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Emission Properties of Dioxorhenium(V) Complexes in Aqueous Solutions of Anionic and Nonionic Surfactants: A Sensitive Probe of Hydrophobic Binding Regions

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Abstract: The emission properties of $ReO_2(py)_4^+(ReO_2^+)$ in aqueous solutions of anionic and nonionic surfactants have been investigated. The optical properties of this complex are extremely sensitive to water and therefore it is an excellent probe of hydrophobic as well as hydrophilic regions. The emission and absorption maxima of ReO_2^+ are dependent on the water content of its environment. Emission lifetimes vary over four orders of magnitude upon shifting from aqueous to nonaqueous environments. The emission lifetime has a large (8.6) isotope effect ($k(H_2O)/k(D_2O)$) that reflects its sensitivity toward the environment. These properties have been used to develop a structural and kinetic model for the interactions of ReO_2^+ with sodium dodecyl sulfate (SDS). A hydrophobic ReO_2^+ derivative, $ReO_2(3\text{-Ph-py})_4^+$ (3-Ph-py = 3-phenylpyridine), has been used to probe micelles of nonionic surfactants and these results are consistent with those obtained with SDS.

The photochemistry of small guest molecules included in microheterogeneous environments is an area of continuing interest in biomimetic chemistry.[1] Transition-metal complexes are attractive candidates for inclusion in these environments because of the diversity of their photophysics and redox properties.[2] The 2-fold purpose of this research is to probe the structure and dynamics of the environment using novel properties of the guest molecule and to develop new photochemistry of the guest molecule through the use of a novel environment.[3] The trans-dioxo Re(V) complex, $ReO_2(py)_4^+$, abbreviated hereafter as ReO_2^+, is a potentially sensitive probe of interfacial regions of microheterogeneous environments because its emission lifetime varies over four orders of magnitude upon shifting from aqueous to increasingly nonaqueous regions. The Re(V) complex can be photochemically oxidized to $ReO_2(py)_4^{2+}$, and this Re(VI) complex is reactive toward a number of organic substrates.[4]

In order to develop fully the microheterogeneous photochemistry of ReO_2^+, we have studied its emission properties in aqueous solutions of anionic and neutral surfactants. A model for cationic metal complexes in anionic surfactant solutions has been developed through numerous detailed investigations involving $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine).[5] Because the emission lifetime of $Ru(bpy)_3^{2+}$ is not strongly dependent on the aqueous character of its environment, bimolecular quenching experiments were employed to develop this model.[6-8] We will show that a similar model can be developed for ReO_2^+ by varying surfactant concentration, H_2O/D_2O ratio, incident laser power, and ionic strength.

Previous work with $Ru(bpy)_3^{2+}$ and sodium dodecyl sulfate (SDS) has shown that a number of different interactions between cationic metal complexes and anionic surfactants can occur. At very low surfactant concentration, insoluble dodecyl sulfate (DS^-) salts can precipitate (Figure 1, **1**).[9] Above the critical micellar concentration (cmc(SDS) = 8.1 mM), these salts are solubilized by the anionic micelles (**2**).[6,7,9] At intermediate concentrations below the cmc (3–6 mM), clusters have been shown to form that resemble very diffuse inverse micelles with one or more $Ru(bpy)_3^{2+}$ cations in the center (**3**).[8] On the basis of our data, we propose that ReO_2^+ obeys the model shown in Figure 1. This model is consistent with similar $Ru(bpy)_3^{2+}$ schemes, and we have been able to show for the first time that extramicellar clusters (**3**) persist at surfactant concentrations well above the cmc.

Table I. Lifetime Data for $[ReO_2(py)_4]PF_6$

surfactant	solvent	τ
	H_2O	<10 ns
	CH_3CN	10 μs
	CH_2Cl_2	12.5 μs
SDS	H_2O	67 ns/900 ns
SDS	D_2O	570 ns/900 ns
SDS	4:1 H_2O/D_2O	120 ns/900 ns
SDS	4:1 H_2O/D_2O, 0.2 M NaCl	70 ns/900 ns
Brij 35	H_2O	<10 ns
CTAB	H_2O	<10 ns

Dioxorhenium(V) and SDS

Steady-State Electronic Spectra. The absorption spectrum of ReO_2^+ in aqueous solution exhibits band maxima at 445 (ϵ 1200) and 331 nm (ϵ 19 400 M^{-1} cm^{-1})[10] (Figure 2A). The low-energy band has been assigned[11] to $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{xz},d_{yz})^1$. The intense band at 331 nm is attributable to d(Re) $\rightarrow$ π^*(py) MLCT on the basis of its shift upon protonation of the oxo group.[10] Several experiments in our laboratory support this assignment.[12] The MLCT λ_{max} shifts to lower energy in less polar solvents (Figure 2C).

