $Ru(phen)_2(CN)_2$ is much less water soluble than $Ru(bpy)_3^{2+}$, we attribute the larger K_{DM} to a hydrophobic interaction. Similarly, $Ru(Ph_2phen)_2(CN)_2$ is insoluble in water but very soluble in SDS and, therefore, has an effectively infinite SDS binding constant.

Both titrations with $Ru(phen)_2(CN)_2$ had icmc's near 7.7 mM, which is in good agreement with the literature value. The K_{DS_2} values of 0.11 and 0.028 mM^{-2} are substantial. The fits for the N_2- and air-saturated data are presented in Figure 3.

As with the $Ru(phen)_3^{2+}$–SDS system, changing ionic strength (40 mM NaCl) perturbs the $Ru(phen)_2(CN)_2$–SDS binding. K_{DM} is 538 000 M^{-1}, but there is a very large uncertainty in this value because of the small post icmc τ changes. The icmc of 3.2 mM agrees well with the literature value of 3.1 mM for a 30 mM NaCl solution.[21] However, τ_D and τ_{DM} are essentially unchanged in deoxygenated solutions with or without salt. Thus, ionic strength affects the driving force for binding but not the deactivation pathways.

We turn to the question of the premicellar aggregation size (i.e., n) for the SDS interactions (Table II). To do this, we varied n and examined the quality of the fits and the chemical plausibility of the calculated parameters. In both the N_2- and air-saturated fits, the calculated micelle-bound lifetimes, τ_{DM} (531–535 ns for N_2 and 340 ns for air), are remarkably consistent. The titrations have plateaued, and this parameter is easy to determine. K_{DM} is also very consistent for the different fits. Only in the N_2-saturated case with $n = 4$ does it deviate far from 300 000 M^{-1}. Additionally, the icmc remains in the expected 7.5–8.0 mM range.

Except for the $n = 1$ case, τ_{DS} is also consistent for the titrations (424–452 ns for N_2 and 251–275 ns for air). DS_n is never a dominant species and, therefore, cannot be as well characterized. In the DS_1 case, our model explains the decreasing lifetimes below the icmc by assuming a small DS fraction with a very short lifetime. We cannot directly compare K_{DS_n} for different n's because the calculated binding constants are dimensionally different.

For both titrations, the χ_r^2 error remains relatively close for the fits over the range $n = 1$–3. The error starts to increase at $n = 4$ and becomes much larger at $n > 4$. This implies that the $n = 1$–3 fits are approximately equivalent in describing the titrations. This is not surprising as binding probably involves a range of aggregates from the monomer up to the micelle. However, the degradation of the fit for $n > 3$ indicates that a relatively narrow range of small aggregates dominates the mixture below the icmc. We stress that while the fitting procedure is tolerant of variations in n, some form of premicellar aggregation is essential to prevent catastrophic failure of the model.

$Ru((Ph\text{-}SO_3)_2phen)_3^{4-}$. $Ru((Ph\text{-}SO_3)_2phen)_3^{4-}$ is the largest and most anionic probe investigated. When bound to SDS, it has greater solvent exposure than the cationic and neutral complexes ($F = 0.53$).[8a] There was no evidence for premicellar aggregation. The K_{DM} of 31 100 M^{-1} is much weaker than either the cationic or neutral Ru(II) complexes. The icmc of 1.5 mM again indicated probe-induced micelle formation.

$Ru(phen)(CN)_4^{2-}$. $Ru(phen)(CN)_4^{2-}$ is the only small anionic probe investigated. No binding to SDS was detected in deoxygenated or aerated solutions either by changes in τ or by emission spectral shift on addition of SDS.[7a] These results are expected on the basis of the electrostatic repulsion between the anionic probe and the micelle.

While both are anionic, the charge is distributed very diffusely in $Ru((Ph\text{-}SO_3)_2phen)_3^{4-}$ in contrast to $Ru(phen)(CN)_4^{2-}$. The cationic metal center is well separated from the anionic substituents, and electrostatic binding can occur by intercalation of the surfactant head groups between the sulfonated phenyl rings. With $Ru(phen)(CN)_4^{2-}$, no large charge separation exists and interaction with the anionic surfactant is prohibited.

