On the efficiency of the photosensitized production of singlet oxygen in water suspensions of a tris(bipyridyl)ruthenium(II) complex covalently bound to an insoluble hydrophilic polymer

J.L. Bourdelande [a,1], J. Font [a], G. Marques [a], A.A. Abdel-Shafi [b,*],
F. Wilkinson [b], D.R. Worrall [b]

[a] *Unitat de Química Orgànica, Departament de Química, Facultat de Ciències,
Universitat Autònoma de Barcelona, 08193 Barcelona, Spain*
[b] *Department of Chemistry, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK*

Abstract

It is shown that molecular oxygen in D_2O is efficient in deactivating the lowest excited state of an insoluble hydrophilic polymeric equivalent of $[Ru(bpy)_3]^{2+}$ (see structure **1**). The rate constant for quenching by molecular oxygen of the lowest excited triplet charge transfer state of **1** in D_2O saturated gel is found to be $4.4 \pm 0.5 \times 10^8 \, M^{-1} \, s^{-1}$. Singlet molecular oxygen, which is characterized by its emission at 1270 nm, is generated during quenching and decays with a lifetime of $18 \pm 3 \, \mu s$. The lifetimes for the decay of singlet oxygen, when it is generated by exciting D_2O-solved sensitizers in the presence and absence of the unfunctionalized polymeric skeleton in the form of a D_2O saturated gel, are 34 ± 3 and $63 \pm 5 \, \mu s$, respectively. These shorter lifetimes for singlet oxygen in the polymeric gels are consistent with quenching of singlet oxygen by the hydroxyl groups present in the polymer. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Singlet oxygen sensitization; Tris(bipyridyl)ruthenium(II) complex; Hydrophilic polymer; Heterophase

1. Introduction

The generation of singlet oxygen in water by photochemical sensitization is a well studied process when the sensitizer is water soluble, and hence homogeneously distributed through out the aqueous phase [1–5]. However, data concerning the use of photochemical singlet oxygen sensitizers in heterogeneous systems is scarce [6–8]. Systems where the sensitizer is bound to a solid substrate are attractive since they can be removed from the reaction mixture easily by simple filtration once the photochemical reaction has finished [see [9], and references therein].

In a previous publication, we described the synthesis of an insoluble hydrophilic polymeric equivalent of tris(bipyridyl)ruthenium(II), **1**, and the study of its photophysical properties in polar solvents [10]. The oxidative quenching by methylviologen (MV^{2+}) and the reductive quenching by *N,N*-dimethylaniline (NNDMA) of solid sus-

pensions of excited **1** were found to be as efficient as for the homologous $[Ru(bpy)_3]^{2+}$ (bpy = 2, 2′-bipyridine) in solution. Rate constants for the quenching of the excited states of $[Ru(bpy)_3]^{2+}$, $[Ru(bpac)_3]^{2+}$ (bpac = 4, 4′-dicarboxy-2, 2′-bipyridine) and **1** by MV^{2+} are reported to be 0.8, 2.5 and $2.1 \times 10^9 \, M^{-1} \, s^{-1}$ in H_2O, respectively [10].

In this publication, we have explored the efficiency of **1** as a singlet oxygen sensitizer in D_2O suspensions and report on the deactivation by molecular oxygen of the excited state **1** in a D_2O gel. This deactivation is found to be efficient resulting in the generation of singlet molecular oxygen, which is characterized by its emission at 1270 nm.

2. Experimental section

Polymer **1** has been prepared as previously described [10] by reaction of $[Ru(bpac)_3]^{2+}$ with sephadex G-25 (Pharmacia) which had a part of its hydroxyl groups protected with epichlorohydrin. $[Ru(bpac)_3]^{2+}$ was available from a previous study [10]. $[Ru(bpy)_3]^{2+}$, D_2O and acetonitrile are all of available in high purity from Aldrich and were used as received.