The energy of the MLCT transition is linearly dependent on the solvent polarity parameter, Z (Figure 3).[13] These data correlate equally well with the Gutmann acceptor number,[14] a phenomenon that has been observed frequently for MLCT transitions in other complexes.[15] Figure 2B shows that this band also shifts to lower energy upon addition of 20 mM SDS to an aqueous solution of ReO_2^+. This energy can be used to calculate an average

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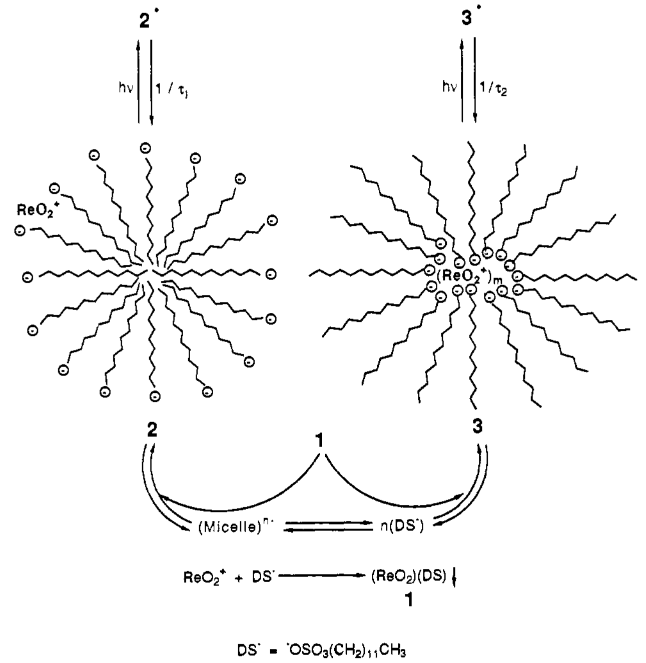

Figure 1. Model for SDS/ReO_2^+ interactions.

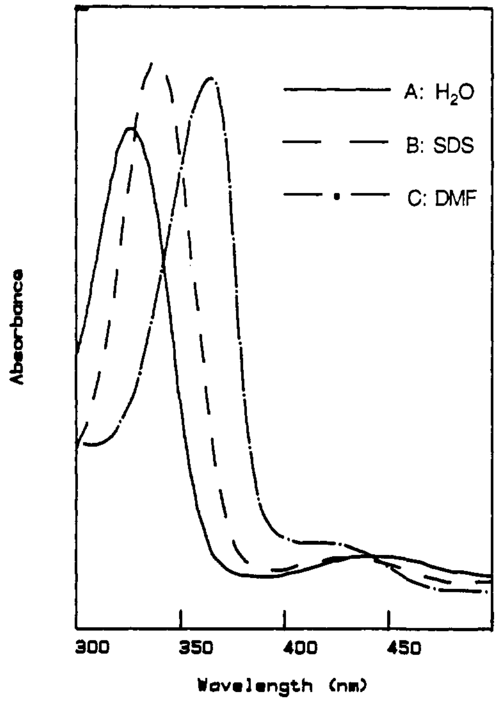

Figure 2. Absorption spectra of ~1 mM solutions of $[ReO_2(py)_4]PF_6$ in (A) water (dotted line), (B) 20 mM SDS (solid line), and (C) *N,N*-dimethylformamide (dashed line).

