ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 95 (1996) 235–238

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Tris(bipyridyl)ruthenium(II) complex covalently bound to an insoluble hydrophilic polymer: reductive and oxidative quenching

J.L. Bourdelande [a,*], J. Font [a], G. Marquès [b], M. Valiente [b]

[a] *Unitat de Química Orgànica, Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain*
[b] *Unitat de Química Analítica, Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain*

Received 31 July 1995; accepted 20 September 1995

Abstract

The synthesis of a new insoluble, hydrophilic, polymeric equivalent of the $Ru(bpy)_3^{2+}$ complex is described. Sephadex is used as a hydrophilic polymeric skeleton. Its photophysical properties are similar to those of $Ru(bpy)_3^{2+}$ in solution. The deactivation of this polymeric excited complex by methyl viologen (oxidative quenching) and *N,N*-dimethylaniline (reductive quenching) is very efficient in polar solvents, making it both a powerful oxidant and reductant species in photochemical reactions accomplished in heterogeneous phase.

Keywords: Ruthenium complex; Insoluble polymer; Reductive quenching; Oxidative quenching

1. Introduction

Tris(bipyridyl)ruthenium(II) complexes have been used successfully as oxidizing or reducing species in photochemical reactions [1]. The immobilization of the ruthenium complexes in heterogeneous environments has been studied to facilitate the charge separation involved in photoinduced redox processes [2]. We have already described the photochemical and photophysical behaviour of some polymeric equivalents of $Ru(bpy)_3^{2+}$ (bpy = bipyridyl) in which one of the bipyridyl ligands is covalently bound to an insoluble cross-linked polystyrene through polymethylene hydrophobic or polyethoxylated hydrophilic spacers [2a–2d]. The oxidative quenching of the luminescence of the excited states of these polymeric complexes by methyl viologen (MV^{2+}) in dioxan:water and the reductive quenching by *N,N*-dimethylaniline (DMA) in dioxan were studied in heterophase. The oxidative quenching was found to be 40 times less efficient than that described for the monomeric $Ru(bpy)_3^{2+}$ in solution; it was proposed that the hydrophobicity of the polymeric backbone could prevent the approach of the water-solvated MV^{2+}, thus minimizing the photoinduced electron transfer (PIET) process [2a,2d]. The reductive quenching was carried out using dioxan as a solvent to allow a good contact between the quencher, DMA, and the polymeric surface. Then, the solid complex was 20 times more efficient than the monomeric $Ru(bpy)_3^{2+}$ in solution, but only 25% of the initial emission was quenched [2d]. It was proposed that only those chromophores lying on the surface of the polymeric bead (responsible for the 25% of the emission) were available to be deactivated while the rest were "hidden" in the interior part of the bead, surrounded by the polymeric skeleton. The hydrophobicity and the reticulation of the cross-linked structure account for such poor results.

We wish to report here the synthesis of an insoluble hydrophilic polymeric equivalent of $Ru(bpy)_3^{2+}$, **1**, and the study of its photochemical and photophysical properties in polar solvents. Sephadex is now used as a hydrophilic polymeric skeleton and both the oxidative and the reductive quenching of the luminescence of the excited **1** have been found to be as efficient as in solution.

2. Experimental section

2.1. Materials

Sephadex G-25 (Pharmacia) and all other materials were obtained from commercial sources and used as received.

Tris-(4,4′-dicarboxy-2,2′-bipyridine) ruthenium (II) chloride, **2**, was prepared from 4,4′-dicarboxy-2,2′-bipyridine (bpac) [2b,3] and *cis*-dichlorobis(2,2′-bipyridine)-ruthenium(III) [4] as already described [2b].

---

* Corresponding author.

1010-6030/96/$15.00
SSDI 1010-6030(95)04221-0

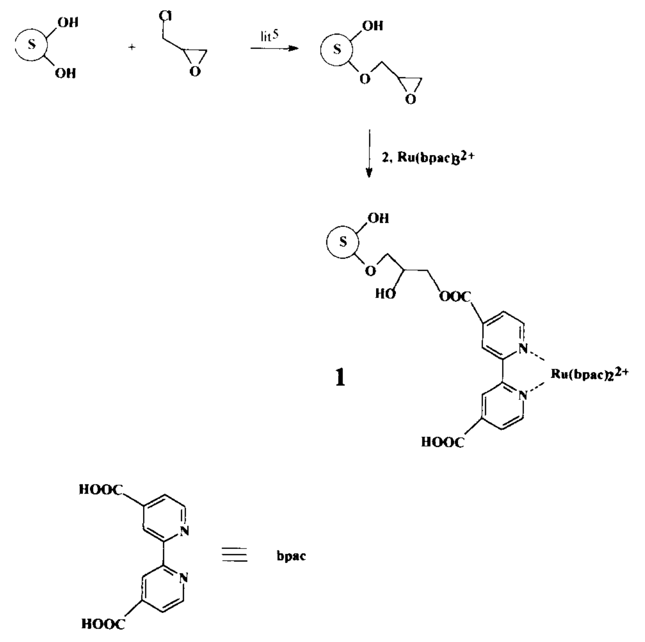
2.1.1. Covalent linkage of 2 to Sephadex, 1

