

Effect of humidity on photoluminescence from $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into a polysaccharide solid film and its application to optical humidity sensor

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Received 6 February 2004; received in revised form 12 April 2004; accepted 21 May 2004

Available online 29 July 2004

Abstract

The effects of humidity on photoluminescence from $\text{Ru}(\text{bpy})_3^{2+}$ dispersed in polysaccharide solid films have been investigated. In a κ -carrageenan solid film, peaks of relative emission intensity (I_R) and lifetime (τ) appeared around 20% (under Ar) and 30% (under air) relative humidity (RH). In a chitosan solid film, only small changes were observed in I_R and τ of the photoluminescence up to 20% RH. However, over 20% RH, the I_R and τ decreased with the increase in RH. These results were interpreted by mobility of $\text{Ru}(\text{bpy})_3^{2+}$ as well as electrostatic and hydrophobic interactions between polysaccharide and $\text{Ru}(\text{bpy})_3^{2+}$. Larger effect of humidity was observed under air than under Ar depending on the polysaccharide used, which was explained by the quenching reaction by the O_2 dissolved in water phase in the polysaccharide domain.

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Keywords: $\text{Ru}(\text{bpy})_3^{2+}$; κ -Carrageenan; Chitosan; Polysaccharide solid; Photoluminescence; Optical humidity sensor

1. Introduction

$\text{Ru}(\text{bpy})_3^{2+}$ is attracting a great deal of attention not only as a photocatalyst for photoenergy conversion [1–7], but also as a photoluminescent probe which absorbs and emits visible light [8–18]. Polysaccharides are natural polymer abundant in nature. They have various characteristics depending on the character of the polymer chain. It is possible to provide them with various functions by utilizing the polymer domain of a polysaccharide. Photoluminescent $\text{Ru}(\text{bpy})_3^{2+}$ is a nice probe to investigate the microenvironment of such materials [13–18], and our group and other ones have reported the photoluminescence from $\text{Ru}(\text{bpy})_3^{2+}$ dispersed in polysaccharide such as cellulose [11,12]. However, there have been no report about the effect of humidity on the photoluminescence from $\text{Ru}(\text{bpy})_3^{2+}$ incorporated in polysaccharide solids. We have found strong humidity effect on the photoluminescence from $\text{Ru}(\text{bpy})_3^{2+}$ incorporated in polysaccharide.

Humidity sensors have been fabricated using hygroscopic polymers by utilizing their resistance or capacitance change [19]. The effect of humidity on the photoluminescent inten-

sity could lead to fabrication of new humidity sensors based on the photoluminescence. Optical sensors have many advantages, for example, since it does not use electric current, it can be used even in flammable vapor (antiexplosive), under electromagnetic field (such as in an electric oven), etc., by using an optical fiber.

In the present paper, we have incorporated the photoluminescent probe $\text{Ru}(\text{bpy})_3^{2+}$ into polysaccharide solid films and investigated humidity effect on its photoluminescence. Chitosan, κ -carrageenan, agar, cellulose, locust bean gum/xanthan gum (1:1 mixture) and curdlan were used as a polysaccharide. The fundamental behavior will be reported and the possibility to apply it to optical humidity sensor is discussed.

2. Experimental

2.1. Materials

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ was purchased from Sigma–Aldrich Co., chitosan from Tokyo Kasei Kogyo Co. Ltd., κ -carrageenan from Wako Pure Chemical Industries Ltd., agar from Kishida Chemical Co. Ltd., cellulose paper from Toyo Roshi Kaisha Ltd., locust bean gum from Wako Pure

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Chemical Industries Ltd., xanthan gum from Tokyo Kasei Kogyo Co. Ltd. and curdlan from Wako Pure Chemical Industries Ltd.; they were used as received.

Chemical structures of polysaccharides used are presented in Fig. 1.