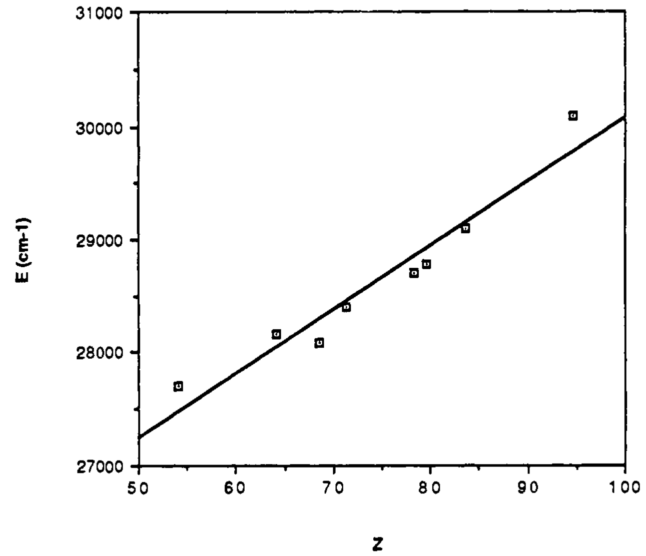

Figure 3. Plot of ReO_2^+ MLCT energy (absorption maximum) against the solvent polarity parameter, *Z*.

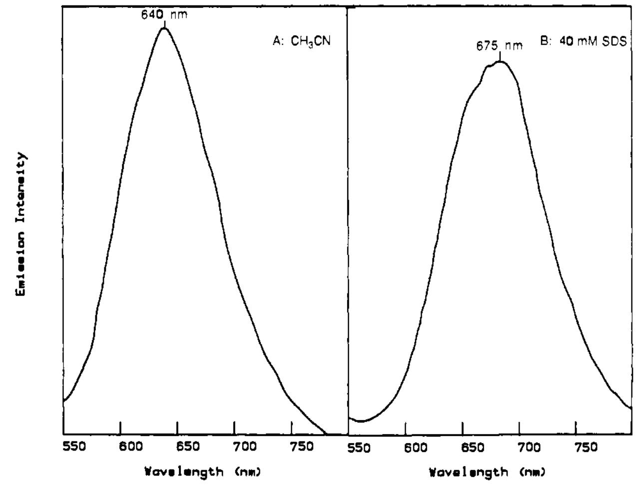

Figure 4. Uncorrected room temperature emission spectra of $[ReO_2(py)_4]PF_6$ in (A) acetonitrile solution and (B) 40 mM SDS/H_2O.

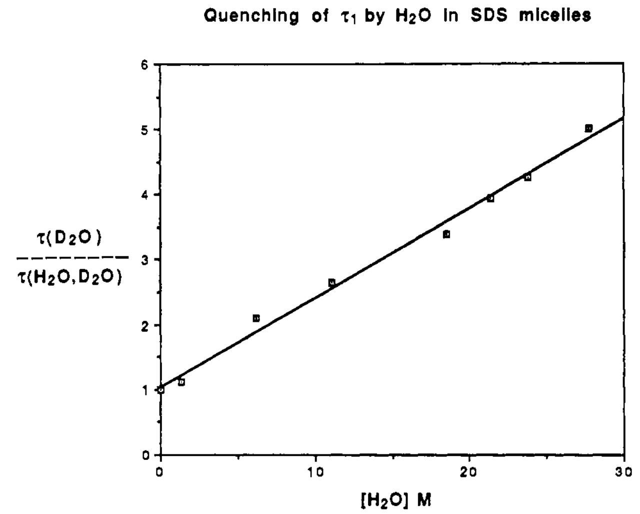

Figure 5. Stern–Volmer plot for eq 1.

polarity of the SDS environment that is between MeOH and EtOH, a result consistent with other measures of the SDS micellar polarity near the interfacial region.[16]

The emission properties of ReO_2^+ were first investigated by Winkler and Gray.[11] The emission spectrum of this complex in nonaqueous solution (Figure 4A) is essentially featureless with $\lambda_{max}(CH_3CN)$ at 640 nm. The lifetime of this emission varies slightly with solvent, ranging from 10 to 17 μs depending on the nonaqueous medium (Table I). The emission is quenched by protic solvents with a large isotope effect (in pyridine), $k(H_2O)/k(D_2O) = 8.6$; $k_Q(H_2O) = 8.2 \times 10^5$, $k_Q(D_2O) = 9.4 \times 10^4$ M^{-1} s^{-1}.[11b] In neat H_2O or D_2O this emission is completely quenched ($\tau < 10$ ns). Addition of SDS to aqueous solutions of ReO_2^+ leads to emission with λ_{max} at 675 nm (Figure 4B); precisely the same behavior is observed in experiments on nonaqueous (pyridine) solutions of ReO_2^+ to which small amounts of H_2O have been added.[11b]

