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ANNELIDES
VIII: LUMINESCENCE PROPERTIES OF AMPHIPHILIC COMPLEXES OF RUTHENIUM IN MICELLAR PHASES

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Summary

The photophysical properties of a new water-soluble amphiphilic ruthenium complex (I) of the annelide type are described. Luminescence measurements show that complex I forms mixed micelles with alkyl poly-oxyethylene glycol monoether surfactants. The local concentration of the photosensitizer I at the surface of the micelles was varied by changing the ratio of the concentration of I to the surfactant concentration. The quantum yield of luminescence and the lifetime of the excited state of the ruthenium derivative were determined at each concentration. The lifetime of the excited state of complex I is influenced by intramicellar self-quenching effects. Studies of the relative variations in the luminescence quantum yield and of the emission lifetime as functions of the local concentration of ruthenium enabled the self-quenching mechanism to be determined.

1. Introduction

The photochemical and photophysical properties of the complex tris(2,2'-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) have been extensively studied [1 - 12]. Its high absorption coefficients in the visible region and the photoredox properties of its excited state make this complex very attractive for solar energy conversion applications [9 - 15]. The collection efficiency of the photons would be greatly enhanced if the photosensitizer could be inserted into organized structures [12, 15 - 22]. Such supermolecular structures might facilitate energy migration from the point at which the photon is absorbed to the reaction centre where ionization and charge separation might take place (antenna effect). Ruthenium complexes substituted with long paraffinic tails have already been synthesized and organized phases have
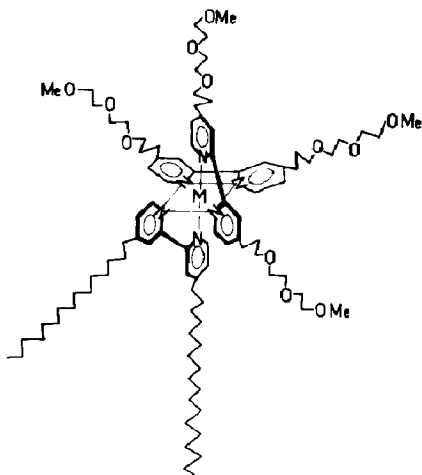
Fig. 1. Amphiphilic ruthenium complex I used in the present study.

been formed [23 - 33]. However, these complexes have a very limited solubility in water and in most cases only monolayers or mixed micelles were studied. A new amphiphilic ruthenium complex with both hydrophilic and hydrophobic chains (Fig. 1) has recently been described [34]. The structure of this complex is closely related to the annelide-type derivatives reported previously [35, 36]. The generic term annelide has been proposed to designate organometallic complexes which are able to form lyotropic or thermotropic mesophases. Examples of all the main organized phases, *i.e.* micelles [35, 36], lamellae [37], cylinders [38] and discotic liquid crystals [39], are known. In this paper the luminescence properties of the complex (4,4'-dinonadecyl-2,2'-bipyridine)bis(4,4'-di(10,13,16-trioxa-undecyl-2,2'-bipyridine)ruthenium dichloride (I) in both homogeneous and micellar media are described. Complex I was incorporated into micellar phases of non-ionic surfactants. The mean distance between the polar heads of the ruthenium derivatives was varied by changing the ratio of the concentration of the non-ionic cosurfactant to the concentration of I. The luminescence lifetime of the excited state and the corresponding quantum yield were determined at each concentration ratio. These two parameters are shown to be dependent on the local concentration of I. An intramicellar quenching process involving the interaction of the excited state with the unexcited polar heads is shown to take place.

2. Experimental details

The synthesis of I has been described elsewhere [34]. Tris(2,2'-bipyridine)ruthenium dichloride hexahydrate was prepared from $RuCl_3$ and 2,2'-bipyridine [40]. The surfactant n-dodecyl-hexaoxyethylene glycol monoether ($C_{12}E_6$) [41] was obtained from Nikkol (Japan) and cetyl-dotria-contaoxyethylene glycol monoether (Texofor A30 or $C_{16}E_{32}$) [42] was

obtained from A.B.M. Chemicals Ltd. (Gt. Britain). These chemicals were used without further purification.