* Corresponding author. Tel.: +44-1509-263171; fax: +44-1509-223925.
E-mail addresses: joseluis.bourdelande@uab.es (J.L. Bourdelande),
a.abdel-shafi@lboro.ac.uk (A.A. Abdel-Shafi).
[1] Co-corresponding author.
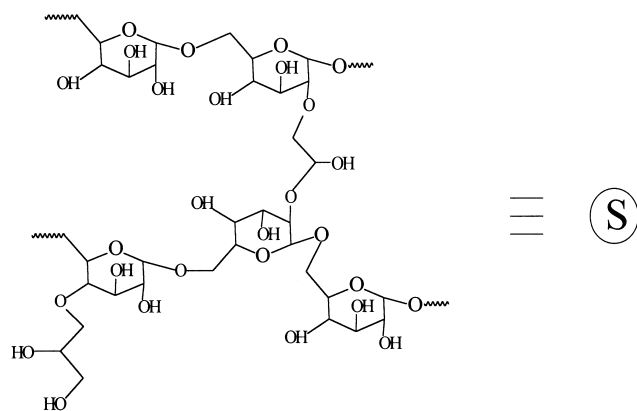
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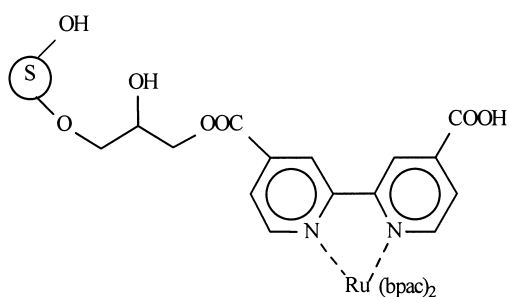
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Singlet oxygen luminescence measurements were carried out using excitation from a Lumonics HY200 Nd:YAG laser (FWHM 8 ns) at 355 nm and a liquid-nitrogen cooled germanium photodiode/amplifier (North Coast model EO-817P) as detector. Luminescence was detected from the front face of the sample, with a 355 nm holographic notch filter (Kaiser Optical) and a 1270 nm interference filter (Newport) interposed between the sample and the detector to markedly reduce laser scatter and sensitizer emission reaching the detector. The signal from the amplifier was digitized using a digital oscilloscope (Tektronix model 2432A) and transferred to a computer for analysis. Sample degassing was achieved using 12 freeze pump thaw cycles.

3. Results and discussion

Polymer **1** carries 0.043 mmol of $[Ru(bpac)_3]^{2+}$ covalently bound to 1 g of sephadex (a hydrophilic resin formed by copolymerization of dextrane and epichlorohydrine). This polymer swells in water to form a gel-like suspension. The transient absorption spectrum recorded for excited **1** in polar solvents resembles that of soluble $[Ru(bpy)_3]^{2+}$ [10] showing maxima at 270, 325, and 380 nm as well as depletions at 300 and 460 nm. When the polymer is suspended in H_2O:MeOH (1:1) the luminescence band due to phosphorescence from the lowest excited triplet charge transfer state of **1** is centred at 605 nm. The diffuse reflectance ground

state spectrum as well as the excitation spectrum of **1** show absorption at 355 nm, and hence the third harmonic of a neodymium YAG laser can conveniently be used for excitation. Fig. 1 shows the decay at 605 nm of the excited metal to ligand charge transfer state (MLCT) with different oxygen concentrations in a D_2O saturated gel. The signal has been recorded using front face detection after pulsed laser excitation at an angle of 45°C. The lifetime of the ^{3}MLCT phosphorescence depends on the amount of oxygen dissolved in the deuterated water. Decay is first order with lifetimes for degassed and oxygen saturated D_2O solid suspensions of 1.53 ± 0.05 and 0.79 ± 0.05 μs, respectively. The inverse of these lifetimes give the pseudo first order rate constants for decay, which show a Stern–Volmer relationship, viz.

$$k_{obs} = k_{TD} + k_q[O_2] \tag{1}$$

where k_{obs} and k_{TD} are first order decay constants of the ^{3}MLCT state in the presence and absence of oxygen, respectively. The slope of the plot shown in the inset of Fig. 1 based on the above equation gives a quenching rate constant of $4.4(\pm 0.5) \times 10^8 \, M^{-1} \, s^{-1}$ using oxygen concentrations of 0.29 and 1.39 mM for air equilibrated and oxygen saturated aqueous solutions, respectively [11]. This quenching constant is sufficiently high for a significant proportion (about 50% in oxygen saturated solution) of the excited states to be deactivated by oxygen quenching. The presence of singlet oxygen can be conveniently detected spectroscopically through its phosphorescence by monitoring emission at 1270 nm. Trace (a) in Fig. 2 shows the transient emission at 1270 nm recorded after the excitation of oxygen saturated suspension of **1** in a D_2O saturated gel with a pulsed laser (355 nm). The initial points in the decay trace are attributable to emission from the ruthenium complex, and hence are not included in the analysis of the singlet oxygen decay [4,5,13].

