A New Probe of Solvent Accessibility of Bound Photosensitizers. 1. Ruthenium(II) and Osmium(II) Photosensitizers in Sodium Lauryl Sulfate Micelles

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Abstract: A new method of measuring solvent accessibility of photosensitizers bound to organized media is presented. In particular, the solvent accessibility of a series of ruthenium(II) and osmium(II) photosensitizers bound to sodium lauryl sulfate micelles has been determined. The method takes advantage of the large solvent deuterium effect on the excited-state lifetimes of these complexes. The solvent accessibility of the bound complexes correlates with the hydrophobicity of the ligands. The potential application of this method to a variety of other systems is mentioned.

Photophysics and photochemistry of organized systems are currently areas of active study.[1] Our group is studying ruthenium(II) and osmium(II) photosensitizers in homogeneous and surfactant containing media. We have measured the binding interactions and photosensitization properties in both ionic and nonionic surfactants.[2-5] In a study of the excited-state electron-transfer reactions between Ru(II) photosensitizers and $HgCl_x^{2-x}$ (x = 2, 3, 4) in sodium lauryl sulfate (NaLS), we have shown that the Marcus electron-transfer theory can be successfully modified to explain the changes in behavior between surfactant-free and micellar systems.[3b] Our results showed that micelle-bound photosensitizers were greatly protected from quenching by the water-borne Hg(II) species. In particular, $[Ru(Ph_2phen)_3]^{2+}$ (Ph_2phen = 4,7-diphenyl-1,10-phenanthroline), which was expected to show the greatest tendency to partition into the hydrocarbon core of the micelles, showed the greatest shielding effect.

The precise solvent environment around the micelle-bound photosensitizers remained unknown. In particular, we wished to quantitate the degree of exposure of the photosensitizers to solvent-borne quenchers. Many approaches have been developed for probing the binding interactions of molecules with organized systems such as micelles.[1b-d,6-8] However, most of these approaches use specially modified probes, require high probe concentrations, or do not answer the above questions. No approach appeared suitable for our photosensitizers at micromolar concentrations.

In an attempt to find a usable method for our systems, we noted that luminescence techniques have been developed for investigating the structure of rare earth complexes and lanthanide-substituted metalloproteins.[9-11] These methods depend on the large deuterium isotope effect on the luminescence lifetimes or intensities of hydrated rare earth ions. A comparison of the lifetimes in a H_2O or D_2O environment permits a direct determination of the number of bound water molecules. This technique has been limited to rare earth probes and has never been used to study the important problem of photosensitizers in organized media.

Even in the absence of chemical aquation the excited-state lifetimes of many transition-metal complexes show a large deuterium effect.[12-14] We demonstrate here that this effect can be extended to organized systems permitting a direct determination of the average solvent accessibility of bound photosensitizers. We report a detailed study on the interactions of Ru(II) and Os(II) photosensitizers on NaLS micelles and discuss the limitations and possible extensions of this approach.

Experimental Section

The ligands and our abbreviations are as follows: 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), 1,10-phenanthroline (phen), 5-chloro-1,10-phenanthroline (Clphen), 5-bromo-1,10-phenanthroline (Brphen), 5-methyl-1,10-phenanthroline (Mephen), 5-phenyl-1,10-phenanthroline (Phphen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen), 5,6-dimethyl-1,10-phenanthroline (5,6-Me_2phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2phen), disulfonated 4,7-diphenyl-1,10-phenanthroline ($(SO_3Ph)_2$phen), 2,2′,2″-terpyridine (terpy), bis(diphenylphosphino)-methane (DPPM), and *cis*-bis(1,2-diphenylphoshino)ethylene (DPPene). The bpy, phen, and terpy ligands were from G. Frederick Smith Chemical Co. and were used without further purification. The phosphines were used as received from Strem Chemicals, Inc.