(a) Functionalization of Sephadex with epichlorohydrin was performed as already described [5]. The resulting polymer was washed with H_2O and MeOH.

(b) 15.6 mg of **2** was dissolved in a mixture of *N,N*-dimethylformamide (20 ml) and an aqueous solution of Na_2CO_3 0.01 M (20 ml). 2 g of the modified Sephadex obtained in (a) was added and the mixture stirred for 16 h at 60–65 °C. After filtering, the polymer was washed with H_2O (2×50 ml), 0.01 M Na_2CO_3(aq) (24×50 ml), H_2O (6×50 ml) and EtOH (4×50 ml). After drying under vacuum, 1.85 g of a red polymer **1** was obtained. IR results (KBr) were as follows: 3420 cm^{-1} (w), 2926 cm^{-1} (s), 2094 cm^{-1} (broad), 1652 cm^{-1} (s), 1458 cm^{-1} (s), 1012 cm^{-1} (s). The nitrogen content (0.36%) indicates the presence of 0.043 mequiv complex g^{-1}. The excitation and emission spectra of **1** are shown in Fig. 1 and the transient absorption of its excited state is shown in Fig. 2.

2.2. Methods

IR spectra were recorded on a Perkin Elmer 16PC FT-IR spectrometer. Luminescence spectra of homogeneous solutions of $Ru(bpac)_3^{2+}$ or $Ru(bpy)_3^{2+}$ and suspensions of polymeric complexes were obtained with a Hitachi F-4500 fluorescence spectrometer. All measurements were conducted at room temperature (22 ± 2 °C). Emission from the static suspensions of the polymeric samples was monitored at right angles to excitation. All the measurements were made in argon-saturated solutions or suspensions at the ionic strength indicated. Laser flash photolysis experiments were performed using an LKS50 instrument from Applied Photophysics. The second harmonic (532 nm) of a *Q*-switched Nd:YAG laser (Spectron Laser Systems, UK; pulse width, ca. 9 ns) was used for laser flash excitation. Typically 17–22 mJ $pulse^{-1}$ were used for sample excitation.



Scheme 1.

3. Results and discussion

Polymer **1** has been prepared according to Scheme 1 by reaction of $Ru(bpac)_3^{2+}$, **2**, with a previously modified Sephadex (copolymer of dextrane and epichlorohydrin). The complex **2** and the modified polymer have been prepared as already described [2b,3–5]. The new hydrophilic insoluble polymer, **1**, carries 0.043 mequiv complex g^{-1}. Fig. 1(a) shows the excitation and the emission spectra recorded from a static gel-like suspension of **1** in MeOH:water (1:1). The excitation spectrum presents maxima at 291 nm (ligand $\pi \rightarrow \pi^*$ transition) and 465 nm (metal-to-ligand $d \rightarrow \pi^*$ charge transfer transition), while the emission spectrum presents a maximum at 603 nm. Both spectra are similar to those of **2** (Fig. 1(b)) in the same solvent, indicating the absence of decomposition or distortion of the complex during its covalent linkage to the polymeric skeleton.

Fig. 2 shows the difference transient absorption spectrum recorded after a pulsed excitation at 532 nm of a static gel-like suspension of **1** in MeOH:H_2O (1:1). Although the sample is solid, its transparency allowed us to record the spectrum by the classic transmission technique. The shape of the transient spectrum matches those of the tris(bi-

