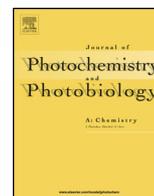




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Short note

Anomalous Hammett's plot in the quenching of Ru(bpy)₃²⁺ phosphorescence by p-substituted phenols



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ABSTRACT

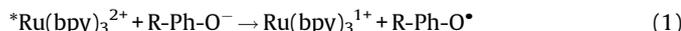
Tris(2,2'-bipyridine) Ru(II) (Ru(bpy)₃²⁺) phosphorescence is readily quenched by p-substituted phenols in a bimolecular process whose rate, in aqueous solution, is determined by the pH of the solution and the electron-affinity of the substituent. A Hammett's type plot based on data obtained at pH 10.4 in terms of σ parameters conforms to a parabola with a minimum rate for phenol and two branches, one comprising compounds with negative σ values (electron donors) and other with positive σ values (electron acceptors groups). This anomalous behaviour takes place at a constant pH and it can be explained in terms of two quenching mechanisms: a simple electron transfer from the phenolate to the Ru(II) complex when $pK_a \ll pH$, and a PCET (proton coupled electron transfer) mechanism for compounds where the protonated phenol predominates ($pK_a > pH$).

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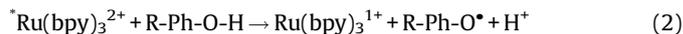
1. Introduction

The interaction between excited tris(2,2'-bipyridine) Ru(II) ions (Ru(bpy)₃²⁺) and phenols has been extensively studied due to their multiple applications, such as photoredox catalysis [1,2], and/or the fact that they can mimic relevant biological processes [3–5]. Furthermore, the quenching of excited Ru(bpy)₃²⁺ is closely related to the quenching of the dye electrochemiluminescence [6] although secondary electrode reactions, favoured by high local concentrations of the intermediates at or near the electrode interface, open new pathways for the quenching process [7].

It has been established that the quenching of the excited Ru(bpy)₃²⁺ phosphorescence by a simple p-substituted phenol is extremely dependent of the substituent, pH, and solvent [8,9]. Furthermore, the quenching process can involve the oxidation of the dye to Ru(bpy)₃³⁺ or its reduction to Ru(bpy)₃¹⁺ with the concomitant reduction or oxidation of the phenol, respectively. This pH dependence of the quenching process can be ascribed to the protonation-deprotonation of the phenol. In fact, the simplest process takes place when working $pH \gg pK_a$ and can be considered as comprising a single electron transfer step:



Sjödin et al. have carried out a detailed study of the reaction of Ru(bpy)₃²⁺ with tyrosine [5], reporting that its deprotonation resulted in a 100-fold increase in the rate constant of process. Furthermore, when $pH \gg pK_a$ the rate of the process become independent of pH over a large range of values. On the other hand, a different mechanism takes place at low pH. In these conditions, protonation of the phenol precludes the occurrence of Reaction (1) and its oxidation must follow a more complex mechanism, such as proton-coupled electron transfer (PCET), where the proton is simultaneously released to the bulk solvent (Reaction 2):



The rate constant of this reaction should increase when the pH and the electron donicity of the substituent decreases (For a detailed review about PCET, please refer to reference [10]). In order to test these proposals, we have measured the rate of ^{*}Ru(bpy)₃²⁺ phosphorescence quenching by a series of p-substituted phenols of different electrophilicity and expressed them in terms of Hammett's plot at pH 10.4, obtaining a parabolic dependence of both parameters. Reasons of this rather peculiar photo-behaviour of ^{*}Ru(bpy)₃²⁺ in presence of simple p-substituted phenols are discussed in the present work.

2. Experimental

Ru(bpy)₃²⁺ chloride, phenol and their p-substituted derivatives (Sigma) were employed as received. The water employed to prepare the buffer solutions was obtained from a Modulab Type II

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equipment. Phosphorescence measurements were performed in a Shimadzu RF-53001 PC spectrofluorometer (Kyoto, Japan). Lifetimes of excited $\text{Ru}(\text{bpy})_3^{2+}$ were measured in a Jobin Yvon/ISA single photon counter.

3. Results and discussion

Typical spectra obtained in $\text{Ru}(\text{bpy})_3^{2+}$ phosphorescence quenching by *p*-substituted phenols at two different pHs are presented in Fig. 1.

According to Fig. 1, it is clear that the electro-donating compound (*p*-methoxyphenol) is more sensible to the pH than *p*-nitrophenol (electro-attraction substituent). In particular the small quenching observed for *p*-methoxyphenol could be due to the large proportion of the protonated phenol at the two working pHs (pKa 10.1). Moreover, it can be appreciated that neither the form nor the position of the phosphorescence band of $\text{Ru}(\text{bpy})_3^{2+}$ was modified by the quencher concentration. Similar results to those shown in Fig. 1, were obtained for the others *p*-substituted phenols employed in the present work (data not shown). This would point to a negligible formation of secondary products and/or direct photo-decomposition of $\text{Ru}(\text{bpy})_3^{2+}$ [2].