The aqueous solutions were prepared using triply distilled water and were degassed by the freeze–pump–thaw technique under a vacuum of 10^{-4} Torr. The freeze–pump–thaw cycle was repeated five times before the cell was sealed under vacuum. The spectroscopic properties of the solutions prepared in this way were stable over long periods of time.

The quantum yields were recorded at 25 °C in cells of dimensions 10 mm × 10 mm using a FICA 55 absolute spectrofluorometer. The emission spectra were corrected up to 600 nm. The excitation wavelength was 450 nm. The optical densities of the solutions were between 0.09 and 0.15. Quantum yields were determined either from the area under the luminescence spectra or from the maximum heights of the emission curves; both methods gave identical results.

The lifetimes were determined by the single-photon technique [43]. The source was a hydrogen flash lamp (6 - 8 bar). The excitation wavelength of 450 nm was selected using a Jobin–Yvon H-10 grating monochromator. The emission at right angles was detected using a high gain RCA 8850 photomultiplier. The impulses were analysed using a time–amplitude converter (Ortec components) and were collected using an Intertechnique 400-channel analyser. A Kodak Wratten filter 23A was placed in front of the photomultiplier to eliminate the scattered light. The luminescence decay obeyed a single-exponential law $I(t) = I(0) \exp(t/\tau)$, and therefore the lifetime could be calculated directly from the slope of the plot of ln I versus time.

The experimental conditions for the light scattering measurements have been described elsewhere [34].

3. Results

It has been shown by surface tension measurements that the amphiphilic ruthenium complex I does not form micelles in aqueous solution in the concentration range 10^{-8} - 10^{-4} M [34]. However, I can be incorporated into preformed non-ionic micelles using cosurfactants [34]. The photophysical properties of annelide I and of the unsubstituted complex $[\text{Ru(bpy)}_3]^{2+}$ in the presence and the absence of non-ionic micelles formed from $C_{12}E_6$ are compared in Table 1. The critical micellar concentration of $C_{12}E_6$ is 9.0 × 10^{-5} M [41]. Surfactant solutions with concentrations almost 100 times greater than the critical concentration were used. The addition of ruthenium complexes is not expected to change the critical micellar concentration (CMC) so dramatically that micelles would no longer be present. The quantum yield of luminescence and the emission lifetime of the unsubstituted complex are unchanged in the presence of the non-ionic micelles. This probably indicates that $[\text{Ru(bpy)}_3]^{2+}$ is not incorporated into the micelles. The behaviour of annelide I is very different; both the luminescence quantum yield ϕ and the emission lifetime τ of I are increased when the

TABLE 1

Luminescence quantum yields and emission lifetimes of complex I and of the corresponding unsubstituted homologue $Ru(bpy)_3Cl_2$ in pure water and in the presence of micellar phases of $C_{12}E_6$

	Quantum yield ϕ[a]		Luminescence lifetime τ (ns)	
	Without $C_{12}E_6$	With $C_{12}E_6$[b]	Without $C_{12}E_6$	With $C_{12}E_6$[b]
$Ru(bpy)_3Cl_2$	0.042	0.039	611	678
Annelide I	0.008	0.016	428	574

[a]The quantum yield of $[Ru(bpy)_3]^{2+}$ ($\phi = 0.042$ at 25 °C) was taken from ref. 44.
[b]Concentration of surfactant, 5×10^{-3} M; concentration of complex, 1.5×10^{-5} M.

TABLE 2

Quantum yields and lifetimes of the excited state of complex I in the presence of various concentrations of $C_{12}E_6$

Surfactant concentration $(\times 10^{-4}$ M)	[complex]/[surfactant]	ϕ[a]	τ[b] (ns)	τ_0[c] $(\times 10^4$ ns)
0	—	0.008	428	5.35
2	0.075	0.009	483	5.37
3	0.050	0.007	378	5.40
4	0.037	0.016	591	3.69
6	0.025	0.017	601	3.54
10	0.015	0.018	651	3.62
50	0.003	0.016	574	3.59