$[Ru(bpy)_3]Cl_2$ (G. F. Smith Chemical Co.) was recrystallized from water. $[Ru(Ph_2phen)]_3Cl_2$ was prepared and purified by the method of Watts and Crosby.[15] The remaining Ru(II) complexes were prepared as reported elsewhere.[3b] The Os(II)[16] and Cr(III)[17] complexes were

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Table I. Excited-State Lifetimes (μ) and F's

complex	no NaLS		10 mM NaLS		F
	H_2O	D_2O	H_2O	D_2O	
$[Ru(bpy)_3]^{2+}$	0.576	0.936	0.800	0.956	0.305 ± 0.047
$[Ru(Me_2bpy)_3]^{2+}$	0.342	0.607	0.559	0.677	0.246 ± 0.036
$[Ru(phen)_3]^{2+}$	0.908	1.09	1.76	1.99	0.357 ± 0.049
$[Ru(Clphen)_3]^{2+}$	0.962	1.09	2.04	2.29	0.438 ± 0.017
$[Ru(Brphen)_3]^{2+}$	1.21	1.50	2.37	2.73	0.348 ± 0.041
$[Ru(Mephen)_3]^{2+}$	1.33	1.71	2.40	2.56	0.156 ± 0.085
$[Ru(4,7\text{-}Me_2phen)_3]^{2+}$	1.65	2.29	3.13	3.60	0.246 ± 0.007
$[Ru(5,6\text{-}Me_2phen)_3]^{2+}$	1.91	2.80	2.94	3.42	0.287 ± 0.051
$[Ru(Me_4phen)_3]^{2+}$	1.75	2.03	1.88	1.99	0.373 ± 0.222
$[Ru(Phphen)_3]^{2+}$	1.63	2.02	1.88	2.08	0.432 ± 0.111
$[Ru(phen)_2(Ph_2phen)]^{2+}$	3.07	4.22	6.11	6.56	0.126 ± 0.063
$[Ru(Ph_2phen)_3]^{2+}$	3.58	5.83	3.96	4.15	0.107 ± 0.090
$[Ru(phen)_2((PhSO_3)_2phen)]$	3.46	5.25	2.79	3.11	0.374 ± 0.113
$[Ru((PhSO_3)_2phen)_3]^{4-}$	3.73	5.84	4.92	6.60	0.534 ± 0.027
$[Ru(bpy)_2(CN)_2]$	0.254	0.456	0.391	0.577	0.473 ± 0.017
$[Ru(phen)_2(CN)_2]$	0.654	0.825	0.572	0.620	0.427 ± 0.167
$[Os(phen)_3]^{2+}$	0.074	0.143	0.115	0.157	0.357 ± 0.025
$[Os(terpy)_2]^{2+}$	0.141	0.234	0.156	0.187	0.377 ± 0.058
$[Os(bpy)_2(CNMe)_2]^{2+}$	0.552	0.892	0.635	0.716	0.258 ± 0.070
$[Os(phen)_2DPPM]^{2+}$	0.554	0.880	0.602	0.713	0.387 ± 0.063
$[Os(phen)_2DPPene]^{2+}$	1.02	1.55	0.903	1.02	0.379 ± 0.097
$[Cr(bpy)_3]^{3+}$	53.9	59.1	42.4	39.6	
pyrene	0.228	0.234	0.357	0.374	

prepared by following literature methods. Electrophoresis Purity Grade NaLS (BioRad Lab.) was purified by recrystallizing from methanol and vacuum drying. Pyrene from Aldrich Chemical Co. was used without further purification.