Other Complexes. Measurements with SDS and the more hydrophobic cationic complexes such as $Ru(5,6\text{-}Me_2phen)_3^{2+}$ and $Ru(Ph_2phen)_3^{2+}$ were precluded. The interaction between the cationic probes and surfactant molecules in the premicellar region often irreversibly bleaches the solution. This detrimental phenomenon is probably due to microcrystallization of a Ru(II)–dodecyl sulfate salt.[3e,f,7a]

Interactions with CTAB. CTAB has an aggregation number of 61[12] and a cmc of 0.98 mM.[21] Previous luminescence studies in CTAB have focused on its interactions with nonpolar aromatic molecules,[23] rather than metal complexes.[8c] Several Ru(II) probes exhibit binding with CTAB. Depending upon the complex, either monophasic (D and DM) or biphasic (D, DS_n, and DM) behavior is observed. The fitting results are summarized in Table I. Unlike the anionic SDS, CTAB micelles have an electrostatic repulsion to cationic Ru(II) probes. Therefore, interactions with these complexes must arise from the hydrophobic effects of the photosensitizer ligands in the alkyl core of the micelle.

$Ru(Ph_2phen)_3^{2+}$. The only cationic complex studied that exhibited a tight CTAB binding was $Ru(Ph_2phen)_3^{2+}$, the most hydrophobic cation probe employed. K_{DM} for CTAB binding was at least a factor of 3 smaller than for binding to the neutral TX-100.[6]

$Ru(Me_4phen)_3^{2+}$. The hydrophobic $Ru(Me_4phen)_3^{2+}$ bound weakly to CTAB. The K_{DM} of 720 M^{-1} was reduced by a factor of about 600 in comparison to TX-100 binding.[6] Interestingly, we observed that $Ru(Me_4phen)_3^{2+}$ formed premicellar aggregates, a phenomenon often observed in SDS interactions, but only otherwise observed in CTAB with anionic Ru(II) complexes. This premicellar binding caused little change in lifetime ($\tau_D = 500$ ns vs $\tau_{DS} = 458$ ns). This interaction may be attributed to the balancing of two properties of $Ru(Me_4phen)_3^{2+}$. It is quite hy-

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drophobic, and despite its hydrophobicity, it is a rather small complex. In contrast, the complexes with the very hydrophobic phenyl-substituted ligands show no biphasic behavior. We cannot preclude premicellar aggregation in these cases; if the lifetimes of D and DS_n are similar, the titrations will show no evidence for the DS_n species.

Ru(phen)$_2$((Ph-SO$_3$)$_2$phen). As with the cationic complexes, neutral and zwitterionic Ru(II) complexes tend to bind more weakly to CTAB than to either SDS or TX-100. Ru(phen)$_2$((Ph-SO$_3$)$_2$phen) binds moderately strongly to CTAB micelles but shows no evidence for premicellar interactions. The K_{DM} in the air-saturated solution is more accurate than that for the N_2-saturated solution because the lifetime changes are larger and the nitrogen-bubbled CTAB solutions are much harder to handle. A fit of the air-saturated titration is presented in Figure 2.

Ru(phen)$_2$(CN)$_2$. The neutral complex, Ru(phen)$_2$(CN)$_2$, was also found to bind weakly to CTAB. Ru(phen)$_2$(CN)$_2$ is very well shielded from solvent by the CTAB micelle.[8c] Although previous work has led us to assume that Ru(phen)$_2$(CN)$_2$ must interact with some premicellar CTAB species,[8c] no lifetime or intensity changes were detected below the icmc. Since binding is not complete over the accessible CTAB concentration range, the titrations do not plateau and the K_{DM}'s cannot be measured very accurately. The variation of the intensity and lifetime K_{DM}'s is deemed to be within experimental error.