The concentration of complex I is 1.5×10^{-5} M in all cases; the CMC of $C_{12}E_6$ is approximately 9.0×10^{-5} M.
[a]Luminescence quantum yield.
[b]Emission lifetime.
[c]Radiative lifetime $\tau_0 = \tau/\phi$.

cosurfactant $C_{12}E_6$ is added. The effect of increasing the concentration of $C_{12}E_6$ on ϕ and τ is shown in Table 2. There are clearly two concentration domains. Below a surfactant concentration of 3×10^{-4} M, the variations in ϕ and τ are small and apparently erratic. The radiative lifetime $\tau_0 = \tau/\phi$ is less sensitive than ϕ and τ to perturbations arising from uncontrolled quenching processes [45]. It can be seen that τ_0 is rigorously constant in this same concentration range and is equal to the value found in aqueous solutions. At surfactant concentrations in the range 3×10^{-4} - 4×10^{-4} M both ϕ and τ increase rapidly to reach values of 0.016 ± 0.002 and 600 ± 50 ns respectively. These values are constant up to detergent concentrations of 5×10^{-3} M. The critical concentration thus found (3×10^{-4} - 4×10^{-4} M) is significantly higher than the CMC of the non-ionic surfactant $C_{12}E_6$.

Another non-ionic detergent, Texofor A30, which has a lower CMC (1.3×10^{-5} M at 25 °C) was also used [42] (Table 3). As in the previous case,

TABLE 3

Luminescence quantum yields and lifetimes of the excited state of complex I in the presence of increasing amounts of Texofor A30

Surfactant concentration $(\times 10^{-5}\,M)$	[complex]/[surfactant]	ϕ	τ (ns)	τ_0 $(\times 10^4\,ns)$
0	—	0.008	428	5.35
2	0.75	0.013	222	1.71
4	0.375	0.013	286	2.20
6	0.25	0.016	373	2.33
10	0.15	0.014	373	2.66
100	0.015	0.018	471	2.62

The symbols are as defined in Table 2. The concentration of complex I is $1.5 \times 10^{-5}\,M$ in all cases. The CMC of Texofor A30 is $1.3 \times 10^{-5}\,M$ at 25 °C.

the incorporation of the amphiphilic ruthenium complex into non-ionic micellar phases induces substantial changes in ϕ, τ and τ_0. More importantly, higher ratios of annelide to cosurfactant could be obtained because of the lower CMC of Texofor A30; τ_0 was found to vary monotonically over this extended range of local concentrations of ruthenium complex from 1.7 at high values to 2.6 at low values. Simultaneously, the lifetime of the excited state increased from 220 to 470 ns.

4. Discussion

It is well known that photoexcited molecules incorporated into micelles show higher luminescence quantum yields and longer excited state lifetimes. This behaviour is observed when the amphiphilic ruthenium complex I is in the presence of a detergent concentration that is significantly higher than the CMC. The micellar medium probably inhibits some bimolecular quenching process by decreasing the overall mobility of the photosensitizer. Thus the photophysical properties observed are those of the complex isolated in the micelle. These properties will be independent of the concentrations of both detergent and complex if the amphiphile is totally incorporated into the micelle, and, indeed, both the luminescence quantum yields and the emission lifetimes remain constant above some critical concentration slightly higher than the CMC of $C_{12}E_6$ (Table 2). The fact that the critical concentration is different from the CMC is not unexpected since it is well known that the CMC of non-ionic surfactants is very sensitive to the presence of additives or to temperature variations [46 - 50].

The behaviour of the ruthenium derivative can be studied in more detail in the presence of Texofor A30. Because of the lower CMC of Texofor A30, the local concentration of the ruthenium derivative at the micellar subsurface can be varied over a larger range. Light scattering measurements [34]

TABLE 4

Calculated distances between the ruthenium complexes at the micellar subsurface for various surfactant concentrations