Complete absence of emission at 1270 nm is observed (see trace (b) in Fig. 2) when an air saturated gel of unfunctionalized sephadex (without any complex attached) in D_2O is excited. These data confirm that it is the ruthenium complex linked to the polymer that is responsible for the formation of singlet oxygen, and not the polymeric skeleton itself.

Table 1 shows the lifetime of singlet oxygen in D_2O saturated gels under different conditions. In this study the lifetime decreases from 63 ± 5 μs with $[Ru(bpy)_3]^{2+}$, $[Ru(bpac)_3]^{2+}$ or phenalenone as sensitizers, down to 18 ± 3 μs when the sensitizer is polymer **1**. In order to see if this effect is related to the polymeric skeleton, we have repeated the experiments with $[Ru(bpy)_3]^{2+}$ and phenalenone in the presence of a large enough amount of non-functionalized sephadex to form a stable suspension of the polymer as a gel. Under these new conditions and recording the emission signal as we did when using polymer **1**, the singlet oxygen lifetime was reduced to 34 ± 3 μs when either $[Ru(bpy)_3]^{2+}$ or phenalenone were used as sensitizers. A similar effect is found for $[Ru(bpy)_3]^{2+}$ in acetonitrile where the singlet oxygen lifetime changes from 80 ± 5 to 66 ± 5 μs when sephadex is added. Hence, it is
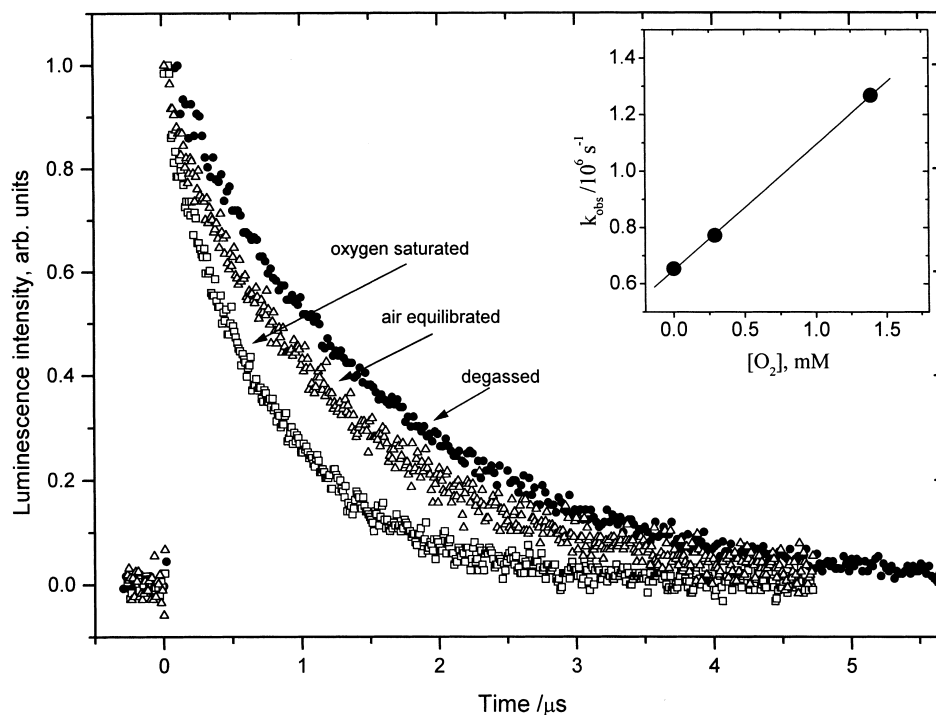
Fig. 1. Decay traces of the emission monitored at 605 nm after laser pulsed excitation (355 nm, 8 ns/pulse) of a degassed (●), air equilibrated (△) or oxygen saturated (□) suspension of polymer **1** in D$_2$O. Insert shows Stern–Volmer relationship for the quenching of the ^{3}MLCT state of **1** by oxygen.

