Singlet Oxygen (¹Δ$_g$) Production by Ruthenium(II) Complexes in Microheterogeneous Systems[†]

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Singlet oxygen (O$_2$(¹Δ$_g$)) production and quenching in homogeneous and microheterogeneous media are reported for two anionic ruthenium(II) complexes ([RuL$_2$L′]²⁻ (where L stands for (1,10-phenanthroline-4,7-diyl)bis(benzenesulfonate) (pbbs) and L′ stands for *N*-(1,10-phenanthrolin-5-yl)acetamide (paa) or *N*-(1,10-phenanthrolin-5-yl)tetradecanamide (pta)) and for the cationic complex [Ru(bpy)$_3$]²⁺ (bpy: 2,2′-bipyridine). Comparative results of photosensitized ¹O$_2$ generation in micelles, reverse micelles, and microemulsions reveal that the nature of the ligands and the size and charge of the [RuL$_3$] complexes are important factors affecting their effective location and ¹O$_2$ production in these media. The rate constants of quenching of the excited state [RuL$_3$]* by molecular oxygen (k_q) are in the range of $(1-3) \times 10^9$ M⁻¹ s⁻¹. The emission lifetimes of [RuL$_3$]* and k_q values depend on the nature of the ligand and on the medium. The complexes are stable singlet oxygen sensitizers, with quantum yields of singlet oxygen production (Φ$_Δ$) in air-equilibrated solutions between 0.30 and 0.75. The efficiency of ¹O$_2$ formation (i.e., the fraction of triplet excited states quenched by oxygen yielding ¹O$_2$, $f_Δ^T$) is a valuable probe of the interactions of the [RuL$_3$] complexes with micelles and microemulsions. The highest $f_Δ^T$ values (≥0.90) were observed in micellar media based on surfactants bearing a charge opposite to that of the [RuL$_3$] complex. In the microheterogeneous systems investigated, the most probable location of the [RuL$_3$] sensitizers is the micellar interfacial region.

I. Introduction

Coordination compounds of Ru(II) with polyazaheterocyclic ligands ([RuL$_3$]) have different applications based on their unique features. Complexes that are stable, inert, water soluble, and have long luminescence lifetimes are extremely valuable as optical sensors (optodes),[1−3] as luminescent probes for investigating microheterogeneous systems,[4,5] as probes for biological systems,[6−8] and as singlet oxygen (¹O$_2$) sensitizers.[9−15] Some Ru(II) complexes that recognize and react with nucleic acids are also regarded as new diagnostic and therapeutic agents.

The interaction of sensitizers with microheterogeneous systems such as micelles, bilayers, colloids, and biopolymers usually results in dynamic binding, and the spectroscopic properties of the sensitizer depend on its location. The distribution of sensitizers in these microheterogeneous environments is markedly influenced by the hydrophobic/hydrophilic character of the surrounding medium and by the presence of electrostatically charged interfaces. Ru(II) complexes usually show a strong interaction with anionic, cationic, and nonionic surfactants, due to a combination of hydrophobic and electrostatic interactions.[16−19] Their luminescence lifetimes generally increase in the presence of the structured microenvironment provided by the surfactants, due to the protection of the complex from quenchers, as well

as to the increased microviscosity that slows down collisional deactivation of the excited species (e.g., quenching by oxygen) by restricting their diffusive motions.

Singlet oxygen production is sensitive to the interfacial characteristics of the microheterogeneous system and the specific microdomain that hosts a sensitizer;[20] therefore, it can be used to probe the surroundings of the sensitizer and its location with respect to the surfactant assembly structure and its interface. Although the quantum yields of ¹O$_2$ production have been determined for some Ru(II)−polypyridyl complexes in homogeneous media[11,13,14] and ¹O$_2$ sensitization by these complexes linked to DNA has been investigated,[9] no data are available in micellar media or microemulsions, which are often used to provide simple models for mimicking cellular environments (e.g., membranes).[21] To examine the effect of the environment on the photosensitized generation of ¹O$_2$, we selected two anionic complexes [Ru(pbbs)$_2$(paa)]²⁻ and [Ru(pbbs)$_2$(pta)]²⁻, which show a strong binding to surfactants (Scheme 1).[19] For comparison purposes, the prototypical cationic complex [Ru(bpy)$_3$]²⁺ was also investigated.