CTAB binding causes the lifetime of Ru(phen)$_2$(CN)$_2$ to change by a factor of 3 in aerated solutions. In N_2-saturated solutions, the decays were complicated by non-single-exponential behavior over much of the useful CTAB concentration region. They were fit by the equation

$$\tau_{obs} = M_1\tau_1 + M_2\tau_2 \qquad (10)$$

where the M_i's and τ_i's represent the weighting factors and lifetimes for the two decay components, respectively. Double-exponential analyses over a CTAB range of 3–6 mM gave an average short lifetime of 620 ns and a long lifetime of 2560 ns.[7a] The short-lifetime component can be attributed to the unbound probe and the long lifetime to the bound probe,[7a,10] and thus, CTAB binding causes a factor of 4 change in lifetime. The larger change of a factor of 6 in I_{DM}/I_D in the intensity titration arose from a combination of two factors. First, increasing the lifetime increases the emission intensity. Second, the intensity titration was monitored near the maximum emission wavelength of the bound form, thus experimentally favoring I_{DM} over I_D.[7a]

Ru(phen)(CN)$_4^{2-}$. The anionic Ru(phen)(CN)$_4^{2-}$ bound strongly to the cationic CTAB in both the micellar and premicellar regions, although the solvent accessibility was large (0.6).[8c] The large K_{DM} is consistent with a strong electrostatic attraction.

As previously observed for cationic Ru(II) complexes interacting with SDS, premicellar aggregates of the oppositely charged surfactant and probe essentially do not emit. Solutions frequently bleach irreversibly probably because of microcrystallization of probe–surfactant salts. The N_2-saturated Ru(phen)(CN)$_4^{2-}$–CTAB solution lost all emission intensity in the premicellar region in titrations approached from either direction. In an air-saturated solution, we were able to carry out the titration through the premicellar region. Fits of the titrations usually gave very small values for τ_{DS}, and we had to model with at least a DS_3 cationic species to obtain meaningful values for τ_{DS}. Results are presented in Figure 4.

Ru(phen)(CN)$_4^{2-}$ did not follow the normal lifetime trend for air-saturated solutions. In both air- and N_2-saturated solutions, $\tau_D > \tau_{DM} \gg \tau_{DS}$. Ru(phen)(CN)$_4^{2-}$ was the only probe in which the lifetime decreased upon binding to CTAB (and also TX-100). Oxygen shielding is normally the largest factor associated with the lifetime increase upon micelle binding. Other factors, such as water accessibility and local solvent properties (i.e., dielectric constant, viscosity, and rigidity), are also important. These properties must overwhelm the reduction in O_2 quenching upon binding.

Ru((Ph-SO$_3$)$_2$phen)$_3^{4-}$. As expected, the anionic Ru((Ph-SO$_3$)$_2$phen)$_3^{4-}$ interacted the strongest with CTAB. The lifetime plateaus to its completely bound value just above the icmc (lifetimes were unchanged above a formal surfactant concentration of about 1.5 mM). Although the fit for Ru((Ph-SO$_3$)$_2$phen)$_3^{4-}$ was not as good as in some of the other systems, the data followed the common trend with $\tau_{DM} > \tau_D > \tau_{DS}$. As with Ru(phen)(CN)$_4^{-2}$, a cationic DS_3 species or larger was required to prevent τ_{DS} from becoming unreasonably small.

Omitted Complexes. In general, the cationic complexes experience a strong electrostatic repulsion from the surface of CTAB micelles. Therefore, binding constants are much smaller than for SDS and are even smaller than for binding to the nonionic TX-100.[6,7a] This effect was so pronounced that a complex such as Ru(5,6-Me$_2$phen)$_3^{2+}$, which bound tightly to TX-100 (K_{DM} = 57 000 M^{-1}),[6] did not exhibit any interaction with CTAB. Similarly, Ru(phen)$_3^{2+}$ and Ru(5-Cl-phen)$_3^{2+}$ show no evidence for binding.