2.2. Preparation of polysaccharide solid film

For a chitosan solid film, 3 wt.% chitosan powder, 1 vol.% acetic acid, $\text{Ru}(\text{bpy})_3^{2+}$ ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) and water were mixed, and heated by irradiating very carefully a high frequency wave (2.45 GHz) in an electric oven to entirely solubilize the materials. The hot solution obtained was

poured into a mold (10 mm \times 26 mm \times 1 mm size) made of glass. After cooling the clear solution to room temperature under ambient conditions, a tight, and elastic solid film was obtained. The solid was slightly turbid because of the chitosan network structure. The solid film containing excess water was transferred on a non-luminescent glass and dried under ambient conditions for about half a day.

For a κ -carrageenan, agar, locust bean gum/xanthan gum (1:1 mixture) and curdlan solid films, the same procedure as the above was applied except using acetic acid, wherein either 2 wt.% κ -carrageenan powder, 2 wt.% agar powder, 1:1 locust bean gum/xanthan gum powder (totally 2 wt.%), or 5 wt.% curdlan powder was used.

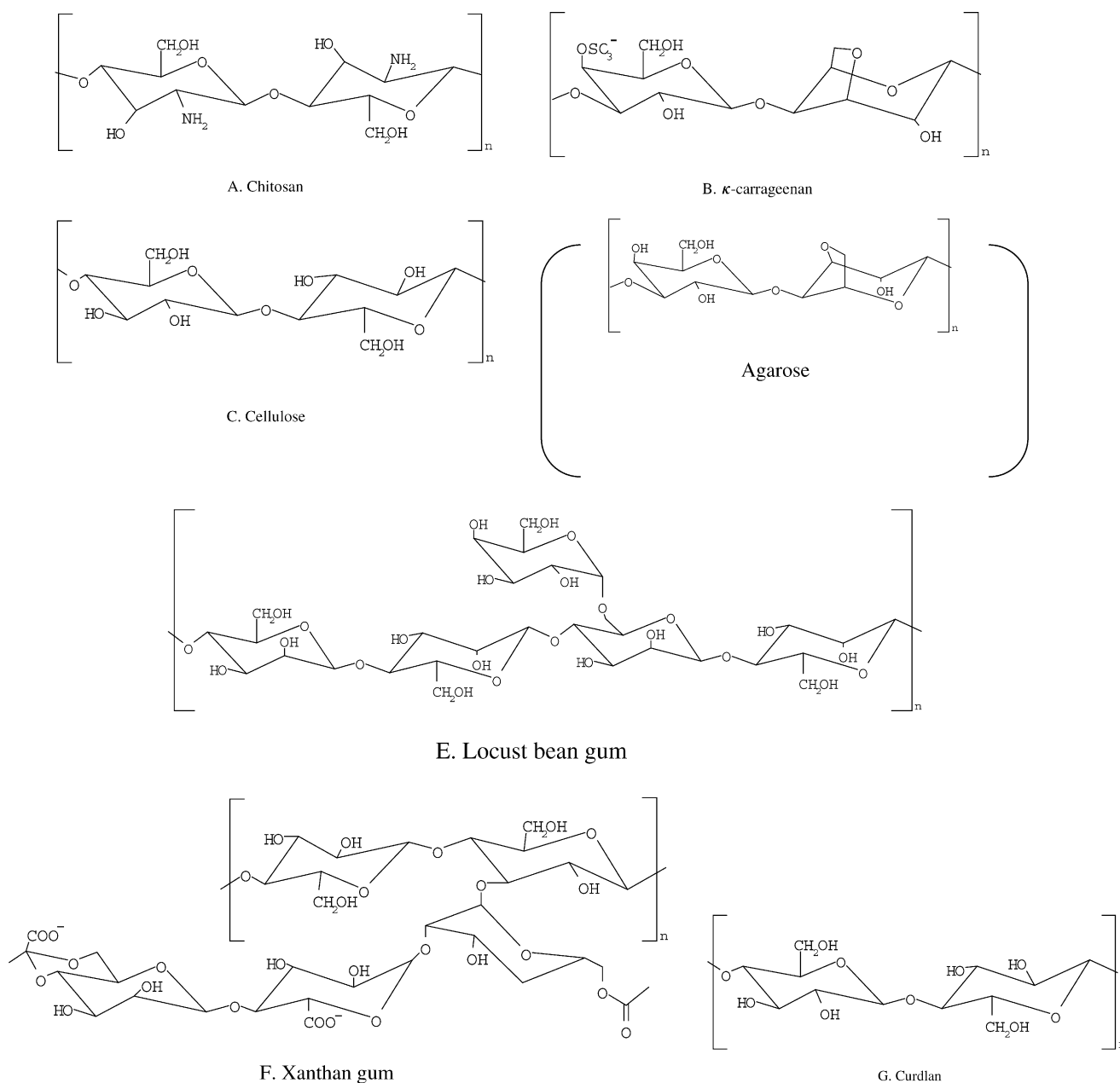


Fig. 1. Chemical structure of polysaccharides used in the present paper.

For a cellulose paper, a cellulose filter paper (125 g/m²) was cut to 14 mm × 40 mm, dipped into a Ru(bpy)₃²⁺ aqueous solution (4.9 × 10⁻⁴ mol dm⁻³) and dried under ambient conditions for about half a day.

2.3. Measurement