II. Materials and Methods

Materials. The complexes [Ru(pbbs)$_2$(paa)]²⁻ and [Ru(pbbs)$_2$(pta)]²⁻ (pbbs, (1,10-phenanthroline-4,7-diyl)bis(benzenesulfonate; paa, *N*-(1,10-phenanthrolin-5-yl)acetamide; and pta, *N*-(1,10-phenanthrolin-5-yl)tetradecanamide) were prepared as previously described,[19] and the chloride salt of [Ru(bpy)$_3$]²⁺ was purchased from Aldrich and used as received. Rose bengal (RB, Aldrich,
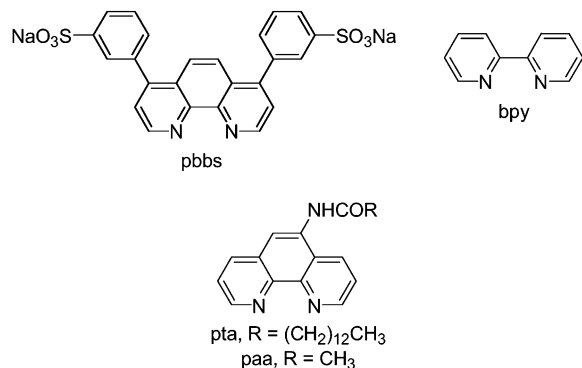
SCHEME 1: Chemical Structure of the Polyazaheterocyclic Ligands of the Ruthenium(II) Complexes Investigated

pbbs

bpy

NHCOR

pta, R = $(CH_2)_{12}CH_3$
paa, R = CH_3

97%) was purified by column chromatography on a silica gel 60 column (dichloromethane/methanol 9:1 as eluent) and a Sephadex G25 column (5×10^{-4} M aqueous NH_4OH as eluent). RB was used as a reference sensitizer.

The following surfactants, cetyltrimethylammonium chloride (CTAC, Fluka), bis-(2-ethylhexyl)sodium sulfosuccinate (AOT, Fluka), Triton X-100 (TX, Fluka), and sodium dodecyl sulfate (SDS, Sigma), were used as received. The deuterated solvents (D_2O and CD_3OD) were from Euriso-top (CEA, France), and the organic solvents isooctane (ISO), cyclohexane (CH), and 1-butanol (BuOH) were from Roth. Purified water (tridistilled quality) was obtained from a Purelab system (USF).

Micellar Media and Microemulsions. Stock solutions containing RuL_3 in water or D_2O were prepared. Micellar solutions contained 0.2 M SDS, CTAC, or TX (critical micellar concentrations (cmc): 8.3×10^{-3}, 1.4×10^{-3}, and 2.6×10^{-4} M, respectively).[22] The composition of the oil-in-water (o/w) microemulsions in weight percent was 8% surfactant (SDS or CTAC), 16% cosurfactant (BuOH), 72% D_2O, and 4% oil phase (CH).[23] In ISO, AOT aggregated into reverse micelles, which were capable of solubilizing large quantities of water into the inner polar core. The size of micelles depended on the molar ratio water/AOT ($w = [H_2O]/[AOT]$).[24] The AOT micelles were prepared with a $w = 40$, employing tridistilled water.

The final $[RuL_3]$ concentrations ranged from 10 to 45 μM, which gave adequate emission intensities and $^1O_2$ luminescence signals (vide infra) and ensured no multiple sensitizer occupation of the micelles. The solutions were gently hand-shacked at room temperature. All measurements were made at 23 $\pm$ 2 °C. The deaerated solutions were prepared under Ar employing a glovebox GB 2201-C (Mecaplex, Switzerland) with an integrated gas circulation system.

Emission Measurements. Emission measurements were carried out using a time-correlated single photon counting FL-900/FS-900 luminescence spectrometer (Edinburgh Instruments, U.K.). For lifetime measurements, excitation of the $[RuL_3]$ complexes was performed employing the 337 nm line of a nitrogen-filled discharge lamp and the luminescence signal was monitored at 620 nm. Luminescence lifetimes were calculated from the single exponential decay profiles using the original Edinburgh Instruments software. No deconvolution of the instrumental response was necessary. The corrected emission spectra were obtained by excitation at 490 nm.

Luminescence lifetimes in air (τ) and in Ar-saturated solutions (τ_0) were used to determine the quenching rate constants of the lowest excited state of the complexes by molecular oxygen (k_q). The temperature and the atmospheric pressure in the laboratory were measured with an electronic barometer (Oregon Scientific).

The O_2 concentrations were calculated from an Ostwald or Bunsen coefficient[25,26] taking into account the barometric pressure, the experimental temperature, and the vapor pressure of the solvent. It was assumed that the solubilities of oxygen in CH_3OH and CD_3OD, H_2O and D_2O, and CTAB and CTAC micelles were the same within each pair. Calculations led to values of ca. 1.9×10^{-3}, 2.9×10^{-4}, and 3.4×10^{-4} M in air-saturated methanol, water, and both SDS and CTAC micellar solutions, respectively. In micellar media, k_q values could only be calculated with two points (i.e., using data for air- and Ar-saturated solutions) because the solutions could not be saturated with oxygen by bubbling (foaming), and the glovebox could not be saturated with oxygen for safety reasons.