At the 10-mM NaLS concentrations used in this study, the micelle concentration is ~30 μM.[18] Sensitizer concentrations were kept below 8 μM to prevent multiple sensitizer occupation of the micelles. Solutions were prepared with deionized water distilled from $KMnO_4$ or with D_2O (Aldrich Gold Label). All solutions were deaerated with solvent-saturated nitrogen prior to lifetime measurements, and measurements were made at 25 °C with use of a temperature controller described elsewhere.[19]

Lifetime measurements were made on a nitrogen laser based decay time apparatus described previously.[3a,20] Excitation was at the 337-nm laser line, and the emissions were monitored at the apparent emission maxima (600 to 750 nm). Decays, recorded on a microcomputer interfaced Tektronix 7912 ultra-high-speed transient digitizer, were exponential over at least 2 half-lives. Mean lifetimes, τ's, were calculated from the slope of a semilogarithmic plot of intensity vs. time with the use of a linear least-squares fit. The 10-ns laser pulse was short enough compared to the decay times that it could be treated as an impulse excitation. All reported lifetimes are averages of at least three measurements which typically agreed to ±2%.

Results and Discussion

Our lifetime data are presented in Table I. There is no deuterium effect for pyrene within our experimental error. For the remaining species, there are two general trends: (1) the photosensitizer lifetimes all increase on going from H_2O to D_2O; and (2) with a few exceptions, photosensitizer lifetimes increase on binding to NaLS micelles.

Figure 1 demonstrates the dependence of τ^{-1} on the mole fraction of H_2O in surfactant-free H_2O–D_2O mixtures. The linear dependence of τ^{-1} on the mole fraction of H_2O indicates that an H_2O-specific quenching process is present.

Compared to aqueous results, the emission spectra of Ru(II) and Os(II) complexes are red shifted and generally the lifetimes are longer at NaLS concentrations above the cmc.[21] We have

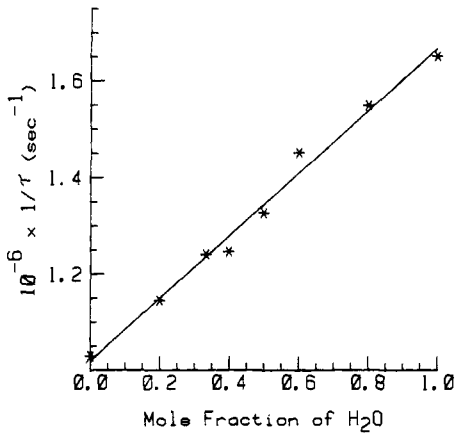

Figure 1. Reciprocal lifetime of $[Ru(bpy)_3]^{2+}$ vs. mole fraction of H_2O.

quantitatively fit titration curves of luminescence lifetimes or intensities vs. $[LS^-]$.[5] These results demonstrate that the cmc and, presumably, gross micelle structure are unaffected by the presence of the sensitizers. Further, the binding to the micelles was shown to be very tight; at the 10-mM [NaLS] used here negligible concentrations of unbound sensitizers existed in solution.[5] These conclusions are further supported by the fact that quenching rate constants for quenchers which do not partition into the micelles are greatly reduced by binding the sensitizer to NaLS micelles.[3b] Analogous arguments hold for the Os(II) and Cr(III) complexes.

It is not surprising that cationic sensitizers are tightly bound to anionic micelles. Even the neutral Ru(II) complexes exhibit strong binding due to a hydrophobic interaction of the ligands and the hydrocarbon core of the micelles.[5] The anionic $[Ru((SO_3Ph)_2phen)_3]^{4-}$ also interacts strongly with NaLS. Presumably, the repulsive effect of the negative charge is ameliorated by its diffuseness, and the LS^- can intercalate between the phenyl rings. The dominant interaction is probably hydrophobic and similar to that between Ru(II) photosensitizers and non-ionic Triton X-100 micelles.[4a] In the subsequent analysis, we assume that photosensitizer micelle binding is tight as has been demonstrated for the current systems.