Visible absorption spectrum was measured with a Shimadzu Multispec-1500 spectrophotometer, and emission spectrum with a spectrofluorometer (Shimadzu RF-5300PC). In all the emission measurements, the sample film on a non-luminescent glass plate was put into a quartz cell at a diagonal position against the excitation light to minimize the effect of scattering light. The emission decay was measured by a time-correlated single photon counting apparatus (Horiba NAES-550) equipped with a nitrogen lamp (10 atm) at 25 °C. The emission was measured at 25 °C in air or argon under a specified humidity. The relative humidity (RH) in the cell was monitored by a Vaisala HMI41 indicator and HMP41 humidity probe. The excitation wave length was 452 nm. The observation wave length in the emission decay experiments was 610 nm.

3. Results and discussion

The visible absorption and emission spectra of a chitosan solid film incorporating Ru(bpy)₃²⁺ are shown in Fig. 2. The spectra are almost the same as those observed in an aqueous solution. In the present relative humidity range, the appearance of all the polysaccharide solid films used in the present paper did not change. The emission around 600 nm changed drastically with the increase of the humidity (vide infra in Fig. 6).

As an example the emission decay of the Ru(bpy)₃²⁺ incorporated into κ-carrageenan under Ar is shown in Fig. 3. The emission decay curves were single exponential in all cases of this experiment. The experimental results of the τ are shown in Table 1 including the chitosan and

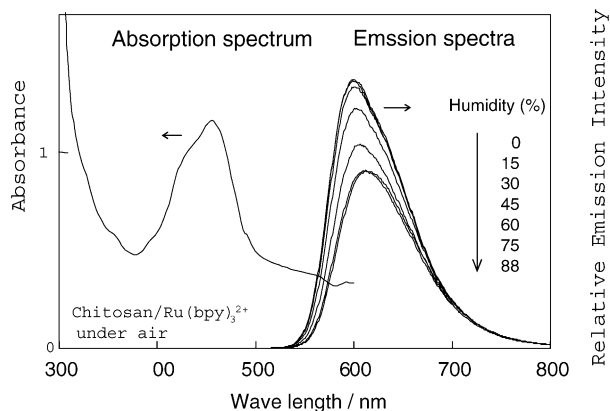


Fig. 2. Absorption spectrum and emission spectral change of Ru(bpy)₃²⁺ (chitosan/Ru(bpy)₃²⁺/under air).