Surfactant concentration $(\times10^{-5}\,M)$	CMC $(\times10^{-5}\,M)$	[complex]/ [surfactant][a]	$\bar{M}_{\mathrm{w}}$		No. of I per micelle[d]	$\bar{d}_{\mathrm{AA}}$[e]
			Experimental[b]	Theoretical[c]		
0	—	—	88000	—	—	—
2	0.7	2.14	—	316500	113	15
4	2.7	0.55	—	143000	22	17
6	4.7	0.32	314000	120000	17	19
10	8.7	0.17	—	100000	9	22
100	98.7	0.015	—	90000	0.8	—

[a]Only surfactant molecules belonging to the micelles are concerned.
[b]Molecular weight of the micelles determined by light scattering experiments.
[c]Theoretical molecular weight of the micelles calculated by assuming that their aggregation number does not depend on the concentration of the ruthenium complex added and that all the complex is incorporated in the micelles.
[d]Mean number of complex I molecules incorporated per micelle according to the assumptions given above.
[e]Mean closest distance between two amphiphilic ruthenium complexes at the micellar subsurface (200 Å^2 has been assumed for the ruthenium polar head and 50 Å^2 for the Texofor A30 [46, 47, 51]).

show that the aggregation number of Texofor A30 in pure water in the absence of the ruthenium complex is 53 (Table 4). This value is in agreement with published data [51]. The average molecular weight $\bar{M}_w$ of the micelles increases substantially in the presence of the amphiphilic ruthenium complex. At an overall ratio of complex to surfactant of 0.25, $\bar{M}_w$ is shown by light scattering measurements to be 314 000. This increase corresponds to a fusion of 2.5 elementary micelles containing 53 molecules of $C_{16}E_{32}$ and 17 molecules of the complex [34] (Table 4). At the highest surfactant concentration used (10^{-3} M) there is less than one amphiphilic complex per nonionic micelle. This precludes any intramicellar interaction between the photoexcited state of the complex and an unexcited polar head. This calculation was performed for a uniform distribution of the molecules of the photosensitizer among the micelles.

In a rigorous treatment a Poisson distribution should be used [52], but this would not significantly change the qualitative conclusions drawn here. The mean distance between the ruthenium polar heads can be estimated by assuming that each Texofor A30 molecule requires an area of 50 Å^2 at the micellar subsurface [46, 47, 51] and that the ruthenium polar head requires 200 Å^2 [34] (Table 4). There is clearly a relation between the calculated mean distance, the luminescence quantum yields and the emission lifetimes of complex I.

The major mode of deactivation of the excited state appears to be an intramicellar self-quenching process:

$$(RuL_3^{2+})^* + RuL_3^{2+} \longrightarrow 2RuL_3^{2+} + heat$$
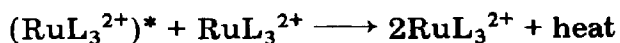
The mechanisms of self-quenching and in particular the dependence of the quenching efficiency on the distance between the metallic complexes are almost completely unknown. Two mechanisms have been postulated for the self-quenching of chromium complexes: catalysed deactivation and catalysed intersystem crossing deactivation [53]. It is not possible to determine which mechanism is effective for ruthenium complexes. However, in all known deactivation processes the variation in the luminescence quantum yield with the concentration of the quencher is always more pronounced than the corresponding variation in the emission lifetime [54]. Clearly, the opposite behaviour is obtained in our case. This supports the hypothesis that the intramicellar self-quenching process occurs by an external heavy atom effect [55] which decreases the natural radiative lifetime of the photoexcited complex. The use of complexes with ions of heavier metals should provide further evidence for this hypothesis.

5. Conclusion

The luminescence properties of a new amphiphilic ruthenium complex in both homogeneous and micellar media have been described. The results suggest that the amphiphilic complex is incorporated in the micelles formed from non-ionic cosurfactants. By varying the local concentration of the amphiphilic complex at the micellar subsurface, it has been possible to demonstrate an intramicellar self-quenching process and to obtain a rough estimate of the dependence of the quenching efficiency on the distance between the polar heads.

More precise determinations which take into account the dynamic properties of the micelles as well as the statistical distribution of the amphiphilic complexes are necessary to elucidate the self-quenching mechanism thoroughly. The synthesis of new amphiphilic derivatives which will form organized phases without the need to use cosurfactants is in progress.

Acknowledgments

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