Determination of Quantum Yields of Singlet Oxygen Production. The $^1O_2$ luminescence in the near-infrared (NIR) (at about 1270 nm) (eq 1) was monitored for determining Φ_Δ of the $[RuL_3]$ complexes.

$$^1O_2 \xrightarrow{k_e} {}^3O_2 + h\nu'' \tag{1}$$
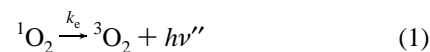
The home-built equipment used for the steady state NIR emission measurements was previously described.[27] Briefly, the sample solution in a quartz cuvette (1 × 1 cm) was irradiated with a xenon/mercury lamp (1 kW) through a water filter, focusing optics, and a monochromator. The $^1O_2$ luminescence was collected with a mirror, chopped at 11 Hz, and after it was passed through a focusing lens, a cutoff filter (1000 nm), and an interference filter (1271 nm), it was detected at 90° with respect to the incident beam using a custom-built cooled germanium photodiode or a photomultiplier (Hamamatsu R5509-42). The $[RuL_3]$ sensitizers were always irradiated at 436 nm (λ) and the reference (RB) at 547 nm (λ^R). The incident radiant power (W, in mW) on the sample cell was measured with a thermopile (Laser Instrumentation, model 154) and used to calculate the relative incident photonic rates ($P_0/P_0^R = W \lambda/W^R \lambda^R$).

The luminescence signals at 1270 nm of the $[RuL_3]$ solutions[13] in air-saturated (S_m^{air}) and in Ar-saturated solutions (E_0) and of a solution containing the reference (S_e^R) were recorded under continuous irradiation for a minimum of 3 min for each sample, alternating between reference and sample with matched absorbances (0.5−1.0). Absorption spectra of all of the solutions under study were recorded before and after each experiment on a Varian Cary 50 spectrophotometer. The absorption spectra of $[RuL_3]$ and RB showed no changes, and both gave stable signals during the irradiation period under the experimental conditions used in this work.

Because of the contribution of the emission tail of the $[RuL_3]$ to the luminescence signal at 1270 nm, the $^1O_2$ luminescence signal (S_e) was calculated using eq 2 (for a more detailed description of the photophysical processes involved, see ref 13).

$$S_e = S_m^{air} - E_0 (\tau/\tau_0) \tag{2}$$

Under the experimental conditions used, $^1O_2$ quenching by the $[RuL_3]$ was found to be negligible as compared to $^1O_2$ quenching by the solvent and Φ_Δ could be calculated using eq 3[27]

$$\Phi_\Delta = \Phi_\Delta^R \frac{S_e P_0^R}{S_e^R P_0} \tag{3}$$

where Φ_Δ^R (0.75 in water and 0.76 in microheterogeneous

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TABLE 1: Absorption Maxima of the RuL$_3$ Complexes in the Investigated Media

	λ_{max} (nm)[a]									
RuL$_3$	ISO[b]	BuOH[b]	CD$_3$OD	D$_2$O	CTAC[e]	CTAC o/w[f]	SDS[e]	SDS o/w[f]	AOT[g]	TX[e]
[Ru(bpy)$_3$]$^{2+}$	276	285		283	284	284	288	287	291	289
			437[d]	437						
		453	449[c,d]	452[c]	452	453	450	453	454	452
[Ru(pbbs)$_2$(paa)]$^{2-}$	275	285	278	272	279	278	278	275	277	279
			437	436	443	441	439	439	444	442[c]
		478	461[c]	458[c]			461[c]			460
[Ru(pbbs)$_2$(pta)]$^{2-}$	277	275	277	274	280	276	278	275	278	272
			434	437		438	436	436		440[c]
		459	458[c]	461[c]	463		461[c]		461	461

[a] ±2 nm. [b] Low solubility. [c] λ_{max}, in general broad absorption band between 380 and 550 nm, with no discernible maximum. [d] Ref 13. [e] Micelles. [f] Microemulsion. [g] Reverse micelles.
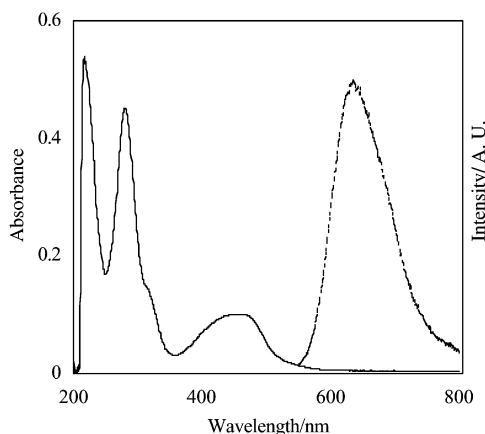

Figure 1. Absorption and emission spectra of [Ru(pbbs)$_2$(pta)]$^{2-}$ in CTAC (0.2 M) micellar media.

media)[28] is the quantum yield of ^{1}O$_2$ production by the reference sensitizer (RB).

III. Results

Absorption and Emission Spectra. The absorption spectra of [RuL$_3$] complexes typically display bands in two regions (Figure 1 and Table 1): at higher energy (approximately 280 nm), an intense band may be ascribed to the ligand-centered $\pi-\pi^*$ transition, whereas the metal-to-ligand charge transfer (MLCT) band appears in the visible region of the spectrum. In some cases, two maxima (between 434 and 463 nm) may be distinguished in the MLCT band, but most often, the band is rather flat (Figure 1). Replacement of bpy ligands in [Ru(bpy)$_3$]$^{2+}$ by phenanthroline (phen) ([Ru(pbbs)$_2$(paa)]$^{2-}$ and [Ru(pbbs)$_2$(pta)]$^{2-}$) causes a slight red shift of the MLCT band (ca. 10 nm), but the corresponding λ_{max} does not vary significantly with the substituents on the ligand (compare [Ru(pbbs)$_2$(paa)]$^{2-}$ to [Ru(pbbs)$_2$(pta)]$^{2-}$, Table 1) or with the nature of the medium.