Since the lifetimes of our complexes are strongly affected by surfactants and by solvent deuteration, these results provide a quantitative measure of solvent accessibility of micelle-bound

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(18) [M] = ([S] − cmc)/A where [M] = micelle concentration, [S] = total surfactant concentration, cmc = critical micelle concentration, and A = aggregation number. For NaLS at 25 °C, cmc = 8.1 mM, A = 62.[6]

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photosensitizers. Following an analysis similar to that used for hydrated rare earth ions,[9] we write:

$$\tau^{-1} = k_0 + F[k_{OH}X(H_2O) + k_{OD}X(D_2O)] \quad (1a)$$

$$k_0 = k_r + k_{nr} \quad (1b)$$

where τ is the observed lifetime and k_r is the radiative rate constant for emission. k_{nr} is the sum of the rate constants of all nonradiative deactivation pathways which do not involve OH or OD oscillators of the solvent. k_{OH} and k_{OD} are the nonradiative rate constants for energy transfer to the OH or OD vibrations of the H_2O or D_2O molecules surrounding the emitting species. $X(H_2O)$ and $X(D_2O)$ are the mole fraction of H_2O and D_2O in the solvent, respectively. F is the fraction of the surface of the complex exposed directly to H_2O and D_2O. k_0 accounts for all processes not directly involving coupling to the OH or OD vibrations. Our notation is different from that used in the rare earth work because we do not know the hydration numbers. For a fixed chemical media, eq 1 predicts a linear dependence of τ^{-1} on $X(H_2O)$ or $X(D_2O)$. Figure 1 demonstrates the expected linear dependence and the validity of eq 1a in our systems.

The large isotope effect on the lifetimes of lanthanide excited states arises from different coupling of the excited state to OH and OD oscillators of coordinated water. Replacing OH oscillators with OD oscillators greatly reduces the rate of energy transfer to solvent and enhances the excited-state lifetimes.[9-11]

A similar deuterium isotope effect occurs for Ru(II) and Os(II) complexes, but there is a difference in the details of the deactivation process. The metal-centered lanthanide excited states are deactivated predominately by coupling to the OH oscillators of coordinated H_2O.[9-11] The charge-transfer (CT) excited states of the Ru(II) and Os(II) complexes involve electron promotion to ligand orbitals; the deactivation occurs via coupling to the ligand-associated solvent molecules in the second coordination sphere. Alternatively, the deuterium isotope effect for CT states of metal complexes may involve charge transfer to solvent states.[12c] The exact details of the interaction are not, however, critical for this current methodology to work.

Equation 1 forms the basis for our analysis. The less exposed the sensitizer is to the solvent, the smaller the isotope effect. Thus, the more that binding to the micelles shields the photosensitizer from the solvent, the smaller the deuterium isotope effect. If the photosensitizer were completely shielded by the micelle from any solvent exposure, there would be no deuterium effect on the lifetime of the bound photosensitizer.

Our model does not directly provide details of the microscopic structure of the micelle–solvent organization around the photosensitizer. It provides only a measure of their time-averaged solvent exposure. We wish to stress that we do not measure the properties of sensitizer-free micelles. The sensitizers may be large enough to represent a significant perturbation on the micelle structure. Our measurements probe only the structures of the micelle–sensitizer complexes, and any attempt to infer micelle structure from these data should be made with great caution.

For the pure solvent and the micelle measurements, eq 1 can be written as

$$\tau(s)^{-1} = k_0 + [k_{OH}X(H_2O) + k_{OD}X(D_2O)] \quad (2a)$$

$$k_0 = k_r + k_{nr} \quad (2b)$$

$$\tau(m)^{-1} = k_0' + F[k_{OH}X(H_2O) + k_{OD}X(D_2O)] \quad (2c)$$

$$k_0' = k_r' + k_{nr}' \quad (2d)$$

where the primes denote rate constants for micellar bound forms. The X's are the mole fractions of H_2O or D_2O in the aqueous solvent. $X(H_2O)$ and $X(D_2O)$ are unity for pure H_2O and D_2O solvents, respectively. F accounts for the fraction of the complex not shielded from the aqueous phase by the surfactant molecules. (s) and (m) designate pure solvent and micelle values, respectively.