clear that there is a significant quenching of singlet oxygen by the polymer. Probably the interaction of the singlet oxygen with the non-deuterated hydroxyl groups within the polymeric skeleton leads to quenching of singlet oxygen due to energy transfer into the vibrational modes of the hydroxyl groups similar to that observed when H$_2$O is used as a solvent [2,3]. In polymer **1**, the complex units are covalently bound to the polymeric skeleton and as such are intimately mixed with the polymer; hence any singlet oxygen generated will be in close proximity to the hydroxyl groups. In contrast, when the polymer is added to a solution of a sensitizer in D$_2$O there are no such constraints on the distribution of sensitizer relative to polymer. This is consistent with the effect being larger when the singlet oxygen is formed following irradiation of polymer **1** yielding the shortest lifetime, as observed.

The quantum yield of singlet oxygen production (Φ_Δ) arising from oxygen quenching of the triplet, metal to ligand charge transfer state (^{3}MLCT) of the ruthenium complexes is given by

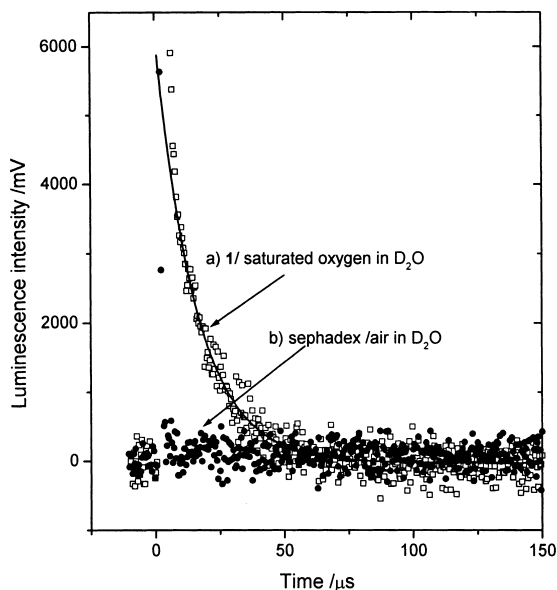$$\Phi_\Delta = \Phi_\mathrm{T} P_\mathrm{T}^{O_2} f_\Delta^\mathrm{T} \qquad (2)$$

Fig. 2. Decay traces of the emission monitored at 1270 nm after laser pulsed excitation (355 nm, 8 ns/pulse) of: (a) oxygen saturated suspension of polymer **1** in D$_2$O (□) and (b) air saturated suspension of sephadex in D$_2$O (●).

Table 1
Lifetimes of singlet oxygen in different media using different sensitizers

Solvent	Sensitizer	$\tau(^1\Delta_\mathrm{g})$ (μs)
D$_2$O	[Ru(bpy)$_3$]$^{2+}$	62 ± 5
D$_2$O	[Ru(bpac)$_3$]$^{2+}$	65 ± 5
D$_2$O	Phenalenone	66 ± 5
D$_2$O saturated gel	[Ru(bpy)$_3$]$^{2+}$ + sephadex	33 ± 3
D$_2$O saturated gel	[Ru(bpac)$_3$]$^{2+}$ + sephadex	31 ± 3
D$_2$O saturated gel	Phenalenone + sephadex	36 ± 3
D$_2$O saturated gel	**1**	18 ± 3
CH$_3$CN	[Ru(bpy)$_3$]$^{2+}$	80 ± 5
CH$_3$CN	[Ru(bpy)$_3$]$^{2+}$ + sephadex	66 ± 5

Table 2
Lifetimes of the excited ^{3}MLCT states of the studied ruthenium (II) complexes, $\tau_0(= 1/k_{TD})$, rate constants for quenching of ^{3}MLCT states by oxygen, k_q, calculated according to Eq. (1), the fraction of the ^{3}MLCT state quenched by oxygen, $P_T^{O_2}$, defined by Eq. (3), quantum yield of singlet oxygen, ϕ_Δ, and the efficiency of singlet oxygen production during oxygen quenching of the ^{3}MLCT state, f_Δ^T