Excitation of [RuL$_3$] complexes is followed by a fast intersystem crossing (ISC) leading to the formation of the MLCT excited state with a dominant triplet character (^{3}[RuL$_3$]*):

$$[RuL_3] + h\nu \rightarrow {}^1[RuL_3]^* \xrightarrow{k_{ISC}} {}^3[RuL_3]^* \qquad (4)$$
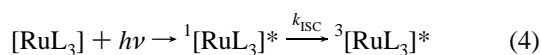
Competing monomolecular processes from ^{3}[RuL$_3$]* are radiative (r) and nonradiative (nr) deactivation:

$$^3[RuL_3]^* \xrightarrow{k_r} [RuL_3] + h\nu' \qquad (5)$$

$$^3[RuL_3]^* \xrightarrow{k_{nr}} [RuL_3] \qquad (6)$$
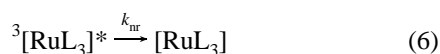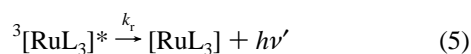
All of the complexes show a strong emission band in solution when irradiated in the MLCT absorption band (Figure 1), and their luminescent properties are perturbed in the presence of surfactants. The emission maxima vary in the range of 620−650 nm (Table 2). For ([Ru(bpy)$_3$]$^{2+}$, the emission maxima in the microheterogeneous media based on anionic surfactants are red-shifted as compared to water and methanol, with the largest shift (27 nm) being observed in the AOT reverse micelles. In cationic and nonionic systems, a slight hypsochromic shift was observed. In contrast, the emission maxima of the anionic [RuL$_3$] are red-shifted as compared to water and methanol in cationic (CTAC) and nonionic (TX) systems, whereas a small hypsochromic shift was observed in SDS micellar media (Table 2).

Emission Lifetimes and Quenching by Molecular Oxygen. The emission lifetimes of the investigated [RuL$_3$] were measured in Ar− (τ_0) and in air-saturated solutions (τ) (Table 2). In the absence of oxygen, lifetimes of the cationic [Ru(bpy)$_3$]$^{2+}$ are all ca. 1 μs in D$_2$O and in microheterogeneous media based on D$_2$O; however, the lifetime drops by 20% in CD$_3$OD. In contrast, the anionic [RuL$_3$] complexes display a 13% lower emission lifetime in D$_2$O as compared to CD$_3$OD and exhibit small changes in the investigated media (±0.6 μs). The significantly lower τ_0 values measured in AOT reverse micelles for both the cationic and anionic complexes may be due to the fact that these microheterogeneous systems were prepared with H$_2$O, where the emission lifetimes of the complexes are lower than in D$_2$O (see Table 2).[19,29]

The MLCT excited states of the complexes are quenched by molecular oxygen. Linear Stern−Volmer relationships (eq 7) were obtained in homogeneous solution:

$$\tau_0/\tau = 1 + k_q\tau_0[O_2] \qquad (7)$$

where τ_0 and τ are the emission lifetimes in the absence and presence of oxygen, respectively, and k_q is the global rate constant of quenching of ^{3}[RuL$_3$]* by O$_2$. Calculation of k_q requires the knowledge of the oxygen concentration in the corresponding medium. In contrast to homogeneous solutions and SDS or CTAC micellar media (Materials and Methods), the oxygen concentration is not available in microemulsions or TX and reverse AOT micelles. Therefore, k_q could not be evaluated in these media. Values of k_q are listed in Table 3. The values determined in this work in ionic micellar media are somewhat lower than those obtained previously.[19] However, it should be noted that a much higher (10 times) concentration of surfactant (0.2 M) was used in the present work, an increase in surfactant concentration leading to bigger aggregates, a larger volume of the dispersed micellar hydrophobic phase and thus to a higher oxygen concentration in the solution.

The observed quenching rate constants of the ^{3}[RuL$_3$]* by ^{3}O$_2$ are generally higher in aqueous solution than in CD$_3$OD

TABLE 2: Luminescence Maxima and Lifetimes of the RuL₃ Complexes in the Investigated Media[a]

