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# $Ru(bpy)_3^{2+}$ bound to an insoluble polymeric phase. Reductive luminescence quenching

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## Abstract

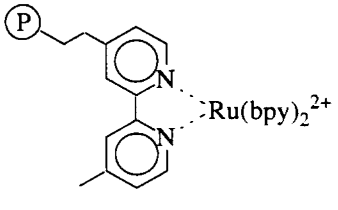
The reductive quenching of excited $Ru(bpy)_3^{2+}$ (bpy, bipyridyl) covalently bound to insoluble polystyrene shows two different polymeric environments and two very different photochemical behaviours of the complex. They are related to the complexes linked to the surface of the bead (functional groups, up to 1.5%), and those linked to the interior of the bead.

*Keywords:* Reductive luminescence quenching

## 1. Introduction

The oxidative quenching of the luminescence of excited $^*Ru(bpy)_3^{2+}$ (bpy, bipyridyl) has been widely studied in homogeneous solution or immobilized on a suitable substrate [1]. In addition, we have described the spectroscopic properties and photochemical and transient behaviour of a polymeric equivalent of this ruthenium complex, **1**, in which one of the bipyridyl ligands is covalently bound to insoluble cross-linked polystyrene [2–4]. **1** was found to be much less efficient than monomeric $Ru(bpy)_3^{2+}$ in photoinduced electron transfer (PIET) processes using methyl viologen ($MV^{2+}$) as electron acceptor and dioxan–water as solvent ($k_q$ was 40 times smaller) [3]. We proposed that the high hydrophobicity of the polymeric backbone could prevent the approach of water-solvated $MV^{2+}$ to the polymer, thus minimizing the PIET process and the photodissociation of water [4].

In this paper, we report the reductive quenching of excited polymeric $Ru(bpy)_3^{2+}$, which suggests the existence of two different polymeric environments and two very different photochemical behaviours of the excited complex. Polymer **1** was prepared as described in Ref. [2], and contains 0.36 mmol of $Ru(bpy)_3^{2+}$ per gram of polymer (2% divinylbenzene cross-linked polystyrene beads) corresponding to six functional groups out of 100 pendant phenyls (6%).



## 2. Results and discussion

We have already shown that Stern–Volmer diagrams can be plotted for the quenching of the excited states of chromophores linked to insoluble polymers such as **1** when these remain in the solvent as a static suspension (gel-like dispersion) [3,4]; the deduced $k_q$ values are in agreement with the overall photochemical behaviour observed for these polymeric chromophores.

Fig. 1(a) shows the steady state Stern–Volmer plot for the luminescence quenching by *N*,*N*-dimethylaniline (DMA) of the excited complex **1** suspended in dioxan. The lifetime of a suspension (gel-like dispersion) of ***1** in dioxan was quantified by diffuse reflectance laser flash photolysis (Applied Photophysics LKS.50) as described previously [3] and found to be in the region 650–700 ns. From the slope of the Stern–Volmer plot, we can deduce $k_q = (1.5 \pm 0.5) \times 10^9$ $mol^{-1}$ $dm^3$ $s^{-1}$. The described quenching constant for soluble $Ru(bpy)_3^{2+}$ in acetonitrile is $7.1 \times 10^7$ $mol^{-1}$ $dm^3$ $s^{-1}$ [5]; as a

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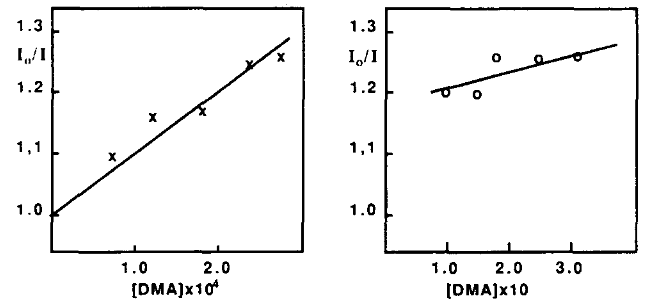

Fig. 1. Stern–Volmer plot of luminescence quenching by DMA of the excited complex **1** suspended in $N_2$-purged dioxan: (a) at very low DMA concentrations; (b) at large DMA concentrations.

consequence, the polymeric complex is 20 times more efficient. A similar effect (but not so intense) has been described for modified $Ru(bpy)_3^{2+}$, in which a large, non-polar substituent is linked to a bipyridyl ligand ($k_q$ increases up to $k_q = (3.7 \pm 0.5) \times 10^8$ $mol^{-1}$ $dm^3$ $s^{-1}$) [5]. It seems that our non- polar, bulky polystyrene support multiplies this effect and substantially improves the PIET process in reductive quenching.

