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APPLICATION OF POLYMER-EMBEDDED TRIS(2,2'-BIPYRIDINE)-RUTHENIUM(II) TO PHOTODETECTION OF OXYGEN

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ABSTRACT

A Nafion film containing tris(2,2'-bipyridine)ruthenium(II) as a luminescence probe was applied to photodetection of oxygen in a gas by utilizing the luminescence quenching by dioxygen. The linear Stern-Volmer plots of the emission intensity with respect to the oxygen concentration allowed quantitative determination of the oxygen. From the emission decay studied by a single-photon counting method, it was concluded that the quenching of the excited state Ru complex by oxygen proceeds by a conventional dynamic mechanism.

INTRODUCTION

Since tris(2,2'-bipyridine)ruthenium(II) complex (abbreviated to $\text{Ru}(\text{bpy})_3^{2+}$) strongly absorbs and emits visible light, it is an excellent candidate as a luminescence probe in the visible light region. The high reactivity of its photoexcited state toward redox reagents [1] allows its use as a probe to detect these reagents. When the complex is embedded in a polymer film, it can be used as a film-state photosensing device. One of the present authors has prepared various polymer-pendent $\text{Ru}(\text{bpy})_3^{2+}$ complexes [2] and reported the quenching of the excited Ru complex by acceptors such as methylviologen and oxygen

[3]. However, if a low molecular weight complex probe can be easily embedded in a polymer film, e.g., simply by adsorption, instead of by preparing a complicated polymer-pendent complex, and if the complex-embedded film remains stable, it provides an easy method for fabricating photosensing devices. In this report, $\text{Ru}(\text{bpy})_3^{2+}$ is adsorbed in a Nafion film, and its applicability to photodetection of oxygen is studied. For a solid-state luminescence probe, the linear relationship of the sensing response with respect to the substrate concentration is always a problem that is concerned with the mechanism of the process. These important points are studied and discussed here.

EXPERIMENTAL

$\text{Ru}(\text{bpy})_3^{2+}$ was prepared and purified as reported elsewhere [4]. For the Nafion film, a purchased film (Nafion 117 from Aldrich Chemical Co. Inc., thickness $173\ \mu\text{m}$) or a cast film was used. Casting was carried out from a Nafion solution (5 wt% solution in lower aliphatic alcohols and 10% water) on a Teflon plate by dropping the solution at $10\ \mu\text{L}/\text{cm}^2$, air-dried at room temperature, and further dried at about 50°C . The estimated film thickness was $6.0\ \mu\text{m}$. The Ru complex was adsorbed into the Nafion film by dipping the film into the aqueous solution of $10\ \text{mM}\ \text{Ru}(\text{bpy})_3^{2+}$ for 30 min, air-dried at room temperature and then at around 50°C . The emission spectrum was measured with a Hitachi fluorospectrophotometer MPF-4 with the film sample placed diagonally in a quartz cell. Emission decay was measured by a single-photon counting apparatus (Hitachi-Horiba NAES-1100) equipped with a hydrogen lamp at 10 atm H_2 . Excitation was done at 450 nm for both measurements.

RESULTS AND DISCUSSION

The absorption and the emission spectra of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed in a Nafion film are shown in Fig. 1. The absorption and the emission peaks (450 and 603 nm, respectively) are almost the same as for the complex present in an aqueous solution. From the adsorbed amount (1.6×10^{-7} mol), film thickness ($1.73\ \mu\text{m}$), film area ($3.90\ \text{cm}^2$), and the absorbance (0.84), the apparent molar extinction coefficient of the Ru complex adsorbed in Nafion was calculated to be $2.0 \times 10^4\ \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, which is higher than that of the complex in an aqueous solution ($1.44 \times 10^4\ \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$).

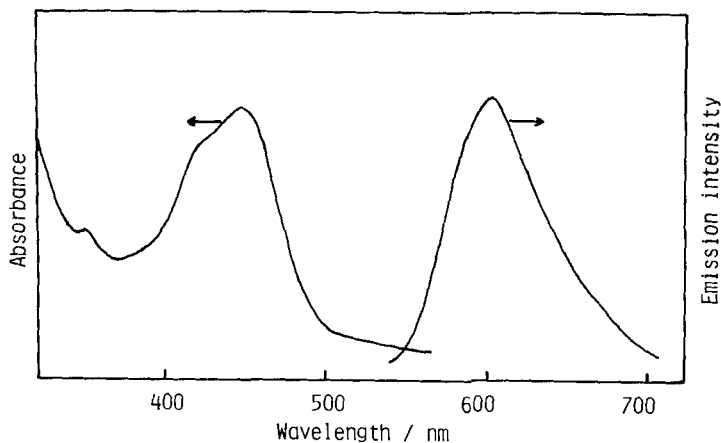


FIG. 1. Absorption and emission spectra of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed in a Nafion film (thickness $173 \mu\text{m}$).