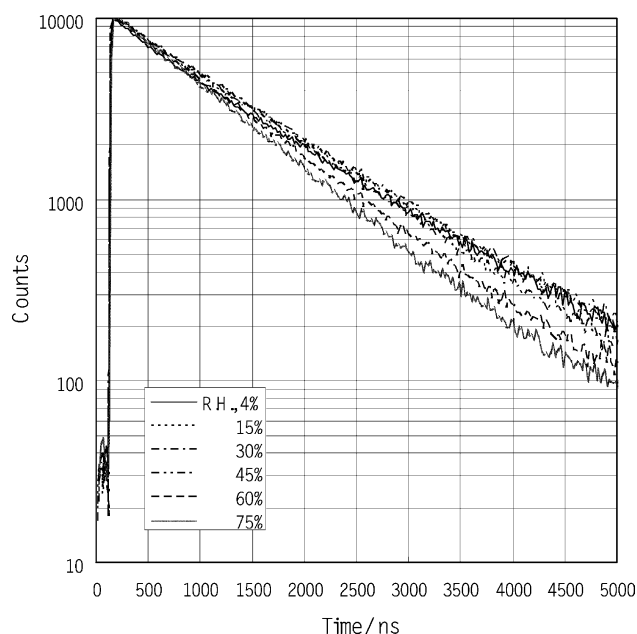


Fig. 3. Emission decay curves of Ru(bpy)₃²⁺ adsorbed in κ-carrageenan solid films, excited at 452 nm, observed at 610 nm, under Ar.

κ-carrageenan samples. The residuals of the analysis (χ^2) are from 1.03 to 1.28 showing that the single exponential analysis is reasonable. These results are shown later in the Figs. 5 and 7 for further discussion. As for the I_R relative

Table 1
Lifetime of the Ru(bpy)₃²⁺ adsorbed in a polysaccharide film

	RH (%)	τ (ns)	Pre-exponential term	χ ²
κ-Carrageenan film				
Under Ar	4	1040	0.077	1.28
	15	1060	0.116	1.21
	30	1080	0.124	1.03
	45	1020	0.191	1.19
	60	936	0.211	1.12
	75	855	0.218	1.04
Under air	4	1010	0.116	1.28
	15	1070	0.151	1.15
	30	1070	0.212	1.21
	45	1020	0.264	1.19
	60	934	0.307	1.19
	75	809	0.359	1.25
Chitosan film				
Under Ar	6	1280	0.159	1.27
	15	1270	0.151	1.25
	30	1270	0.151	1.20
	45	1250	0.170	1.15
	60	1210	0.195	1.18
	75	1050	0.249	1.12
	88	843	0.376	1.22
	Under air	6	1310	0.263
15		1300	0.308	1.10
30		1290	0.300	1.15
45		1170	0.557	1.27
60		1010	0.536	1.21
75		801	0.768	1.05
90	751	0.817	1.15	

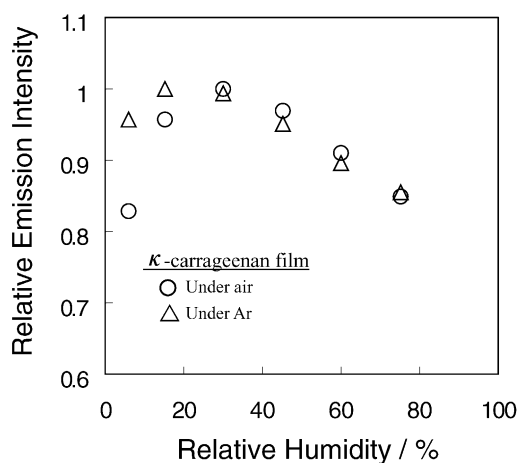


Fig. 4. Relative emission intensity changes of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into a κ -carrageenan solid film against relative humidity at 610 nm.

emission intensity of κ -carrageenan film versus RH see the Fig. 4. In a κ -carrageenan solid film, peaks of I_R appeared around 20% (under Ar) and 30% (under air) RH. In a κ -carrageenan solid film, peaks of τ (Fig. 5) appeared around 20% both under Ar and air; they show almost the same change.