Compound	Solvent	τ_0 (μs)	k_q ($\times 10^9$ M^{-1} s^{-1})	$P_T^{O_2}$	ϕ_Δ	f_Δ^T
[Ru(bpy)$_3$]$^{2+}$	D$_2$O	0.93	2.7	0.42	0.22[a]	0.52
[Ru(bpac)$_3$]$^{2+}$	D$_2$O	1.42	2.4	0.51	0.28	0.55
1	D$_2$O saturated gel	1.53	0.44	0.15	≤ 0.1	≤ 0.6

[a] Ref. [12].

where f_Δ^T is the fraction of triplet states quenched by oxygen which yield singlet oxygen (O$_2^*$($^1\Delta_g$)) and Φ_T is the efficiency of population of the lowest excited spin forbidden ^{3}MLCT. All indications are that the quantum yield of intersystem crossing to the lowest excited ^{3}MLCT state is unity for [Ru(bpy)$_3$]$^{2+}$ and other Ru(II) complexes [5,13], therefore it is assumed that it is also unity for the polymer **1**. $P_T^{O_2}$ is the fraction of the ^{3}MLCT states quenched by oxygen and is given by Eq. (3),

$$P_T^{O_2} = \frac{k_q[O_2]}{k_{TD} + k_q[O_2]} \tag{3}$$

Quenching by oxygen of the ^{3}MLCT excited states of [Ru(bpy)$_3$]$^{2+}$, [Ru(bpac)$_3$]$^{2+}$ and **1** in D$_2$O occurs with k_q values equal to 2.7×10^9, 2.4×10^9 and 0.44×10^9 M^{-1} s^{-1} leading to the production of singlet molecular oxygen with quantum yields of 0.22, 0.28 and ≤ 0.1, respectively. Table 2 lists the lifetimes of the excited ^{3}MLCT states of the studied ruthenium (II) complexes, τ_0, rate constants for quenching ^{3}MLCT states by oxygen, k_q, the fraction of the ^{3}MLCT state quenched by oxygen, $P_T^{O_2}$ and quantum yield of singler oxygen production, Φ_Δ.

It is interesting to note that k_q is about five times less when the ^{3}MLCT excited states of **1** is quenched by oxygen in the aqueous gel compared with that for [Ru(bpac)$_3$]$^{2+}$ in the homologous solution. Quenching by MV^{2+} gives rate constants of 2.5, 2.1 and 0.8×10^9 M^{-1} s^{-1} for, [Ru(bpac)$_3$]$^{2+}$, **1** and [Ru(bpy)$_3$]$^{2+}$ in H$_2$O [10]. Rate constants for quenching by MV^{2+} are higher for [Ru(bpac)$_3$]$^{2+}$ and **1** than for [Ru(bpy)$_3$]$^{2+}$ because of the presence of electron withdrawing substituents on the bipyridine rings which increases the one electron reduction potential of the complex and/or probably due to increased static quenching in the first two cases because of the presence of partial negative charge on the carboxyl groups. In the case of oxygen quenching, rate constant for [Ru(bpy)$_3$]$^{2+}$ is slightly higher than for [Ru(bpac)$_3$]$^{2+}$ due to the small difference in the energy of the excited ^{3}MLCT states being 205 and 206 kJ mol^{-1}, respectively [5,13]. Upon the addition of non-functionalized sephadex to the D$_2$O solved sensitizer to form a stable suspension of the polymer as a gel, the quenching rate constants

drop to 1.8×10^9 and 1.9×10^9 M^{-1} s^{-1} for the two complexes, respectively, as diffusion of oxygen in the saturated D$_2$O gel decreased. Quenching of the excited ^{3}MLCT state by oxygen of **1** is about four times less than the quenching by oxygen of the D$_2$O saturated gel of [Ru(bpac)$_3$]$^{2+}$ due to more steric hindrance in this case as the complex is covalently bound within the sephadex polymer. It is not clear why oxygen suffers a steric hindrance whereas MV^{2+} does not. However, polymer **1** contains may CO$_2^-$ groups in aqueous solution and quenching by MV^{2+} will be favoured by electrostatic interactions which apparently outweigh steric hindrance in this case.

To summarize, we have shown that molecular oxygen is quite efficient in deactivating the excited state of **1** in a suspension in water. It is apparent that the hydrophilic polymeric equivalent of [Ru(bpy)$_3$]$^{2+}$ leads to the production of singlet oxygen and that polymer **1** has good potential as a sensitizer of singlet oxygen in water suspensions.

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