The emission from the excited state of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed in a Nafion film was quenched by oxygen in the gas phase. The Stern Volmer plots for the quenching by oxygen in Fig. 2 show a good linear relationship, indicating that the oxygen concentration is determined by measuring the emission intensity of the Nafion-embedded Ru complex. Here the apparent concen-

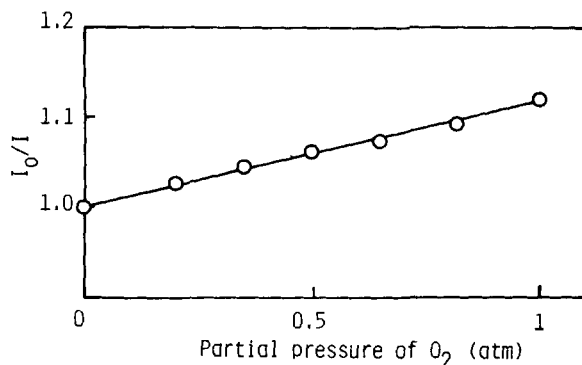


FIG. 2. Stern-Volmer plots of the relative emission intensity (I_0/I) of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed into a Nafion film (Nafion 117, thickness $173 \mu\text{m}$) with respect to partial pressure of oxygen in the gas mixture of oxygen and argon.

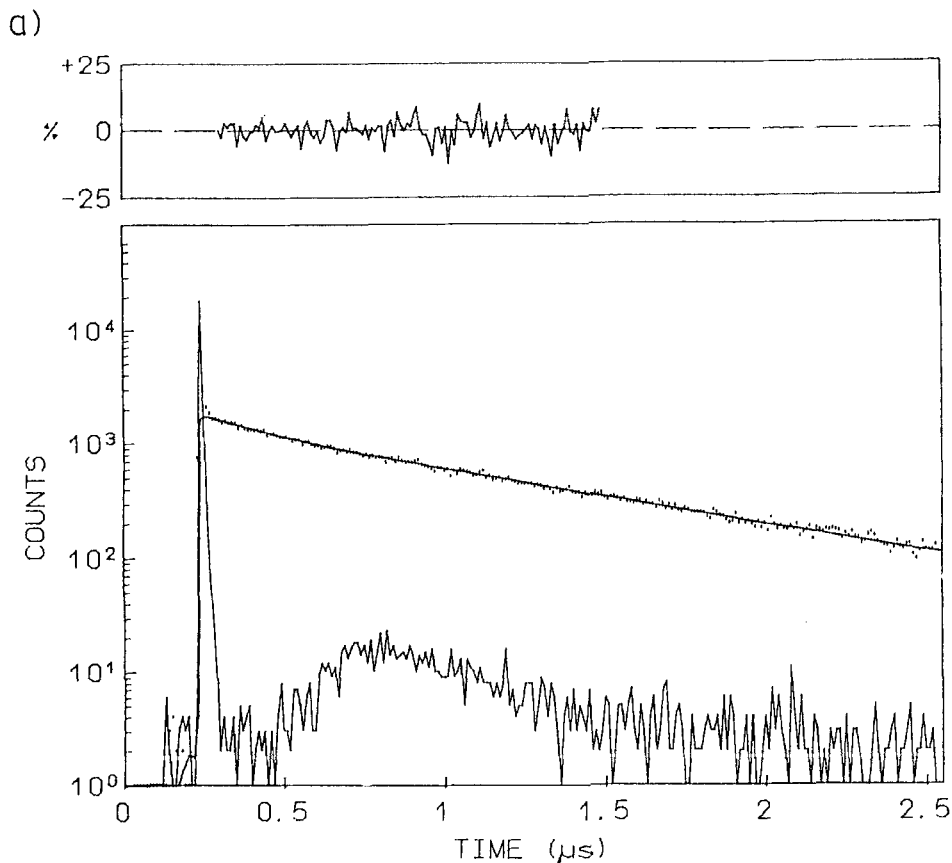


FIG. 3. Emission decay of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed in a cast Nafion film (thickness $6\ \mu\text{m}$). Excited at $450\ \text{nm}$ and monitored through a cutoff filter of O-58. (a) Under argon. (b) In air. The upper figures show residuals.

tration of the complex was calculated to be $2.4\ \text{mM}$ from the film thickness ($173\ \mu\text{m}$), absorbance (0.84), and the molar extinction coefficient (described above). The Ru complex embedded in a cast Nafion film showed essentially a similar behavior as the Nafion 117 film in Fig. 2.