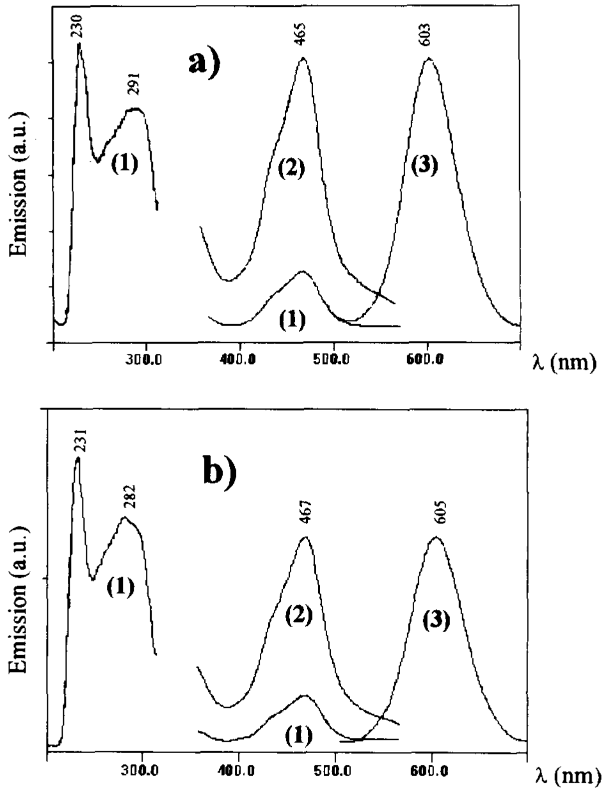


Fig. 1. Excitation and emission spectra, in MeOH:H_2O (1:1), of (a) polymer **1** and (b) complex **2**: spectra 1, excitation, $\lambda_{det} = 655$ nm; spectra 2, excitation, $\lambda_{det} = 602$ nm; spectra 3, emission, $\lambda_{ex} = 468$ nm.

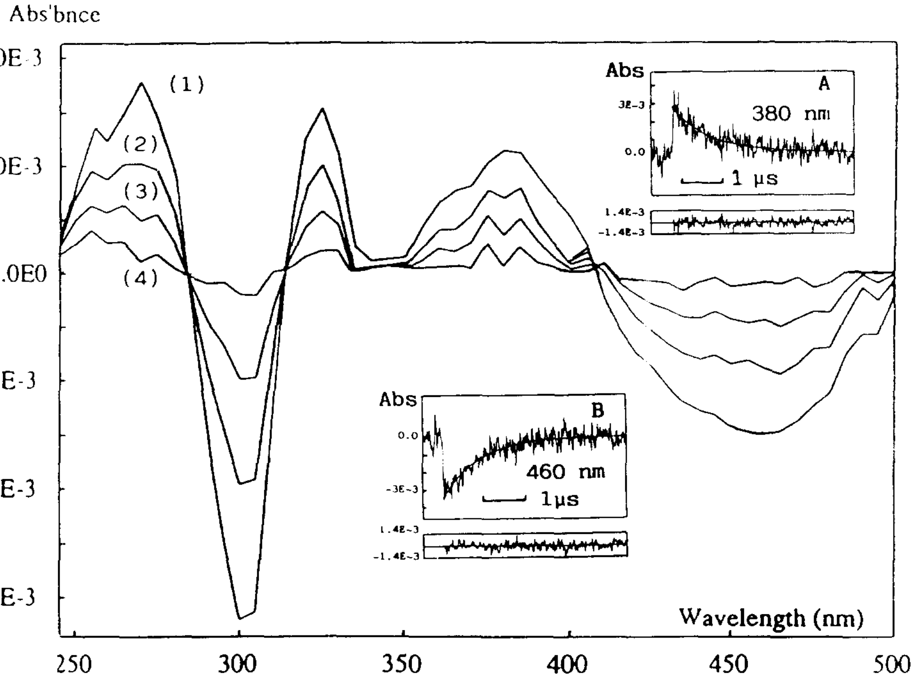


Fig. 2. Transient difference spectra of polymer **1** in N_2-purged MeOH:H_2O (1:1) following 532 nm excitation: spectrum 1, 150 ns after laser flash; spectrum 2, 600 ns after laser flash; spectrum 3, 1200 ns after laser flash; spectrum 4, 2400 ns after laser flash. Also shown are transient decay at 380 nm and first-order fit (spectrum A) and transient decay at 460 nm and first-order fit (spectrum B).

pyridyl)ruthenium(II) complexes [1,2c,2e,2f,6,7]. The decays at the maximum of the absorption at 380 nm and the depletion at 460 nm (Fig. 2, insets A and B) are identical, following a first-order kinetics. The deduced lifetime in this mixture is 1.0 ± 0.1 μs and its dependence on the solvent is very small (Table 1).