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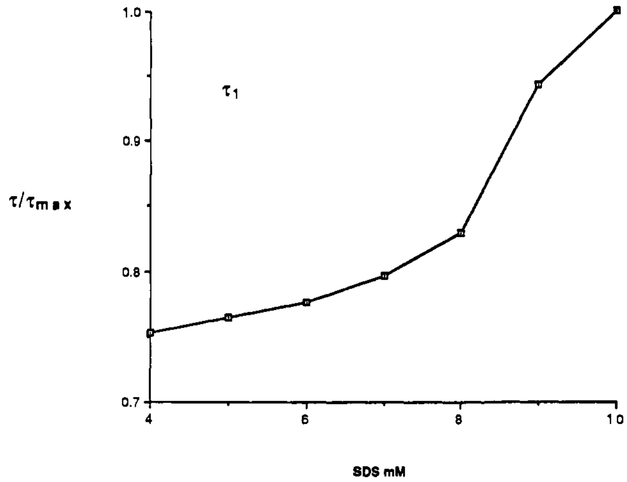

Figure 6. Dependence of τ_1 on SDS concentration.

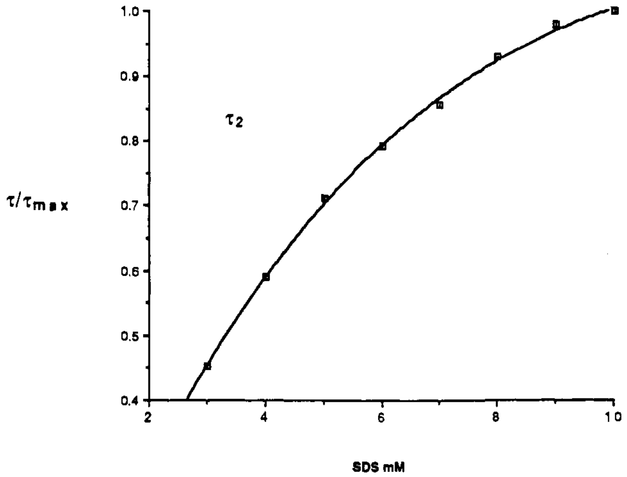

Figure 7. Dependence of τ_2 on SDS concentration.

Emission Lifetime Measurements. The decay curves of aqueous micellar SDS solutions of ReO_2^+ are biphasic with $\tau_1 = 67$ and $\tau_2 = 900$ ns, as expected from the model shown in Figure 1. The value of τ_1 is increased in D_2O (570 ns) with $k(H_2O)/k(D_2O) = 8.6$, the same ratio that was obtained in homogeneous nonaqueous solution.[11b] Data obtained in H_2O/D_2O mixtures show a linear dependence of τ_1 on $[H_2O]$ following eq 1 (Figure 5).

$$\tau_1(D_2O)/\tau_1(H_2O,D_2O) = 1 + k_Q(H_2O)*\tau_1(D_2O)*[H_2O] \quad (1)$$

From this equation we estimate values of $k_Q(H_2O) = 2.4 \times 10^5$ $M^{-1}\ s^{-1}$ and $k_Q(D_2O) = 2.8 \times 10^4\ M^{-1}\ s^{-1}$. These rate constants are of the same order as those measured in homogeneous solution, thereby suggesting that the same deactivation mechanism is operating under these conditions. The similarity of these results with those obtained in homogeneous solution indicates that τ_1 arises from ReO_2^+ residing in an environment of reduced water concentration. In contrast, the component τ_2 is independent of the H_2O/D_2O ratio, suggesting that it is not exposed to the bulk aqueous medium.

The magnitude of τ_1 is strongly dependent on the surfactant concentration (Figure 6). There is a marked increase of τ_1 in the vicinity of the cmc, indicative of association with a normal SDS micelle as shown in **2**.[3] The longer component, τ_2, shows a different dependence on surfactant concentration (Figure 7). The lifetime increases as a function of the surfactant concentration and maximizes at the cmc. At low surfactant concentrations, clusters containing more than one ReO_2^+ can participate in triplet–triplet annihilation, resulting in shorter lifetimes.[8] As the surfactant concentration is increased, more clusters are formed and the multiply occupied clusters are reduced in concentration. Since the ReO_2^+ concentration is constant, the probability for two probes to be within the same cluster decreases with increase in the SDS concentration and therefore a lengthening of the lifetime can be observed.