Attention should be paid to the low deactivation level: in Fig. 1(a), only 25% of the initial emission intensity is quenched. We have explored the effect of large concentrations of DMA and have recorded the Stern–Volmer plot shown in Fig. 1(b). It can be seen that the emission remains almost unquenched and the quenching constant deduced from the new slope decreases dramatically to $k_q' = (4.0 \pm 0.5) \times 10^5$. Therefore about 25% of the initial emission is easily available for small amounts of DMA, but the remaining 75% is essentially unavailable. As polymer **1** contains a loading degree of 6%, this means that the actual amount of functional groups available to be quenched after irradiation is only 1.5%. Polymer **1** has been prepared following the concept of solid-phase synthesis, in which the reactants are linked to a solid sample of the insoluble matrix (usually cross-linked polystyrene beads). Some of the reactants remain linked to the surface, while the others are forced to travel to the interior of the polymer. The reactivity of the linked functional groups will depend on their macromolecular environment and it is useful to clarify how they are distributed in the polymer chain. Very little is known about this distribution because these materials are generally unsuitable for study by standard analytical methods [6]. In our case, the functional groups are luminescent chromophores and can be studied using diffuse reflectance techniques. For instance, the lifetime of the excited state of polymer **1** has been evaluated using diffuse reflectance laser flash photolysis.

The emission originating from excited **1** can be deactivated in two very different ways. To account for this result, we suggest that approximately 1.5% of the functional phenyl groups are located on the surface of the bead, while the others are linked in the interior (Fig. 2). The former are easily deactivated by DMA after irradiation, while the latter are surrounded by the polymeric skeleton inhibiting the approach of DMA. This is in agreement with the distribution already suggested for benzoylated polystyrene beads [7]. To evaluate the rigidity of the polymer, we have performed steady state polarization studies on the emission of a suspension of **1** in dioxan–water. Polymer **1** shows two characteristic emission bands: one centred at 320 nm due to the excimer of the phenyl rings of the backbone and another centred at 610 nm due to the metal-to-ligand charge transfer (MLCT) complex [4]. Polarization is found to be $P = 0.84$ at 320 nm and $P = 0.34$ at 610 nm, suggesting a very rigid skeleton. If the polymer is so rigid, the diffusion of DMA will be hindered and it will not be able to reach the excited complex linked to the interior; this is in agreement with the low quenching efficiency shown in Fig. 1.

To summarize, we can conclude that only those $Ru(bpy)_3^{2+}$ units linked to the surface of the beads (functional groups, up to 1.5%) can be deactivated by DMA by rapid reductive quenching after irradiation

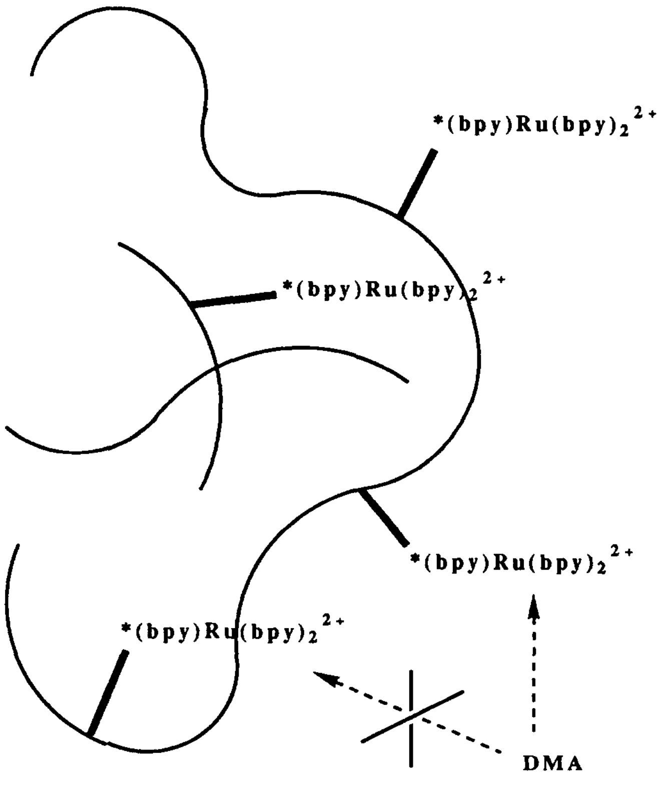

Fig. 2. Distribution model for $Ru(bpy)_3^{2+}$ covalently bound to 2% divinylbenzene cross-linked polystyrene beads.

and the rest remain unavailable in the interior of the bead.

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