To determine the fundamentally important F, four luminescence lifetime measurements, $\tau_{H(s)}$, $\tau_{D(s)}$, $\tau_{H(m)}$, and $\tau_{D(m)}$, are required. $\tau_{H(s)}$ and $\tau_{D(s)}$ are the lifetimes of the complex in surfactant-free media when either pure H_2O or pure D_2O is used as the solvent. $\tau_{H(m)}$ and $\tau_{D(m)}$ are the lifetimes of the micelle-bound complex in pure H_2O or pure D_2O solutions, respectively. From eq 2

$$F = \frac{[\tau^{-1}_{H(m)} - \tau^{-1}_{D(m)}]}{[\tau^{-1}_{H(s)} - \tau^{-1}_{D(s)}]} \quad (3)$$

where F denotes the fractional exposure of the micelle-bound photosensitizer to the aqueous solvent. Equation 3 has few inherent assumptions. It does not require that k_0 and k_0' be equal. Further, explicit values of k_{OH} and k_{OD} are not needed; they must only be the same for the free and bound complex. Equation 3 also requires that the probes be tightly bound to the micelle. If this assumption is incorrect, then eq 3 yields a fractional accessibility averaged over the bound and unbound forms. If the equilibrium constant for binding is known, it is then possible to correct the data to obtain true F's. Alternatively, the concentration of micelles could be raised to drive the equilibrium in favor of the bound form. In the current work, the binding is tight and we ignore any contribution from free probes.

The F's calculated for all Os(II) and Ru(II) complexes studied are summarized in Table I. The indicated uncertainties were calculated by assuming a 2% uncertainty in each τ measurement. In general, the values range from 0.25 to 0.40 and average about 0.33. Thus, typically, about one-third of the ligand environment is exposed to the solvent. This figure is quite reasonable, especially for the complexes with three similar bpy or phen ligands. The hydrophobic ligands tend to associate with the hydrocarbon region of the micelle; opposing this tendency is the need for the metal ion to associate with charged counterions. Embedding most of the complex in a hydrocarbon region while allowing partial solvent access counterbalances these two interactions.

Figure 2 schematically shows several possible models for photosensitizer binding to the micelles. In all cases LS^- in the photosensitizer's second coordination sphere excludes water from that portion of the complex located inside the micelles. For simplicity we have shown the roughly spherical micelle appropriate for the unperturbed LS micelles, but the perturbations caused by the sensitizers may distort this spherical shape.

Figure 2A is consistent with the Dill–Flory version of the barrier model[22] for micelles. The micelle core is considered to be a nearly dry hydrocarbon region. A fraction of the sensitizer is embedded in this core and protected from the water phase. The portion of the complex projecting into the water is responsible for the water exposure.

Figure 2B is more nearly in accord with the fjord model.[7] In this case the sensitizer is buried in the micelle, but water exposure arises from penetration of the micelle surface via deep clefts or fjords. We have explicitly shown only fjords extending to the charged photosensitizer. Even if fjords penetrate to our photosensitizers, this does not imply that the rest of the micelle is honeycombed with fjords or that photosensitizer-free micelles possess a fjord structure.

Figure 2C shows the sensitizer in a partially aqueous region which is cut off from the bulk solvent. We have explicitly shown both major water aggregates and isolated parcels of one or two water molecules trapped in the clefts between the ligand rings.

In reality no single picture is likely to be a complete description. Micelles are very dynamic structures and during an extended period a bound photosensitizer may sample two or more of the suggested structures. If this sampling of structures is rapid compared to the excited-state lifetime, the sensitizer will sense an average aqueous environment, and the F determined will represent a time-averaged quantity over all possible structures. Also, as long as these configurational changes occur rapidly, the luminescence decays will be exponential with no evidence of heterogeneity of binding.