RuL₃		CD₃OD	D₂O[b]	CTAC[c]	CTAC o/w[c]	SDS[c]	SDS o/w[c]	AOT[d]	TX[c]
[Ru(bpy)₃]²⁺	λ (nm)	623[g]	622[g]	623	620	637	645	649	620
	τ_0 (μs)[e]	0.79[g]	1.0[g] (0.61)[h]	1.0	1.0	0.99	0.94	0.60	1.0
	τ (μs)[f]	0.23[g]	0.56[g] (0.39)[i]	0.57	0.55	0.62	0.34	0.26	0.64
[Ru(pbbs)₂(paa)]²⁻	λ (nm)	622	629	634	638	619	620	633	630
	τ_0 (μs)[e]	7.5	6.4 (3.8)[i]	6.7	5.9	6.2	6.3	4.7	7.0
	τ (μs)[f]	0.29	1.3 (0.99)[i]	1.9	0.90	1.5	1.0	1.3	3.1
[Ru(pbbs)₂(pta)]²⁻	λ (nm)	620	624	635	630	619	619	628	630
	τ_0 (μs)[e]	7.0	6.1 (3.7)[i]	6.9	6.2	5.7	5.5	4.1	6.7
	τ (μs)[f]	0.30	1.6 (1.05)[i]	1.6	0.81	1.7	1.0	1.3	2.9

[a] $\lambda \pm 3$ nm, $\tau \pm 5\%$. [b] Values in parentheses are in H₂O. [c] Prepared with D₂O. [d] Reverse micelles prepared with H₂O and ISO. [e] Ar-purged solutions. [f] Air-equilibrated solutions. [g] Ref 13. [h] Ref 29. [i] Ref 19.
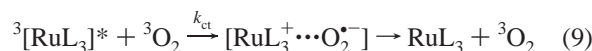
TABLE 3: Kinetic Constants k_q and k_{et} for the Deactivation of ³RuL₃* by O₂

RuL₃	k^a (10^9 M⁻¹ s⁻¹)	CD₃OD	D₂O	CTAC/D₂O	SDS/D₂O
[Ru(bpy)₃]²⁺	k_q	1.9[b]	3.3[b]	2.3	1.8
	k_{et}	1.9	1.6	1.5	1.7
[Ru(pbbs)₂(paa)]²⁻	k_q	1.5	2.1	1.1	1.5
	k_{et}	1.2	1.2	1.1	1.0
[Ru(pbbs)₂(pta)]²⁻	k_q	1.5	1.6	1.3	1.4
	k_{et}	1.1	0.77	1.3	1.0

[a] ±15%. [b] Ref 13.

and micelles. Such a dependence of k_q with the media has already been reported for several [RuL₃] complexes.[13,19,30]

Singlet Oxygen Production. In aerobic solutions, the quenching of ³[RuL₃]* by molecular oxygen (O₂(³Σ_g⁻), ³O₂) can occur via energy transfer to generate ¹O₂ (eq 8), charge transfer to form RuL₃⁺ and the superoxide radical anion (eq 9), or physical deactivation (i.e., oxygen-enhanced ISC, eq 10).

$$^3[RuL_3]^* + {}^3O_2 \xrightarrow{k_{et}} [RuL_3] + {}^1O_2 \quad (8)$$

$$^3[RuL_3]^* + {}^3O_2 \xrightarrow{k_{ct}} [RuL_3^+ \cdots O_2^{\bullet -}] \rightarrow RuL_3 + {}^3O_2 \quad (9)$$

$$^3[RuL_3]^* + {}^3O_2 \xrightarrow{k_{dO_2}} [RuL_3] + {}^3O_2 \quad (10)$$

Taking into account reactions 8–10, the quantum yield of ¹O₂ production (Φ_Δ) is defined as:[31]

$$\Phi_\Delta = \Phi_T \phi_{et} = \Phi_T \frac{k_{et}[O_2]}{k_r + k_{nr} + k_q[O_2]} \quad (11)$$

where Φ_T is the quantum yield of triplet formation (ISC), ϕ_{et} is the efficiency of energy transfer from ³[RuL₃]* to ³O₂, and $k_q = k_{et} + k_{dO2} + k_{ct}$.

Equation 11 can also be written as

$$\Phi_\Delta = \Phi_T P_{O_2}^T f_\Delta^T \quad (12)$$

where $P_{O_2}^T$ (the proportion of triplet excited states quenched by ³O₂) is given by:

$$P_{O_2}^T = \frac{k_q[O_2]}{k_r + k_{nr} + k_q[O_2]} = 1 - \frac{\tau}{\tau_0} \quad (13)$$

with $\tau_0 = 1/(k_r + k_{nr})$ and $\tau = 1/(k_r + k_{nr} + k_q[O_2])$, and $f_\Delta^T (= k_{et}/k_q)$ is the fraction of triplet excited states quenched by ³O₂ yielding ¹O₂.

The quantum yield of triplet formation of most [RuL₃] in solution is known to be close to unity.[13,32–35] The quantum yields

of singlet oxygen production (Φ_Δ) and $P_{O_2}^T$ were experimentally determined (eqs 3 and 13, respectively), then f_Δ^T could be calculated using eq 12. The values of these parameters in air-equilibrated media are listed in Table 4 and shown in Figure 2.