The emission from the photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ is changeable with both non-radiative decay (depending on the mobility of the photoluminescent probe) and quenching by quencher (such as O_2). For the non-radiative decay, the electrostatic and hydrophobic interaction of the probe with the polymer matrix changes the probe mobility, so that the adsorbed moisture can change the mobility of the probe, i.e., its luminescent intensity. Generally, non-radiative decay takes place easier when the mobility of the photoluminescent probe molecule is higher, resulting in lower emission intensity of the probe.

The emission from photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ at 610 nm are caused by the triplet state, and the quantum yield (Φ) is

shown by the next Eq. (1).

$$\Phi = \frac{k_e}{k_e + k_d} \quad (1)$$

k_e is the rate constant of emission from the triplet state; and k_d the rate constant of nonradiative decay from the triplet state.

When the molecular mobility of $\text{Ru}(\text{bpy})_3^{2+}$ are suppressed, the Φ and τ (photoexcited state lifetime) increase due to the decrease of the k_d . For example, the emission intensity and τ of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ increased by the suppressed molecular mobility of $\text{Ru}(\text{bpy})_3^{2+}$ when incorporated into a polymer solid matrix by electrostatic or hydrophobic interaction [7]. The Φ can change when the polymer matrix adsorbs other molecules (in the present case, H_2O) because of the change of the micro environment around the adsorbed $\text{Ru}(\text{bpy})_3^{2+}$. When some deactivation process (such as quenching, k_q) takes place by a coexisting molecule, the Φ is represented by the next Eq. (2).

$$\Phi = \frac{k_e}{k_e + k_d + k_q[\text{Q}]} \quad (2)$$

k_q is the 2nd-order rate constant of quenching reaction of the triplet state; $[\text{Q}]$ the quencher concentration.

That is, Φ decreases by the existence of a quencher, so that emission intensity and τ of the photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ decreases. It is known that the triplet state of $\text{Ru}(\text{bpy})_3^{2+}$ are quenched by O_2 , so that the emission intensity and τ of the photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ decrease by the presence of O_2 .

In the κ -carrageenan film the behavior at less than 20% RH in the Fig. 4 could be interpreted as follows. In a dry condition, $\text{Ru}(\text{bpy})_3^{2+}$ would be adsorbed in a hydrophilic region around the $-\text{OSO}_3^-$ groups at the main chain by electrostatic interaction between $-\text{OSO}_3^-$ and $\text{Ru}(\text{bpy})_3^{2+}$. When a small amount of H_2O (less than 20% RH) was adsorbed, the $\text{Ru}(\text{bpy})_3^{2+}$ molecules with hydrophobic bpy ligands would interact with the hydrophobic region of the κ -carrageenan main chain because of the increase of the polarity of the microenvironment. Generally, hydrophobic interaction makes the I_R and τ of the $\text{Ru}(\text{bpy})_3^{2+}$ probe longer due to suppression of the molecular mobility. This is shown by the increase of τ with the increase of the hydrophobicity of the medium for the $\text{Ru}(\text{bpy})_3^{2+}$ (Table 2). At the RH less than 20%, the τ and I_R under air are smaller than those under Ar. This is interpreted by that in a dry condition the $\text{Ru}(\text{bpy})_3^{2+}$ probes are located in hydrophilic region formed by $-\text{OSO}_3^-$ groups because of the electrostatic interaction,

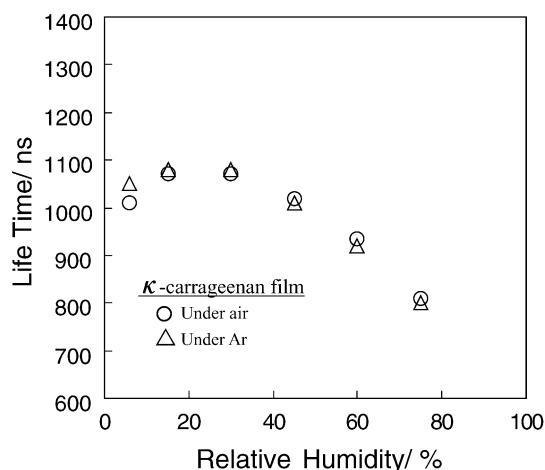


Fig. 5. Lifetime changes of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into a κ -carrageenan solid film against relative humidity at 610 nm.