The data obtained in Fig. 1 at pH 10.4 were plotted according to Stern-Volmer's equation (Fig. 2). The linearity of these plots allows the evaluation of the Stern-Volmer constant and, considering the lifetime of the excited state of $\text{Ru}(\text{bpy})_3^{2+}$ (400 ns in the present experimental conditions), can be derived the bimolecular quenching constant. These values are plotted as a function of Hammett's σ

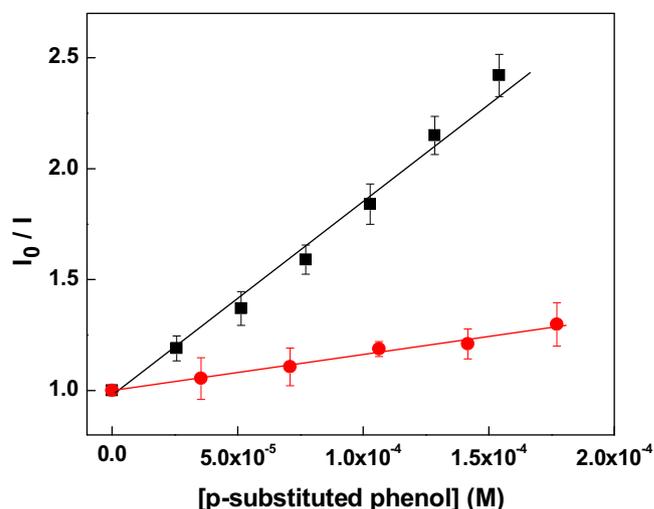


Fig. 2. Stern-Volmer's plot of the phosphorescence intensity ratio of $\text{Ru}(\text{bpy})_3^{2+}$ as the function of quencher analytical concentration. (■) *p*-nitrophenol; (●) *p*-methoxyphenol. In this plot, the analytical quencher concentration was corrected to take into account the presence of a small fraction of protonated phenol in the right branch and that of the unprotonated quenchers in the left.

parameter (Fig. 3). Contrary to expectations, the data show a non-linear behaviour, with a clear minimum for the rate of the reaction with phenol and higher rates for compounds with positive (high electron affinity) and negative (electron donating) values of the

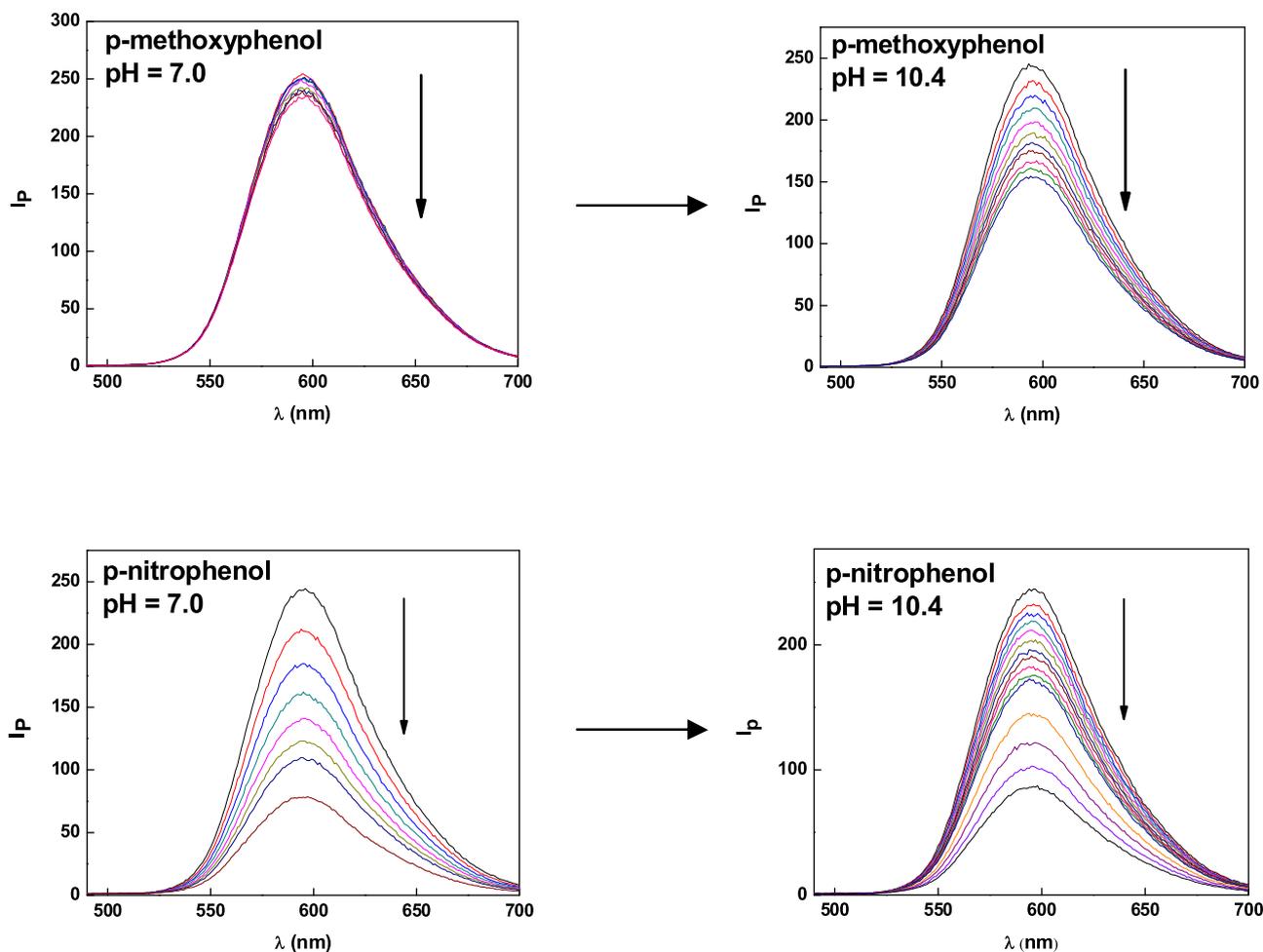


Fig. 1. Phosphorescence profiles for the quenching of $\text{Ru}(\text{bpy})_3^{2+}$ by *p*-substituted phenols at pH 7.0 (left) and pH 10.4 (right).

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