Fig. 3 shows the Stern–Volmer diagram for the oxidative quenching of the excited state of **1** by MV^{2+} in H_2O. Also are displayed data for **2** and the parent $Ru(bpy)_3^{2+}$. The deduced k_q values are collected in Table 1. The rate constant for **2** is much larger than for the parent $Ru(bpy)_3^{2+}$, probably because of the substitution of the bipyridine rings with electron-withdrawing groups which increase the one-electron-reduction potential of the complex [2e]. The rate constant for **1** is, also, much larger than for $Ru(bpy)_3^{2+}$ and only somewhat smaller than for **2**, indicating that the hydrophilic polymeric complex **1** is more efficient than the parent complex in the PIET process and that it is a good candidate to be used in the photochemical decomposition of water to O_2 and H_2 [1,2a].

Fig. 4 shows the Stern–Volmer diagram for the reductive quenching of the excited state of **1**, **2**, and $Ru(bpy)_3^{2+}$ by

Table 1
Summary of results

Complex	Solvent	τ (ns) [a]	Quencher	$k_q \times 10^{-8}$ ($M^{-1} s^{-1}$)
$Ru(bpy)_3^{2+}$	H_2O	610 ± 10	MV^{2+}	7.9 ± 0.2
$Ru(bpac)_3^{2+}$, **2**	H_2O	770 ± 10	MV^{2+}	24.6 ± 0.3
1	H_2O	830 ± 10	MV^{2+}	21.2 ± 0.3
$Ru(bpy)_3^{2+}$	MeOH:H_2O, 1:1	710 ± 5	*N,N*-DMA	1.0 ± 0.1
$Ru(bpy)_3^{2+}$	MeOH:H_2O, 1:2	625 ± 5	*N,N*-DMA	1.0 ± 0.1
$Ru(bpy)_3^{2+}$	Dioxan:H_2O, 1:1	770 ± 10	*N,N*-DMA	0.5 ± 0.1
$Ru(bpy)_3^{2+}$	Dioxan:H_2O, 1:2	670 ± 5	*N,N*-DMA	1.1 ± 0.1
$Ru(bpac)_3^{2+}$, **2**	MeOH:H_2O, 1:1	1060 ± 10	*N,N*-DMA	7.6 ± 0.2
$Ru(bpac)_3^{2+}$, **2**	MeOH:H_2O, 1:2	830 ± 10	*N,N*-DMA	11.1 ± 0.3
$Ru(bpac)_3^{2+}$, **2**	Dioxan:H_2O, 1:1	910 ± 10	*N,N*-DMA	2.9 ± 0.1
$Ru(bpac)_3^{2+}$, **2**	Dioxan:H_2O, 1:2	450 ± 5	*N,N*-DMA	11.8 ± 0.3
1	MeOH:H_2O, 1:1	1000 ± 10	*N,N*-DMA	6.5 ± 0.2
1	MeOH:H_2O, 1:2	910 ± 10	*N,N*-DMA	8.6 ± 0.2
1	Dioxan:H_2O, 1:1	1000 ± 10	*N,N*-DMA	1.9 ± 0.1
1	Dioxan:H_2O, 1:2	1000 ± 10	*N,N*-DMA	4.4 ± 0.2

[a] For [quencher] = 0.

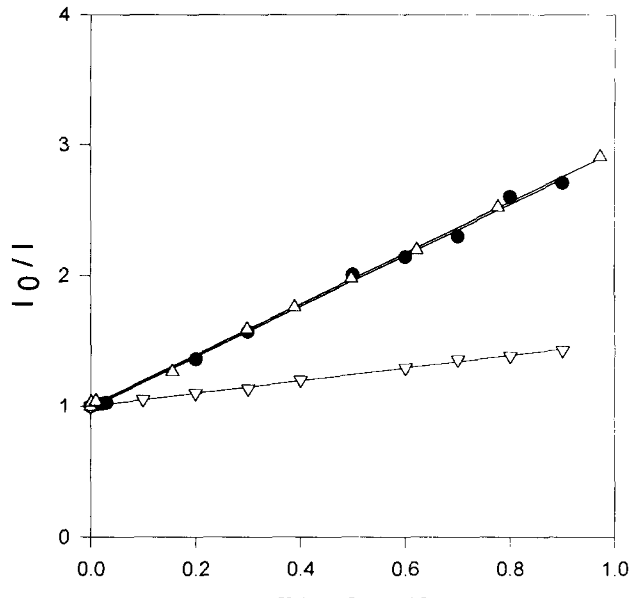


Fig. 3. Stern–Volmer plots for the luminescence quenching of excited **1** (△), **2** (●) and $Ru(bpy)_3^{2+}$ (▽), by MV^{2+} in N_2-purged H_2O, ionic strength 0.1 M (Bu_4NBr).