Interactions with TX-100. TX-100 is a polyether nonionic micelle-forming surfactant with N = 140 and cmc = 0.32 mM.[13] TX-100 binding interactions with Ru(II) probes have been covered previously.[6,9,10] In this section, we investigate three additional complexes.

Ru(phen)$_2$(5-Ph-phen)$^{2+}$. For the mixed-ligand Ru(phen)$_2$(5-Ph-phen)$^{2+}$, we found K_{DM} = 126 000 M^{-1}. This K_{DM} is intermediate in strength between that for the more hydrophobic Ru(phen)$_2$(Ph$_2$phen)$^{2+}$ (K_{DM} = 333 000 M^{-1}) and less hydrophobic Ru(phen)$_3^{2+}$ (K_{DM} = 0).[6] The lifetime increased upon binding, and the icmc was in the expected region.

Ru(phen)$_2$(CN)$_2$. Ru(phen)$_2$(CN)$_2$ binds weakly to TX-100. The intensity titration gave a large I_{DM}/I_D ratio of 4.4, but the lifetime titration exhibited double-exponential behavior and was not carried out in detail. The K_{DM} of 17 000 M^{-1} cannot arise from electrostatic attraction but must be due to a hydrophobic interaction with the sparingly water-soluble complex. The icmc was small, indicative of premicellar species or induced micelle formation. The best fit for the intensity titration is presented in Figure 5.

Ru(phen)(CN)$_4^{2-}$. Ru(phen)(CN)$_4^{2-}$ also binds weakly to TX-100. The K_{DM}'s in deoxygenated (18 500 M^{-1}) and air-saturated (12 500 M^{-1}) solutions indicate a similar strength binding as for the neutral Ru(phen)$_2$(CN)$_2$. As discussed with the CTAB interactions, τ for Ru(phen)(CN)$_4^{2-}$ decreased upon binding to TX-100 in both the air and N_2 solutions. Also, as with Ru(phen)$_2$(CN)$_2$, the decays of Ru(phen)(CN)$_4^{2-}$ exhibit some double-exponential character. Best fit for the air-saturated titration is presented in Figure 6.

Conclusions

While our equilibrium model utilizes a small number of species, it fits remarkably diverse systems, including all combinations of cationic, neutral, and anionic probes and surfactants. It provides insight into the solution composition above and below the cmc. This information would form the basis for interpretation of photochemical and thermal kinetics of micellar systems.

Qualitatively, binding follows the expected trend based upon electrostatics: electrostatic attraction increases binding while repulsion decreases it. Compare Ru(bpy)$_3^{2+}$ and Ru(bpy)$_2$(CN)$_2$ in SDS where the electrostatic attraction increases the binding constant by at least 10-fold. Also, there is no detectible binding of the anionic Ru(phen)(CN)$_4^{2-}$ to SDS. Conversely, Ru(phen)(CN)$_4^{2-}$ binds tightly to CTAB while Ru(bpy)$_3^{2+}$ shows no binding.

Indeed, without electrostatic interactions, small polar cationic complexes (e.g., Ru(bpy)$_3^{2+}$ or Ru(phen)$_3^{2+}$) rarely interact with micelles. These complexes are normally the first investigated in surveys of luminescent probes, but we find them to be poor indicators of potential interactions between metal complexes and microheterogeneous environments.

Binding shows a strong correlation with hydrophobicity in that complexes with very hydrophobic ligands bind more strongly. Compare Ru(phen)$_2$(CN)$_2$ with Ru(bpy)$_2$(CN)$_2$ in SDS where the more hydrophobic phen versus bpy ligand increases binding 10-fold. With CTAB, K_{DM} follows the trend Ru(Ph$_2$phen)$_3^{2+}$ ≫

$Ru(Me_4phen)_3^{2+} \gg Ru(phen)_3^{2+}$. These trends were also observed for binding to TX-100.[6] Relatively modest structural changes can radically alter binding. The addition of one phenyl group to $Ru(phen)_3^{2+}$ converts a nonbinder on TX-100 to the strongly binding $Ru(phen)_2(5\text{-Ph-phen})^{2+}$.