The emission decay of cast Nafion-embedded Ru complex was measured under argon as well as in air and is shown in Fig. 3(a) and (b). The apparent concentration of the complex in the film is $0.19\ M$. Although the decay

b)

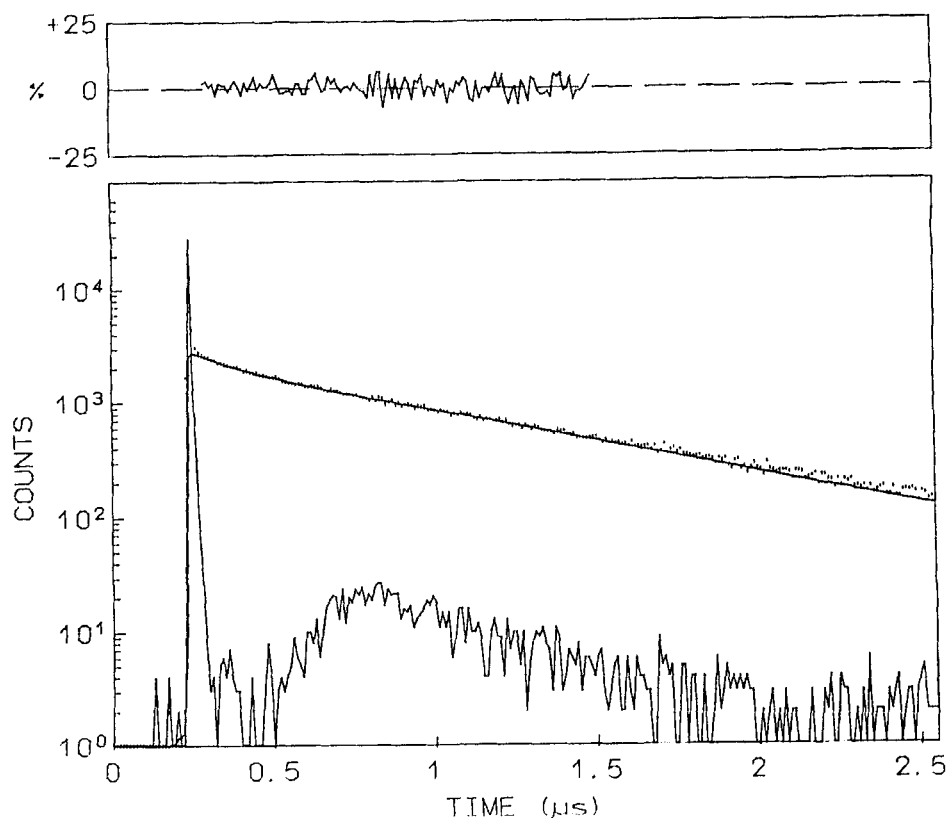


FIG. 3 (continued)

curves show the presence of a shorter lifetime component at 238 and 121 ns, the main component (over 90%) shows a lifetime of around 800 ns (Table 1). It is surprising that this lifetime is much longer than that of the complex present in a homogeneous solution, which is about 600 ns in the absence of oxygen although the apparent concentration of the complex is very high (0.19 M) in this film sample. In a solution system, the so-called concentration quenching occurs at a concentration of higher than mM order, making

TABLE 1. Lifetime of the Excited $\text{Ru}(\text{bpy})_3^{2+}$ Adsorbed in a Nafion Film (as calculated from Fig. 3)

Components	Atmosphere			
	Argon		Air	
	Lifetime, ns	Ratio, % ^a	Lifetime, ns	Ratio, % ^a
1st	238	9.0	121	4.6
2nd	839	91.0	752	95.4

^aRelative quantum yield of the emission

the excited-state lifetime remarkably low. In the present film system, the concentration quenching of the excited state that should prevail at such high concentrations in a solution system is dramatically hindered. The even longer lifetime of the film system would be explained by the hindering of the molecular motion of the excited molecule. The shorter lifetime component in Table 1 would be due to the small fraction of the complex present in a specific environment where nonradiative decay of the excited state occurs easily.

The very similar linear decay curve in air (Fig. 3b) compared to that under argon suggests that the quenching of the excited complex by oxygen proceeds by a dynamic mechanism. Table 1 shows that both lifetime components are quenched by oxygen, indicating that the quenching can be explained by a dynamic model.

The relative emission intensity (I_0/I) in the absence and presence of oxygen does not depend much on the film humidity, but the emission intensity itself depends on the humidity. Figure 4 shows that the emission intensity under argon increases with decreasing film humidity. This kind of humidity effect was also observed for the $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed onto cellulose paper [4]. The increase of the emission intensity would be due to the decrease of the molecular motion of the probe with decreasing water content. Such hindering of the molecular motion can hinder nonradiative decay of the excited state, and therefore can increase both lifetime and emission intensity.

The advantages of the present oxygen detection system are 1) easy fabrication of the sensing device, 2) stability, and 3) applicability to various phases such as gas, liquid, and solid. Studies on other emission probe systems are in progress.

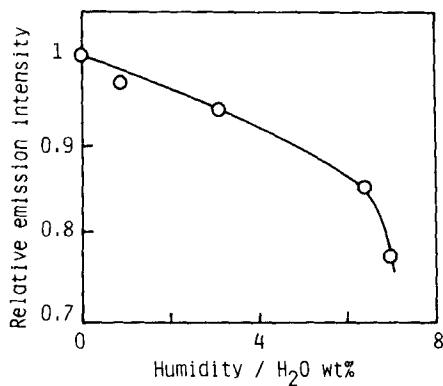


FIG. 4. Dependence of emission intensity on the film humidity (Nafion film, as in Fig. 1). Under argon.

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