We now make several observations concerning the possible configuration of Figure 2. We can exclude the solvent-entrapment model (Figure 2C) as the sole source of water exposure. Our extensive quenching results with $HgCl_x^{2-x}$ (x = 2, 3, and 4) show that all bound complexes are accessible to water-borne quenchers

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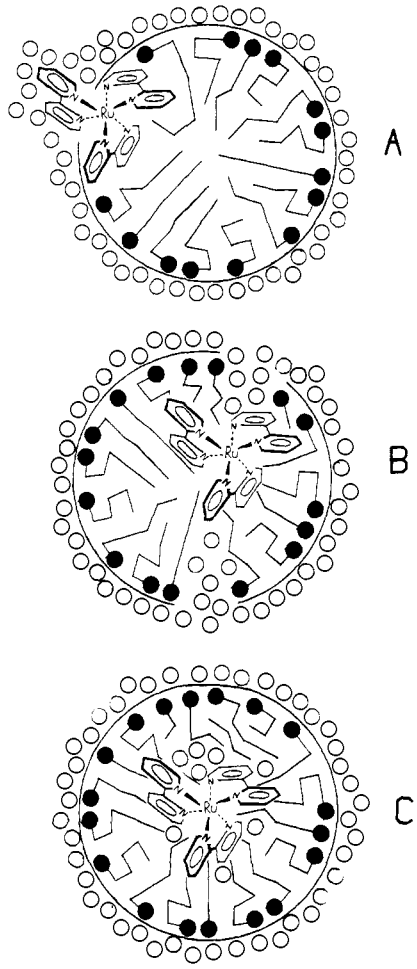

Figure 2. Schematic representations of a typical micelle-bound Ru(II) photosensitizer. $[Ru(bpy)_3]^{2+}$ is used in the figure. Solid circles represent the ionic head groups of the surfactant molecules and their attached solid lines represent the hydrophobic tails. The open circles represent the water molecules. The large circle represents the micelle surface. Part A, modified Dill–Flory model; part B, simplified fjord model; part C, idealized solvent-entrapment model.

and that there is no static quenching.[3b] Thus, during the excited-state lifetime, all sensitizers must have free access to bulk solvent-borne quenchers.

The fjord model (Figure 2B) could account for the solvent-accessibility results since it gives the solvent access to the sensitizer. A variation of the fjord model might involve fjords rapidly opening and closing. This dynamic fjord-entrapment model would also be consistent with our observed F's.

It is difficult to rationalize the $HgCl_x^{2-x}$ data with a fjord model. In particular, it is difficult to account for the observed facile quenching of a buried sensitizer by a bulky and charged water-borne $HgCl_3^-$ which must penetrate through a narrow fjord to quench. Further, with use of a simple geometric shielding model derived from the Dill–Flory structure of Figure 2A, the F values measured here are consistent with quenching by $HgCl_2$ and $HgCl_3^-$. It is difficult to envision how a fjord or fjord-entrapment model could provide such consistency.

We therefore conclude that a structure similar to the Dill–Flory model of Figure 2A currently provides the best picture of the predominant binding mode of Ru(II) and Os(II) photosensitizers to LS^- micelles. However, we cannot rule out some time-averaged combination of all three structures in Figure 2. In the subsequent discussion we principally use the model of Figure 2A, but with minor changes in semantics the other models of Figure 2 can be accommodated.

For the model of Figure 2A the metal center is located near the surface of the micelle to maximize ionic interactions between the negatively charged micelle surface and the metal ion. On the average, two ligands are buried in the hydrocarbon region to provide favorable hydrophobic interactions with the hydrocarbon chains. The third ligand is found in the Gouy–Chapman layer and is solvent accessible. Deactivation by the OH oscillators occurs via the exposed ligand.