For systems that can exhibit both hydrophobic and electrostatic interactions, there can be a balancing of the two effects. The reduction of binding due to electrostatic repulsions can be partially or largely offset by hydrophobic interactions. Consider $Ru(phen)(CN)_4^{2-}$ and $Ru(Ph_2phen)_3^{2+}$ in CTAB; the cationic and anionic complexes have virtually identical micelle binding constants. Thus, the hydrophobic interactions are powerful enough to overcome a strong electrostatic repulsion of the cationic complex and bind it as tightly as a strongly attracted, less hydrophobic, anionic species. These results show the relative importance of electrostatic and hydrophobic interactions and their effect on the strength of probe binding and provide semiquantitative data for the design of probes that will bind to different substrates or microenvironments.

Our model and data clearly reveal the presence and importance of premicellar aggregates. Our luminescence data directly provide evidence for aggregates and their structure. In many cases, premicellar aggregates are essential for data fitting. Typically, aggregates are composed of a relatively small number of surfactant monomers associated with the probe. In particular, when the probe and monomer are of opposite charge, premicellar binding tends to be important and the aggregate sizes that give the best fits are close to those necessary for charge neutralization. Detectible premicellar aggregation is also common with the CN systems.

The high environmental sensitivities of $Ru(phen)_2(CN)_2$ and $Ru(bpy)_2(CN)_2$, coupled with their small perturbation of the cmc for SDS, suggest that they may be useful as luminescent probes for rapid measurement of cmc's of anionic micelles. Our data for the other systems in which the icmc is much lower than expected were not taken in a manner that allows us to judge their suitability as cmc probes for these classes of micelles. In general, neutral complexes are more reliable for cmc determination.

Oxygen quenching can be quite useful in separating τ_D and τ_{DM} (see Figure 3). Frequently, under one set of conditions the lifetimes are too close to allow parameter extraction, but by removing or introducing oxygen, the τ's can be separated and successful fits can be obtained.

We stress that invariance of τ before the cmc does not prove the absence of premicellar interactions. If association has little effect on the probe lifetime, our methodology fails to detect association. Indeed, using solvent exposure studies, we demonstrated the presence of premicellar aggregates in the CTAB–$Ru(phen)_2(CN)_2$ system even though lifetime or intensity titrations fail to detect it.[8c]

We point out that both the neutral and charged cyano complexes exhibit enormous environmental sensitivity.[24] The origins of this effect are unclear but probably involve specific interactions of the CN's with the local environment. This very high sensitivity is likely to provide cyano complexes with a unique role in the development of new probes of microstructure. Further work is in progress.

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Registry No. SDS, 151-21-3; TX-100, 9002-93-1; CTAB, 57-09-0; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(phen)_3^{2+}$, 22873-66-1; $Ru(bpy)_2(CN)_2$, 58356-63-1; $Ru(phen)_2(CN)_2$, 14783-57-4; $Ru((Ph\text{–}SO_3)_2phen)_3^{4-}$, 63244-81-5; $Ru(phen)(CN)_4^{2-}$, 114737-30-3; $Ru(Ph_2phen)_3^{2+}$, 63373-04-6; $Ru(Me_4phen)_3^{2+}$, 64894-64-0; $Ru(5,6\text{-}Me_2phen)_3^{2+}$, 14975-40-7; $Ru(5\text{-}Clphen)_3^{2+}$, 47860-47-9; $Ru(phen)_2((Ph\text{–}SO_3)_2phen)$, 63244-80-4; $Ru(phen)_2(5\text{-Ph–phen})^{2+}$, 93503-35-6.

Supplementary Material Available: Simple equilibrium expressions for the fractions of free donor, f_D, DS_n, f_{DS_n}, and micelle-bound probe, f_{DM} (2 pages). Ordering information is given on any current masthead page.

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