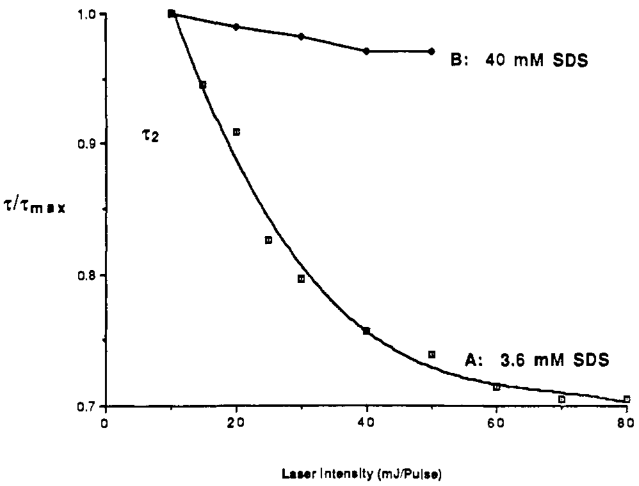

Figure 8. Dependence of τ_2 on laser power intensity in (A) 3.6 mM SDS and (B) 40 mM SDS.

The inverse dependence of τ_2 on the incident laser power further supports this model (Figure 8). At SDS concentrations below the cmc (3.6 mM), τ_2 is inversely dependent on the laser power and levels off to a maximum at low excitation intensities. This is consistent with the self-annihilation mechanism associated with clusters containing more than one ReO_2^+ ion, i.e., structure **3** in Figure 1. At SDS concentrations well above the cmc (40 mM), τ_2 is only slightly dependent on the laser power, indicating that most of the clusters are singly occupied at these SDS concentrations.

The value of τ_1 can be significantly reduced by the addition of NaCl (Table I). Greater ionic strength increases the average micellar size and raises water concentration at the interface.[17] Increased exposure to water results in a reduced value of τ_1. In contrast, τ_2 is not dependent on [NaCl]. The decay profiles of ReO_2^+ in cationic cetyltrimethylammonium bromide (CTAB) and nonionic Brij 35 ($CH_3(CH_2)_{11}(OCH_2CH_2)_{23}OH$) micellar solutions are single exponentials and short, as in water. This further supports the proposal that the long-lived emission observed in SDS arises from a unique environment associated with SDS. The negatively charged surfactant can cluster with the positively charged (ReO_2^+) probe ions and a probe embedded in such a cluster is least exposed to the bulk aqueous environment. On the other hand, the short-lived emission arises from probe ions bound to micelles at the negatively charged interfacial region.

Time-Resolved Emission Spectra. In acetonitrile solution, the steady-state emission spectrum of ReO_2^+ (Figure 4A) is typical of complexes of this type. Time-resolved emission measurements in CH_3CN show that this emission spectrum remains unchanged (λ_{max} 640 nm) over a period of 10 μs. The corresponding decay curves are strictly monoexponential and independent of the monitoring as well as the excitation wavelength (300–550 nm). Thus, only one emissive state is observed in homogeneous, nonaqueous solution.

The steady-state emission spectrum of ReO_2^+ obtained in SDS is red-shifted relative to CH_3CN (Figure 4B). Qualitatively, the spectrum broadens slightly and the emission maximum is moved to lower energy. Time-resolved emission spectra taken in SDS at 50-ns intervals over a period of 200 ns show a blue shift in the emission maximum with time (Figure 9). This is consistent with two emissive states, a short-lived species with emission at longer wavelengths and a longer-lived state with emission at shorter wavelengths.[18] The fact that the longer-lived component emits at higher energy suggests that this species is less relaxed by the