Table 2

Relationship between photoexcited lifetime of $\text{Ru}(\text{bpy})_3^{2+}$ and medium hydrophobicity

Medium	Increase of hydrophobicity	Lifetime (τ) (ns)
H_2O	Small	600
MeOH	↓	664
DMF	Large	959

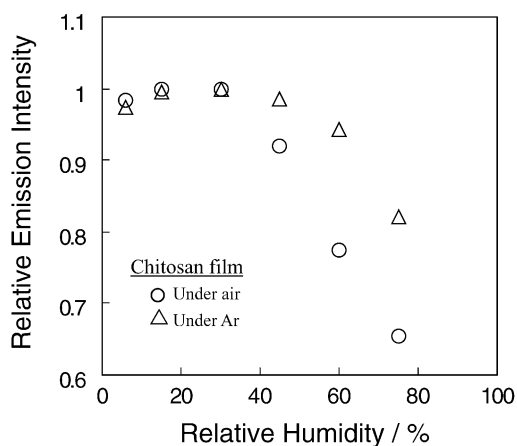


Fig. 6. Relative emission intensity changes of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into a chitosan solid film against relative humidity at 610 nm.

so that by adsorbing a small amount of water the O_2 present in the adsorbed water phase would quench the photoexcited $\text{Ru}(\text{bpy})_3^{2+}$.

At more than 20% RH in the κ -carrageenan film, the mobility of $\text{Ru}(\text{bpy})_3^{2+}$ would increase probably because the electrostatic interaction is suppressed by the adsorbed water, which reduces the τ and I_R of the probe with the increase of the RH. At the RH more than 20% the behavior under air and Ar is very similar, i.e., oxygen molecules are not working as a quencher showing that the $\text{Ru}(\text{bpy})_3^{2+}$ complex does not exist in water phase. However, it is not clear that the adsorbed moisture could access to the $\text{Ru}(\text{bpy})_3^{2+}$. Anyway the adsorbed water (at higher than 20% RH) makes the probe labile, which decreases the emission intensity.

The dependence of the I_R from the photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into a chitosan solid film on RH is shown in Fig. 6. In a chitosan solid film, only a small increase in I_R was observed up to 20% RH. However, the I_R decreased with the increase in the RH over 20% RH. The I_R was more strongly influenced by the RH under air

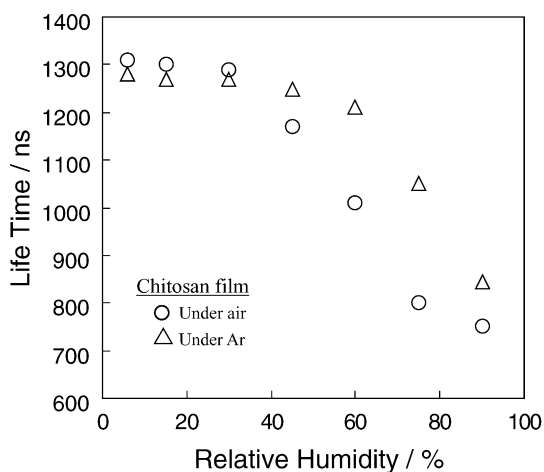


Fig. 7. Lifetime changes of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into a chitosan solid film against relative humidity at 610 nm.