IV. Discussion

Absorption and Emission Characteristics. The investigated complexes display a typical MLCT band in the visible region of the absorption spectrum. No significant information with respect to the localization of the complexes in the microheterogeneous systems could be obtained considering only the data in Table 1, due to the small effects of the media on the absorption spectra of the complexes. The emission properties of the ³MLCT excited state of the [RuL₃] complexes depend on the type of ligand and on the microenvironment around the complex. In general, the emission maximum of the complexes investigated in this work shifts to the red in micellar media based on surfactants with a charge opposite to that of the complex, in comparison with water (Section III, Table 2). This result may be interpreted by a closer association between the [RuL₃] complex and the micellar interface of opposite charge. The electron-withdrawing pbbs ligands strongly increase the polarity of the metal-to-ligand charge transfer excited state of the metal complex as compared to its ground state. A strong interaction with surfactants of opposite charge stabilizes such excited state so that a bathochromic shift in the emission band is observed (even for the homoleptic [Ru(bpy)₃]²⁺ complex, Table 2).

In all of the experiments, the surfactant concentration (0.2 M) has been selected to be much larger than that of the Ru(II) sensitizers (≤45 μM). Such a situation ensures single occupancy of the micelles and yields exponential emission decay profiles for the metal dye, which turn out to be multiexponential functions below and slightly above the surfactant cmc as a consequence of premicellization of surfactant molecules around the [RuL₃] complex.[19] The presence of phenyl substituents at positions 4 and 7 on the phen ligand increases the lifetime of the complex (as compared to [Ru(bpy)₃]²⁺ or [Ru(phen)₃]²⁺), as it was reported previously.[19,36] This result is related to the lower value of k_{nr} calculated for the complexes with phenyl substituents. The luminescence lifetimes of the investigated pbbs chelates (Table 2) show a ca. 10% increase in the presence of oppositely charged and neutral (TX) micelles. This fact lends further support to the proposed interaction since it provides partial protection from the water molecules,[19] and it is known that the O–H oscillators of the solvent molecules provide a nonradiative deactivation pathway for the electronically excited Ru(II) polypyridyls. In the presence of oxygen, the emission lifetimes decrease considerably (Table 2). The longer-lived anionic complexes are more efficiently quenched by oxygen than [Ru(bpy)₃]²⁺ (see $P_{O_2}^T$ values, Table 4), so that their

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TABLE 4: Parameters for $^1O_2$ Production by the Investigated RuL$_3$ Complexes in Air-Equilibrated Media[a]

RuL$_3$		CD$_3$OD	D$_2$O	CTAC	CTAC o/w[b]	SDS[b]	SDS o/w[b]	AOT[c]	TX[b]
[Ru(bpy)$_3$]$^{2+}$	Φ_Δ	0.73[d]	0.22[d]	0.30	0.30	0.34	0.51	0.52	0.33
	$P^T_{O_2}$	0.71[d]	0.46[d]	0.44	0.46	0.38	0.63	0.57	0.39
	f^T_Δ	**1.0**[d]	0.48[d]	0.67	0.65	**0.90**	0.81	**0.91**	0.85
[Ru(pbbs)$_2$(paa)]$^{2-}$	Φ_Δ	0.75	0.44	0.74	0.73	0.50	0.60	0.42	0.51
	$P^T_{O_2}$	0.96	0.80	0.72	0.85	0.76	0.83	0.72	0.56
	f^T_Δ	0.78	0.55	**1.0**	0.86	0.66	0.73	0.58	**0.90**
[Ru(pbbs)$_2$(pta)]$^{2-}$	Φ_Δ	0.73	0.36	0.74	0.74	0.51	0.58	0.45	0.55
	$P^T_{O_2}$	0.96	0.74	0.77	0.87	0.70	0.82	0.68	0.57
	f^T_Δ	0.76	0.48	**0.98**	0.85	0.73	0.71	0.67	**0.98**

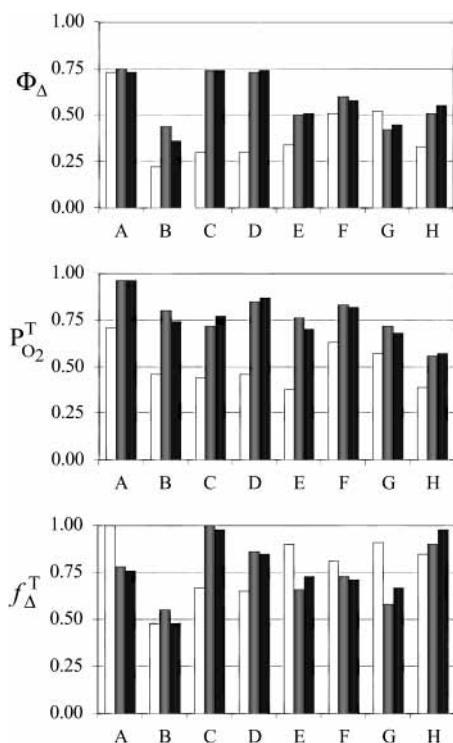[a] ±10%. [b] Prepared with D$_2$O. [c] Prepared with H$_2$O and ISO. [d] Ref 13.