The small perturbations from $F = {}^1/_3$ are due to shifts of different complexes to more or less solvent accessible locations. These shifts probably occur because of differences in the hydrophobic interactions between the ligands and the surfactant molecules.[4,5] Consider the values of F for $[Ru(phen)_3]^{2+}$ and the two dimethyl-substituted analogues, $[Ru(4,7\text{-}Me_2phen)_3]^{2+}$ and $[Ru(5,6\text{-}Me_2phen)_3]^{2+}$. As the number of methyl groups increases, increasing the hydrophobicity of the complex, F decreases. The increased hydrophobicity of the ligand favors a less solvent accessible site in the micelle. Also, the very low F's observed for the complexes with the Ph_2phen ligand arise because the very hydrophobic ligands favor deep burial in the hydrocarbon region. Quenching studies with solvent-borne $HgCl_x^{2-x}$ (x = 2, 3) quenchers demonstrate the very low accessibility of $[Ru(Ph_2phen)_3]^{2+}$ to bulk solvent-borne quenchers.[3b]

$[Ru(Clphen)_3]^{2+}$, $[Ru(Me_4phen)_3]^{2+}$, $[Ru(Phphen)_3]^{2+}$, $[Ru(bpy)_2(CN)_2]$, $[Ru(phen)_2(CN)_2]$, and $[Ru((PhSO_3)_2phen)_3]^{4-}$ have F's well above 0.33. For the Clphen complex, the polar Cl may favor extension of the complex into the aqueous region or local clustering of entrapped water molecules. The Me_4phen and Phphen complexes have such large error limits that quantitative comparisons are not possible. The cis-CN-substituted molecules are asymmetric. Given the high water solubility of most hexacyano metal complexes we would expect the CN side of these complexes to extend into the water. The high F's are consistent with this suggestion. Also, the cyanide ligands present an open face to the solvent which provides less overall shielding and increases the fraction of the complex accessible to the water. This orientation effect has also been observed in Cu^{2+} quenching experiments when the cyano complexes are used.[23,24]

Two possible reasons may be cited for the large F for $[Ru((SO_3Ph)_2phen)_3]^{4-}$. The negative charge on the ligands may sufficiently repel the LS^- to disrupt a tight micelle and thus permit penetration of the water around the complex. Conversely, the large size of the complex (14.5-Å radius) may leave large portions of the ligands in the solvent. Thus, this complex may assume a structure more nearly analogous to that of Figure 2B or a combination of parts B and C of Figure 2. In support of the latter argument, $[Ru((SO_3Ph)_2phen)phen_2]$ appears to exhibit a high F.

In the case of $[Cr(bpy)_3]^{3+}$, the excited state is metal-centered and possesses very little ligand character.[25] Deactivation via OH oscillators would have to occur through metal–H_2O coupling. Since the bpy ligands preclude close coupling between the metal center and the solvent, the small lifetime change must arise because of deactivation via solvent molecules in the second coordination sphere. The extra shielding present in the micelle case prevents the deactivation via a solvent pathway, and the lifetimes in the micelle cases are identical within experimental error.

Our approach appears to be unsuitable for even very long lived singlet excited states of organic molecules. Even the exceptionally long fluorescence lifetime of pyrene exhibits no appreciable solvent–deuterium effect which is a prerequisite for our approach. This is consistent with the well-known insensitivity of singlet-state lifetimes to deuterium effects even when the molecule is deuterated.[26]

Conclusions

We have presented a new method for assessing the average solvent accessibility of photosensitizers in micelles. This method should be equally applicable to many luminescent species bound

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to a variety of other organized media such as micelles, monolayers, bilayers, and vesicles. The assumptions required for the application of the method are not very stringent. Therefore, it should apply to luminescent probes bound to polymers, polyelectrolytes, crown ethers, cyclodextrins, and proteins, as well as to larger colloidal particles such as clays and latex microspheres. It should also work with a variety of covalently and ionically bound or adsorbed species on solid supports. These would include ion-exchange resins, zeolites, and chemically modified electrodes. The latter applications in particular should have important ramifications in catalysis and photoelectrochemistry. Our method is appropriate whenever there is a significant solvent–deuterium effect on the excited-state lifetime.