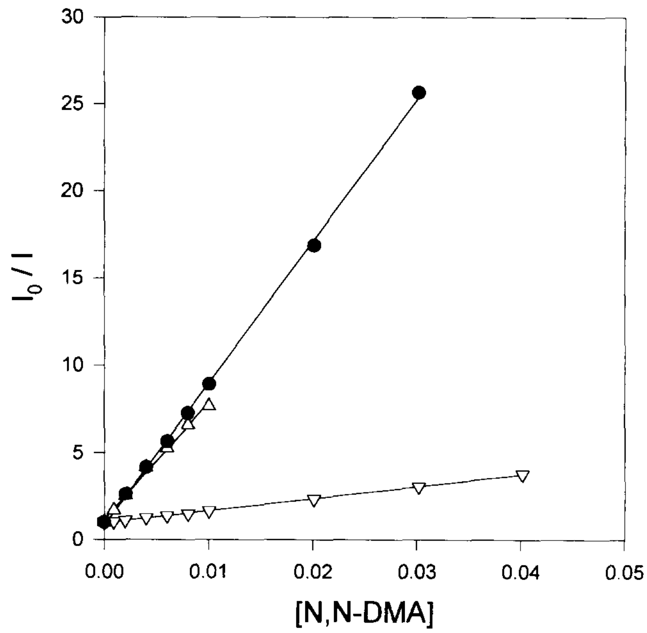


Fig. 4. Stern–Volmer plots for luminescence quenching of excited **1** (△), **2** (●) and $Ru(bpy)_3^{2+}$ (▽), by *N*,*N*-DMA in N_2-purged $MeOH:H_2O$ (1:1), ionic strength 0.1 M (Bu_4NBr).

N,*N*-DMA in $MeOH:H_2O$ (1:1). The deduced k_q values in this and other solvent mixtures are collected in Table 1. Again, the polymeric complex is almost as efficient as **2** and much more than $Ru(bpy)_3^{2+}$ in its reduction process. The new polymer is a good candidate to be used as a powerful reductant in photochemical reactions accomplished in heterogeneous phase.

To conclude, we have prepared a new insoluble, hydrophilic, polymeric equivalent of the $Ru(bpy)_3^{2+}$ complex which is very efficient in both the oxidative and the reductive photoinduced redox processes in polar solvents including water.

Acknowledgements

Financial support from DGICYT and CICYT (Spain), Projects PB 92-0605 and MAT93-0621-C03-01, and from CIRIT (Generalitat de Catalunya) is gratefully acknowledged.

References

[1] K. Kalyanasundaran, *Coord. Rev.*, *46* (1982) 159.

[2] (a) J.L. Bourdelande, C. Campà, J. Font and P. de March, *Eur. Polym. J.*, *25* (1989) 197, and references cited therein; (b) P. Bosch, C. Campà, J. Camps, J. Font, P. de March and A. Virgili, *An. Quím. Ser. C*, *81* (1985) 162; (c) J.L. Bourdelande, C. Campà, J. Font, P. de March, F. Wilkinson and C.J. Willsher, *J. Photochem. Photobiol. A: Chem.*, *44* (1988) 51; (d) J.L. Bourdelande, J. Font, G. Marquès and D. Salvatierra, *J. Photochem. Photobiol. A: Chem.*, *85* (1995) 143; (e) L.A. Kelly and M.A.J. Rodgers, *J. Phys. Chem.*, *98* (1994) 6377; (f) L.A. Kelly and M.A.J. Rodgers, *J. Phys. Chem.*, *98* (1994) 6386.

[3] W.H.F. Sasse and C.P. Whittle, *J. Chem. Soc.*, (1961) 1347.

[4] B.P. Sullivan, D.J. Salmon and T.J. Meyer, *Inorg. Chem.*, *17* (1978) 3334.

[5] E.S. Hemdan and J. Porath, *J. Chromatogr.*, *323* (1985) 247.

[6] D. Meisel, M.S. Matheson, W.A. Mulac and J. Rabani, *J. Phys. Chem.*, *81* (1977) 1449.

[7] C. Creutz, M. Chou, T.L. Ntzel, M. Okumara and N. Sutin, *J. Am. Chem. Soc.*, *102* (1980) 1309.