Figure 2. Quantum yield of singlet oxygen production (Φ_Δ), proportion of excited triplet states quenched by molecular oxygen ($P^T_{O_2}$) and fraction of excited triplet states quenched by molecular oxygen yielding singlet oxygen (f^T_Δ) for [Ru(bpy)$_3$]$^{2+}$ (white bars), [Ru(pbbs)$_2$(paa)]$^{2-}$ (grey bars), and [Ru(pbbs)$_2$(pta)]$^{2-}$ (black bars) in various media (A, CD$_3$OD; B, D$_2$O; C, CTAC micelles; D, CTAC o/w microemulsion; E, SDS micelles; F, SDS o/w microemulsion; G, AOT reverse micelles; and H, TX micelles).

luminescence lifetime shows a more pronounced diminution in the presence of oxygen.

Singlet Oxygen Production. The data in Table 4 and Figure 2 demonstrate that the parameters of $^1O_2$ production depend on the charge of the complex and on the media. Under our experimental conditions, the behavior of the two anionic complexes is very similar (see Figure 2, gray and black bars), independently of the presence of the long alkyl chain on ([Ru(pbbs)$_2$(pta)]$^{2-}$. It has been established previously for [Ru(bpy)$_3$]$^{2+}$ (and other [RuL$_3$] complexes) that the quenching of ^{3}[RuL$_3$]* by $^3O_2$ occurs exclusively by energy transfer (reaction 8) in methanol ($f^T_\Delta = 1.0$) and that it is highly sensitive to the particular solvating properties of water.[13] Although energy transfer is not the only quenching process involved in water ($f^T_\Delta = 0.48$),[12,13] no redox products were detected. Presumably, charge transfer quenching occurs but is followed by back electron transfer (reaction 9) faster than escape from the solvent cage, the net result being an enhanced ISC to the ground state.

In the case of [Ru(pbbs)$_2$(paa)]$^{2-}$ and [Ru(pbbs)$_2$(pta)]$^{2-}$, a similar trend was observed with f^T_Δ values of approximately 0.5 in water (Table 4) and higher values in methanol. However, the charge transfer contribution to the quenching of ^{3}[RuL$_3$]* by $^3O_2$ in methanol ($f^T_\Delta = 0.76-0.78$) is more important than in the case of [Ru(bpy)$_3$]$^{2+}$ ($f^T_\Delta = 1.0$). This fact is probably due to the slightly higher reducing power of the photoexcited Ru(II)−pbbs complexes as compared to *[Ru(bpy)$_3$]$^{2+}$.[19] Because of its long alkyl chain, [Ru(pbbs)$_2$(pta)]$^{2-}$ aggregates in aqueous solution when its concentration increases above 1 μM and is fully aggregated at concentrations higher than 50 μM where a plateau is observed for the emission lifetimes.[19] Values of Φ_Δ could not be determined for this complex in the absence of aggregation (concentration <1 μM) due to very low $^1O_2$ luminescence signals under these conditions. However, comparison with [Ru(pbbs)$_2$(paa)]$^{2-}$, which bears a methyl group instead of a long alkyl chain (Scheme 1) and therefore does not aggregate, shows that aggregation of the complex leads only to a small decrease of $P^T_{O_2}$, Φ_Δ, and f^T_Δ (Table 4). We also determined $P^T_{O_2}$ for [Ru(pbbs)$_2$(pta)]$^{2-}$ in H$_2$O in the absence of aggregation and when it was fully aggregated and found a decrease of $P^T_{O_2}$ of about 10%. Therefore, we may conclude that aggregation leads to some protection of the [Ru(pbbs)$_2$(pta)]$^{2-}$ excited state from oxygen quenching, as already proposed.[19]

In the microheterogeneous media, the contribution of energy transfer to the quenching by oxygen of the MLCT excited states (f^T_Δ) of all of the complexes investigated ranges from 58 to 100%, i.e., higher than in water (Table 4). The analysis of the values of the parameters for $^1O_2$ production in microheterogeneous systems (Table 4) leads to the following considerations:

(i) Values of f^T_Δ are equal to or exceed 0.90 in micellar media based on surfactants bearing a charge opposite to that of the [RuL3] complex: that is, for [Ru(bpy)$_3$]$^{2+}$ in SDS micelles and AOT reverse micelles ($f^T_\Delta = 0.90-0.91$) and for [Ru(pbbs)$_2$(paa)]$^{2-}$ and [Ru(pbbs)$_2$(pta)]$^{2-}$ in CTAC micelles ($f^T_\Delta = 0.98-1.0$). These observations, together with the values of the quenching rate constants of the ^{3}[RuL$_3$]* by $^3O_2$ (k_q), which decrease slightly in going from aqueous solution to micelles (Table 3), suggest a reduced accessibility to water for the excited state of the [RuL$_3$] complexes in the oppositely charged surfactant media. This conclusion is in agreement with previous results obtained from emission experiments. Hauenstein et al.[37] proposed that the fractional exposure of [Ru(bpy)$_3$]$^{2+}$ to water is 0.3 in SDS micelles and that the complex ions are located in the vicinity of the Stern layer, where they experience electrostatic interactions with the anionic groups of the SDS micelles.[38−40] It is probable that the location of [Ru(bpy)$_3$]$^{2+}$ in the anionic AOT micelles is similar. A fractional exposure to water of 0.27 and 0.24 in CTAB was calculated for [Ru(pbbs)$_2$(paa)]$^{2-}$ and [Ru(pbbs)$_2$(pta)]$^{2-}$, respectively.[19] If the [RuL$_3$] complexes are located within the interfacial region of

the micelles, where the charge transfer interactions are less favored than in water, there is a high probability that quenching through energy transfer in the collision complex will occur before [RuL$_3$] and $^3O_2$ diffuse apart. In this case, close values of k_q and k_{et} are observed (Table 3).