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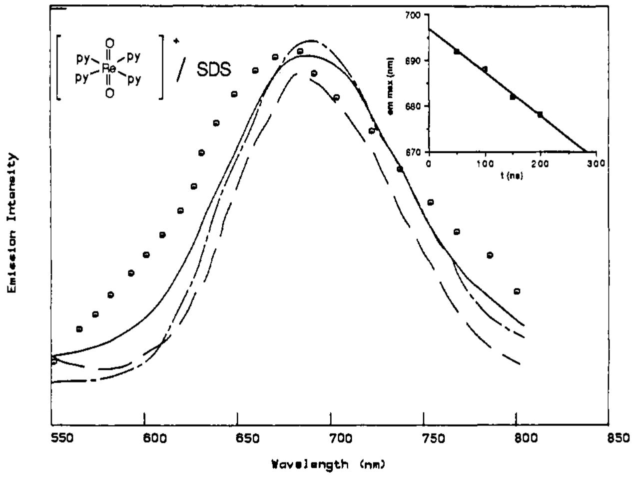

Figure 9. Plot of emission maximum versus time in 40 mM SDS, 4:1 H_2O/D_2O.

Table II. Spectroscopic and Electrochemical Properties

property	$[ReO_2(py)_4]PF_6$	$[ReO_2(3\text{-Ph-py})_4]PF_6$
ν(Re–O),[a] cm^{-1}	815[b]	810
$E_{1/2}(ReO_2^{2+/+})$,[c] V	1.37	1.34
absorption (max),[d] nm	435	425
emission (max),[e] nm	640	625

[a] IR in a Nujol mull. [b] From ref 11b. [c] Acetonitrile solution, 0.1 M tetra-*n*-butylammonium hexafluorophosphate, SSCE reference electrode. [d] Acetonitrile solution. [e] Acetonitrile solution, 400-nm excitation.

surrounding environment. The ordered structure of the cluster would restrict reorganization and therefore could not relax the excited state very effectively. Thus, this species would be expected to emit at higher energies.[19] In steady-state emission experiments involving other aqueous microheterogeneous environments, including nucleic acids and polyelectrolyte films, we have observed that more polar environments (as indicated by MLCT absorption maxima) lead to emission at longer wavelengths.[20]

Dioxorhenium(V) and Nonionic Surfactants

Steady-State Emission Spectra. To extend our investigation of the Re(V) probe, we prepared a hydrophobic ReO_2^+ derivative, $ReO_2(3\text{-Ph-py})_4^+$ (3-Ph-py = 3-phenylpyridine). Substitution of the pyridine ring in this way led to very small changes in the spectroscopic and electrochemical properties of the ReO_2^+ chromophore (Table II). Thus, we were able to increase the hydrophobic properties of the molecule while retaining the desired photophysics. The steady-state emission spectrum of this complex in CH_3CN shown in Figure 10A is unstructured at room temperature. When placed in aqueous solutions of Brij 35, $ReO_2(3\text{-Ph-py})_4^+$ shows vibronically structured emission (Figure 10B). This progression ($\Delta\nu \sim 900\ cm^{-1}$) corresponds to the symmetric Re–O stretch and is similar to that seen in low-temperature emission spectra[11] of $ReO_2(py)_4^+$ and in room temperature emission spectra of $ReO_2(py)_4^+$ intercalated in some types of complex layered oxides.[21] The appearance of this progression indicates that the ReO_2^+ chromophore is in a viscous environment.

Emission Lifetime Measurements. The lifetime data for $ReO_2(3\text{-Ph-py})_4^+$ are given in Table III. In Brij 35, owing to the absence of electrostatic interactions (which can lead to the formation of **3**), it is reasonable to expect that the major interaction that may occur is hydrophobic binding of $ReO_2(3\text{-Ph-py})_4^+$ to the micellar core. Accordingly, in Brij 35, the decay curve is monophasic (τ 500 ns) and shows only a small isotope effect ($k(H_2O)/k(D_2O) = 1.1$). The increased lifetime and the small isotope effect are consistent with local ordering of the chromophore (Figure 10B) with limited exposure to the aqueous environment. Thus, $k(H_2O)/k(D_2O)$ is an effective measure of the solvent accessibility of the probe molecule.[22] In aqueous solutions of Triton X-100 ($CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_{9.5}OH$),[6] a nonionic surfactant with a larger hydrophobic chain that Brij 35, a similar isotope-independent, long-lived emission was observed ($\tau = 1.36\ \mu s$).