In particular, we report on a series of Ru(II) and Os(II) photosensitizers in NaLS micelles. We are able to use the resultant data to shed further light on the structure and interactions in the micelle–sensitizer complexes. Our method appears to be generally applicable to photosensitizers having charge-transfer excited states. The one attempt to apply the approach to a d–d excited state failed, presumably because the d–d state employed was too well shielded from solvent interactions. In many other cases, however, d–d excited states are very susceptible to deuterium perturbation, and our approach should be useful.[13,14]

Our method does not appear to be suitable for organic molecules exhibiting fluorescences due to the absence of a deuterium effect. Triplet states of organic molecules, in contrast, are very sensitive to deuterium effects.[27,28] In view of the great interest in organized systems involving room-temperature phosphorescence, we believe our methodology will be exceptionally useful in probing these systems.

Further work is underway with use of the deuterium isotope effect to explore the structure of transition-metal photosensitizers bound to a variety of organized media. In particular, we are attempting to verify that the assumptions of the model hold under a variety of conditions and that the resultant F's provide new and physically meaningful information about these systems.

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Registry No. $[Ru(bpy)_3]^{2+}$, 15158-62-0; $[Ru(Me_2bpy)_3]^{2+}$, 32881-03-1; $[Ru(phen)_3]^{2+}$, 22873-66-1; $[Ru(Clphen)_3]^{2+}$, 47860-47-9; $[Ru(Brphen)_3]^{2+}$, 66908-45-0; $[Ru(Mephen)_3]^{2+}$, 14975-39-4; $[Ru(4,7\text{-}Me_2phen)_3]^{2+}$, 24414-00-4; $[Ru(5,6\text{-}Me_2phen)_3]^{2+}$, 14975-40-7; $[Ru(Me_4phen)_3]^{2+}$, 64894-64-0; $[Ru(Phphen)_3]^{2+}$, 66862-15-5; $[Ru(phen)_2(Ph_2phen)]^{2+}$, 63373-03-5; $[Ru(Ph_2phen)_3]^{2+}$, 63373-04-6; $[Ru(phen)_2((PhSO_3)_2phen)]$, 63244-80-4; $[Ru((PhSO_3)_2phen)_3]^{4-}$, 63244-81-5; $[Ru(bpy)_2(CN)_2]$, 58356-63-1; $[Ru(phen)_2(CN)_2]$, 14783-57-4; $[Os(phen)_3]^{2+}$, 31067-98-8; $[Os(terpy)_2]^{2+}$, 85452-91-1; $[Os(bpy)_2(CNMe)_2]^{2+}$, 81831-21-2; $[Os(phen)_2DPPM]^{2+}$, 75446-24-1; $[Os(phen)_2DPPene]^{2+}$, 75446-26-3; $[Cr(bpy)_3]^{3+}$, 15276-15-0; NaLS, 151-21-3; H_2O, 7732-18-5; D_2O, 7789-20-0; D_2, 7782-39-0; pyrene, 129-00-0.

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(29) **Note Added in Proof**: A large deuterium isotope effect on the fluorescence of phthalimides in water and in NaLS solutions has been reported (Viktorova, E. N.; Veselova, T. V.; Snegov, M. I.; Cherkasov, A. S. *Opt. Spectrosc. (USSR)* **1982**, *53* (*2*), 148). These molecules are very asymmetric, have an exchangeable proton, and can exhibit strong hydrogen bonding in a restricted region. It is, therefore, unclear that they will respond uniformly to OH or OD groups in contact with different regions. Indeed, it seems likely that the isotope effect will be strongest in regions of strong hydrogen bonding. As a consequence our counting procedure may not work for analyzing the overall exposure of the probe to the solvent, although it may be useful for assessing the exposure of a given region. Our analysis is still correct for our more nearly spherical probes.