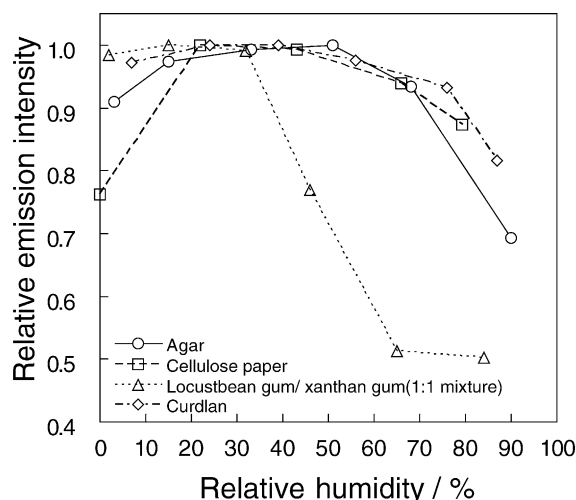


Fig. 8. Relative emission intensity changes of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into other polysaccharide solid films against relative humidity at 610 nm.

than under Ar. Chitosan does not involve any ionic groups so that the adsorbed water would interact mainly with the cationic $\text{Ru}(\text{bpy})_3^{2+}$ complex, i.e., the $\text{Ru}(\text{bpy})_3^{2+}$ complex would be quenched by the dissolved O_2 in the adsorbed water phase.

The dependence of the τ of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into a chitosan solid film on RH is shown in Fig. 7. In a chitosan solid film, only a small decrease of τ was observed up to 30% RH. However, over 30% RH, the τ decreased strongly with the increase in RH probably because the $\text{Ru}(\text{bpy})_3^{2+}$ probe becomes labile by migrating into the water phase. Over 30% RH, the τ was more strongly influenced by the RH under air than under Ar due to the quenching by O_2 dissolved in the adsorbed water phase.

The I_R of various samples (agar, cellulose paper, locust bean gum/xanthan gum (1:1 mixture), curdlan) against RH is shown in Fig. 8. Many of them show a maximum around 30% RH, but agar film shows a maximum around 50% RH. Such a tendency in emission intensity is similar to that of the κ -carrageenan film.

The general behavior of photoluminescence and lifetime of the photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into polysaccharide solid films are shown in Table 3 in comparison with the probe in an aqueous solution. In a dry condition of polysaccharide, since the polymer chain is hydrophobic, hydrophobic interaction would be present between the polymer chain and the hydrophobic bpy ligands of $\text{Ru}(\text{bpy})_3^{2+}$ molecules, so that the molecular mobility of $\text{Ru}(\text{bpy})_3^{2+}$

Table 3
Discussion of mechanism

Medium	Photoexcited $\text{Ru}(\text{bpy})_3^{2+}$		Mobility
	τ (ns)	Emission intensity	
Dry polysaccharide	~1300	Strong	Small
H_2O	600	Moderate	Large

would be small, which would be the reason for the long lifetime of the excited state $\text{Ru}(\text{bpy})_3^{2+}$ (1300 ns, in chitosan film). This lifetime is more than twice that in solution. This is the reason for the strong emission intensity in the solid. We have reported lifetime of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ in a Nafion film to be 1340 ns, which was ascribed to the hydrophobic interaction of the Nafion main chain with the bpy ligand of the Ru complex [13,14]. The present dry polysaccharide film would provide similar hydrophobic microenvironment the same as the Nafion film [14]. On the other hand, when the RH increases to nearly 100%, the lifetime of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ becomes close to 600 ns which is the lifetime in an aqueous solution, showing that in the high RH conditions, the microenvironment around the $\text{Ru}(\text{bpy})_3^{2+}$ probe would be close to water phase where the mobility of the molecule is large (for the chitosan case). However, for the κ -carrageenan case, although high humidity increases the mobility of the probe, the probe would not be present in water phase as clearly shown by the same emission intensity and lifetime both under Ar and air.

Acknowledgements

The present work has been supported by the Grant-in-Aid for Scientific Research (No. 15550101) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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