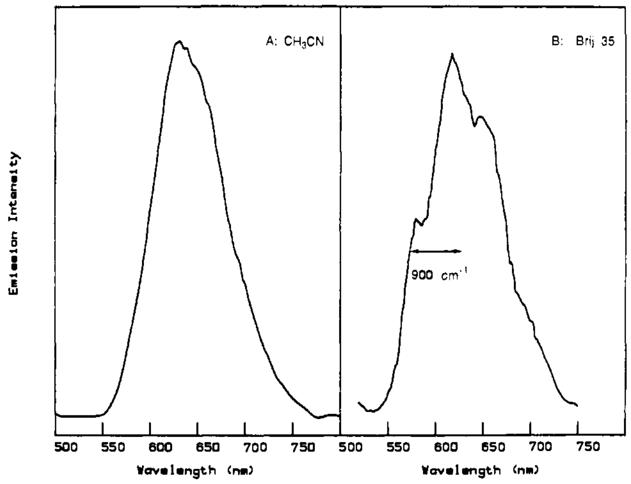

Figure 10. Uncorrected room temperature emission spectra of $[ReO_2(3\text{-Ph-py})_4]PF_6$ in (A) CH_3CN and (B) Brij 35/H_2O.

Table III. Lifetime Data for $[ReO_2(3\text{-Ph-py})_4]PF_6$

medium	τ	medium	τ
H_2O	<10 ns	Triton X-100/D_2O	1.36 μs
CH_3CN	10.4 μs	SDS/D_2O	1.3 μs
Brij 35/H_2O	500 ns	CTAB	<10 ns
Brij 35/D_2O	570 ns		

In micellar SDS solution, the decay curve of $ReO_2(3\text{-Ph-py})_4^+$ is monophasic and shows no isotope effect. The emission properties (lack of an isotope effect, and a long-lived (1.3 μs), single-component decay) indicate that $ReO_2(3\text{-Ph-py})_4^+$ is bound in cluster aggregates (**3**) rather than at the interfacial region of the anionic micelles (**2**). Further, $ReO_2(3\text{-Ph-py})_4^+$ shows no interaction with positively charged CTAB micelles, thereby suggesting that the complex is not sufficiently hydrophobic to allow it to bind to positively charged micelles.

Conclusions

We have shown that the d^2 trans-dioxo complex $ReO_2(py)_4^+$ is a very sensitive probe for hydrophobic binding regions in aqueous surfactant solutions. A number of properties of this chromophore can be used to delineate its microenvironment. These properties include (1) a polarity-dependent UV absorption band and emission maximum, (2) a highly structured emission band when the complex is in an ordered cluster, (3) an emissive excited state that is strongly coupled to the water molecules of its surroundings, and (4) a large H/D isotope effect on excited-state decay in aqueous solution. We have used these properties together with the fact that the excited state of ReO_2^+ is capable of triplet–triplet annihilation to show that the pre-micellar cluster model proposed for $Ru(bpy)_3^{2+}$ can be generalized to dioxo cations (Figure 1).

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(19) In addition, the longer-lived component would be expected to emit at higher energy than the short-lived component from energy-gap law considerations (Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.) Synthesis of ReO_2^+ compounds having different emission maxima confirms that the energy-gap law applies to the ReO_2^+ chromophore.[12]

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(22) Using the ratio of the isotope effect in Brij 35 (HD_{B35}) to the isotope effect in homogeneous solution (HD_{HS}) as a scaling factor, a corrected lifetime that potentially eliminates rigidity can be calculated as in (2).

$$\tau_c = \tau(\text{Brij 35})*(HD_{B35})/(HD_{HS}) \qquad (2)$$

This calculation gives 66 ns, within experimental error of τ_1(SDS), where the isotope effect is the same as in homogeneous solution. This is encouraging since SDS and Brij 35 have the same hydrophobic groups. Further experimentation using a wide range of surfactants and ReO_2^+ derivatives might allow us to quantify the contribution of rigidity to the emission enhancement.

In our case, we have shown that this model is valid by varying the surfactant concentration, incident laser power intensity, H_2O/D_2O ratio, and ionic strength.

We also have synthesized a hydrophobic ReO_2^+ derivative, $ReO_2(3\text{-Ph-py})_4^+$, whose electronic properties are virtually identical with those of the unsubstituted complex. With this hydrophobic derivative, we have been able to probe other environments (e.g., nonionic micelles) by means of the SDS/ReO_2^+ model.