(ii) In the four component o/w microemulsions based on surfactants bearing a charge opposite to that of the [RuL3] complex, values of f_Δ^T are lower (0.81−0.86) than in corresponding micellar solutions. Therefore, the quenching mechanism is affected by the modification of the nature of the interfacial region where most of the cosurfactant of the microemulsions (butanol) is located,[41] allowing some penetration of water molecules.

(iii) In nonionic TX micellar solutions, the cationic and especially the anionic complexes show a high f_Δ^T value (0.85 and 0.90−0.98, respectively). Because of the more complex structure of the surfactant (with an aliphatic chain and phenyl groups in the hydrophobic core and a hydrophilic ethoxyalkyl chain), the probable binding site and location of the complexes are controlled by nonelectrostatic interactions.[16,19] It was proposed that [Ru(bpy)$_3$]$^{2+}$ does not (or weakly) interact with nonionic micelles and that the complex is solvated by H$_2$O rather than by TX.[16] The very small spectral shift of the emission maximum relative to water and the similar τ_0 values (Table 2) would support this hypothesis. However, the much higher value of f_Δ^T in TX micelles as compared to water shows that interaction with the micellar interface does occur. The fractional exposures to water of [Ru(pbbs)$_2$(paa)]$^{2-}$ and [Ru(pbbs)$_2$(pta)]$^{2-}$ in TX micelles were calculated to be 0.52 and 0.29, respectively.[19] Because of the presence of the amphiphilic phenyl-sulfonated phenanthroline ligands, both hydrophobic and hydrophilic interactions are favored and the complexes probably interact with the hydrocarbon−ethoxyalkyl interface of the micelle. The presence of the long alkyl chain in [Ru(pbbs)$_2$(pta)]$^{2-}$ could pull this complex deeper into the hydrocarbon core of the TX micelle and be responsible for the observed larger red shift in the emission maximum and the larger value of f_Δ^T for [Ru(pbbs)$_2$(pta)]$^{2-}$ than for [Ru(pbbs)$_2$(paa)]$^{2-}$. The excited state lifetimes of the anionic [RuL$_3$] complexes in air-saturated nonionic micellar solutions (∼3.0 μs) are about twice the value in water (1.3−1.6 μs) (Table 2) and $P_{O_2}^T$ values decrease by about 40% in the presence of nonionic TX micelles. The high local viscosity around the complex could restrict the oxygen accessibility to the MLCT states. Therefore, the Φ_Δ values are lower than the values in cationic micelles despite the almost similar values of f_Δ^T.

(iv) Complexes in media based on surfactants with the same charge as the complex, as [Ru(bpy)$_3$]$^{2+}$ in CTAC micelles and [Ru(pbbs)$_2$(paa)]$^{2-}$ and [Ru(pbbs)$_2$(pta)]$^{2-}$ in SDS and AOT, exhibit the lowest f_Δ^T in the investigated microheterogeneous systems. The large size of the anionic Ru(II) complexes, the absence of favorable electrostatic interaction with the anionic micelles, and the relative high exposure of the complexes to water in SDS micelles (0.59 and 0.72 for [Ru(pbbs)$_2$(paa)]$^{2-}$ and [Ru(pbbs)$_2$(pta)]$^{2-}$, respectively)[19] explain the lower efficiencies of singlet oxygen production by the anionic complexes in the presence of the anionic surfactants. Because of the insolubility of [RuL$_3$] in ISO and their solubility in water, it is probable that the anionic [RuL$_3$] is confined in the inner aqueous polar core of the AOT/ISO reverse micelles. If the oxygen solubility in the inner water pools is considered similar to that in bulk water, k_q and k_{et} could be estimated to be ca. 1.9 × 10^9

and 1.2 × 10^9 M^{-1} s^{-1}, respectively, for both complexes, indicating that they may be located in the same region of the micelle.

In conclusion, the nature of the ligands and the size and charge of the [RuL$_3$] complex are important factors affecting $^1O_2$ production in microheterogeneous media. The efficiency of $^1O_2$ formation (f_Δ^T) is a valuable probe of [RuL$_3$] interactions with micelles and microemulsions. The determination of quantum yields of singlet oxygen generation by [RuL$_3$] and their localization when incorporated into organized media may provide a valuable tool for the interpretation of their photodynamic effect in vivo.

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