Experimental Section

Materials. Solvents used for syntheses were reagent grade. Photochemical measurements were made in spectrograde solvents that were freshly distilled from appropriate drying agents under an inert atmosphere. Triton X-100 was used as received. Sodium dodecyl sulfate (Aldrich) and Brij 35 (Aldrich) were recrystallized from acetone/water. Water was purified by a nanopure water system. $KReO_4$ (Aersar) was used as received. Deuterium oxide (Aldrich, 99.8 atom %) was placed under vacuum immediately after opening and was distilled just before use.

Dioxo Complexes. The chloride salt of $ReO_2(py)_4^+$ was prepared by the method of Beard et al.[23] The PF_6^- salt was precipitated by addition of saturated aqueous NH_4PF_6 to a water solution of the chloride and recrystallized from 5:1 acetone/pyridine. The 3-phenylpyridine (3-Ph-py) complex was prepared by an analogous method where 3-Ph-py (Aldrich) was substituted for pyridine.

Physical Measurements. Electrochemistry was performed as described elsewhere.[4] Time-resolved emission measurements were performed with use of an OMA system that has been described previously.[24] The spectra were averaged for 15–25 shots and smoothed by two-point smoothing. Electronic absorption spectra were obtained with use of a Shimadzu UV-260 recording spectrophotometer. Steady-state emission spectra[25] and emission decay curves[26] were obtained as described previously. Four parameter biexponential fits were performed with use of a program written by M. Albin. This program is based on the techniques of Marquadt as described by Bevington.[27] In all cases described here, the ratio of integrated intensities τ_1/τ_2 was $\sim$2:1.

Sample Preparation. Solutions for emission lifetime measurements were prepared in a two-compartment cell fitted with a 10-mL Pyrex bulb and a 1 cm pathlength cuvette.[28] Solvent was transferred on a high-vacuum line and degassed by 5 freeze–pump–thaw cycles. For surfactant solutions, the metal complex was added to the bulb and the surfactant was placed in the cuvette. Nanopure water was added directly and D_2O was vacuum transferred into the bulb. Thus, the metal complex was dissolved before mixing with the surfactant. In "Stern–Volmer" experiments, the "quencher" (H_2O, D_2O, NaCl, SDS) was added to the cuvette while the solution was kept in the bulb under vacuum. Liquids were degassed by 3 freeze–pump–thaw cycles before mixing with the solution. Repeating the emission lifetime measurements with use of less rigorous degassing methods did not quantitatively affect the decay curve. Extreme care was taken to ensure that the surfactant, metal complex, and NaCl were completely dissolved. Concentrations of ReO_2^+ were approximately 1 mM in all experiments.

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Stereoselective Syntheses of *erythro*- and *threo*-β-Amino Alcohol Derivatives via Hetero-Diels–Alder Reactions

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Abstract: The reaction of 1,3-dimethoxy-1-[(trimethylsilyl)oxy]butadiene with a variety of N-protected α-amino aldehydes under the influence of Lewis acid has been studied. The reaction provides an α,β-unsaturated lactone that is useful in further transformations. When *N-tert*-butoxycarbonyl-protected amino aldehydes are used with diethylaluminum chloride or tris-[3-[(heptafluoropropyl)hydroxymethylene]camphorato]europium(III) as a catalyst, the reaction provides a diastereomer consistant with a chelation-controlled process. Diastereomeric ratios range from 80:20 (alaninal) to 95:5 (valinal). This stereochemistry is dramatically reversed when *N,N*-dibenzyl-protected amine aldehydes are used. Diastereomeric ratios are consistantly 99:1 in favor of the Cram-type product.

The presence of β-amino alcohols in biological active molecules such as amino sugars, antibiotics, and peptides has raised the interest in the preparation of these type of compounds.[1] In 1982, Danishefsky[2] reported the stereoselective (9:1) syntheses of a statine derivative, using a cycloaddition reaction of a substituted diene with *N*-(*tert*-butoxycarbonyl)leucinal. The stereochemical results could be interpreted as arising from a "chelation-control" process in which the Lewis acid complexes both the aldehyde oxygen and the protected nitrogen. This favors approach of the diene in an "anti-Cram" fashion affording the threo product. Garner and co-workers[3] have studied the cycloaddition of a *N*-Boc-serine-derived aldehyde with Danishefsky's diene. Their results also seem to indicate the participation of the Lewis acid

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