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Room-temperature phosphorescence of 6-bromo-2-naphthol in poly(vinyl alcohol) films containing cyclodextrins

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Abstract

The absorption spectral changes of 6-bromo-2-naphthol (BN) indicate the formation of inclusion complexes of BN with α-cyclodextrin (α-CD) and heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TM-β-CD) in a poly(vinyl alcohol) (PVA) film. The enhanced room-temperature (RT) phosphorescence of BN has been observed for PVA films containing BN and CDs (α-, β-, γ-CD, and TM-β-CD), whereas only the weak RT phosphorescence has been detected for a PVA film without CD. The enhancement of the RT phosphorescence in the presence of α-CD and TM-β-CD is due to the formation of the α-CD–BN and TM-β-CD–BN inclusion complexes, respectively. An induction period has been observed for the enhancement of the RT phosphorescence of BN in a PVA film containing TM-β-CD, although the weak RT phosphorescence has immediately appeared upon the excitation. The appearance of the induction period has been explained in terms of the generation of singlet oxygen by triplet BN bound to the TM-β-CD cavity and the subsequent oxygen consumption. From the analyses of the triplet–triplet absorption decays, triplet lifetimes have been evaluated for BN in PVA films in the absence and presence of CDs.

Keywords: Room-temperature phosphorescence; 6-Bromo-2-naphthol; Cyclodextrins; Poly(vinyl alcohol) film

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides composed of more than five D-glucopyranose residues; CDs having six, seven, and eight D-glucopyranose residues are called α-, β-, and γ-CD, respectively. CDs, which have a hydrophobic cavity, accommodate a guest molecule, leading to the variation of the physicochemical properties of a guest molecule incorporated into the CD cavity.

Because the triplet states of aromatic compounds generally have long natural lifetimes, they are liable to nonradiatively deactivate through quenching by oxygen and/or impurities in solution. Consequently, it is very difficult to observe the phosphorescence of the aromatic compounds in solutions at room temperature, even when solutions are degassed [1–4]. In the presence of CD, however, the phosphorescence of aromatic compounds has often been observed at room temperature, in some cases, even for aerated solutions [5–14]. Inclusion complexes of CD with the aromatic compounds are responsible for the room-temperature (RT) phosphorescence. In addition, the increase in the viscosity of the environment around CD may enhance the phosphorescence intensity furthermore; the increased viscosity of solution by the addition of D-glucose is effective in observing the RT phosphorescence of a guest molecule bound to the CD cavity [15,16].

Phosphorimetry, which is complementary to fluorimetry, is a useful tool for analytical purposes of detecting very small amounts of substances. Therefore, improvement of methods of enhancing the phosphorescence intensity is desirable from the analytical point of view [17,18].

The environment experienced by a solute molecule in a polymer film is considerably harder than that in fluid solution. The rigid environment in a polymer film is expected to promote the appearance and enhancement of the phosphorescence of the solute at room temperature. On the other hand, the formation of an inclusion complex between CD and a solute molecule is decelerated in organic solvents compared to water. Therefore, the embedding of the solute molecule into an organic polymer film may disfavor the inclusional complexation of CD with the solute. As a result, there is a possibility that the intensity enhancement by the addition of CD is not noticeable in a polymer film.

Previously, we have reported that the 2:1 α-CD–6-bromo-2-naphthol (BN) inclusion complex in aqueous solution

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emits the RT phosphorescence of BN [11,12]. Thus, we investigated whether inclusion complexes of CDs with BN are formed or not in poly(vinyl alcohol) (PVA) films and whether the RT phosphorescence of BN in PVA films containing CDs is observed or not. In addition, triplet-state lifetimes were evaluated for BN in PVA films containing CDs.

2. Experimental details

2.1. Reagents

6-Bromo-2-naphthol (BN) purchased from Tokyo Kasei Kogyo Co., Ltd. was recrystallized twice from benzene. α-Cyclodextrin (α-CD), γ-cyclodextrin (γ-CD), and heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TM-β-CD) purchased from Nakalai Tesque, Inc., Wako Pure Chemical Industries, Ltd., and Nakalai Tesque, Inc., respectively, were used without further purification. β-CD purchased from Nakalai Tesque, Inc. was twice recrystallized from water. Poly(vinyl alcohol) (PVA) obtained from Wako Pure Chemical Industries, Ltd., which was partly saponificated, was used as received. In this study, PVA of polymerization degree of 500 was used unless otherwise stated.

2.2. Preparation of samples

A 0.5 ml aliquot of methanolic BN (1.50×10^{-3} mol dm^{-3}) solution was added to 2 ml of aqueous PVA (30 g m^{-3}) solution. In the preparation of PVA films containing CD, CD was beforehand dissolved in the aqueous PVA solution. A 0.3 ml aliquot of the mixture of methanolic BN solution and aqueous PVA solution was spread out on a quartz plate 1.7 cm in width by 5.0 cm in length, and was dried at room temperature for about 15 h after the spreading of the mixture. The widths and lengths of PVA films thus prepared were about 1.5 and 2.0 cm, respectively. A PVA film on the quartz plate was used for the measurements of absorption and phosphorescence spectra. The concentrations of CDs in the sample solutions were 1.33×10^{-7} mol kg^{-1}, unless otherwise stated.

2.3. Apparatus

Absorption and phosphorescence spectra were recorded on a Shimadzu UV-260 spectrophotometer and a Shimadzu RF-501 spectrofluorometer equipped with a cooled Hamamatsu R-943 photomultiplier, respectively. A cylindrical chopper was employed for the measurements of the phosphorescence spectra. A PVA film on a quartz plate was held in an arrangement of front surface excitation. The phosphorescence was observed at right angles to the direction of the excitation light. The phosphorescence spectra were corrected for the spectral response of the fluorometer. Triplet–triplet (T–T) absorption spectra were measured with a conventional flash photolysis apparatus [19]. The measurements of the UV and T–T absorption spectra and the phosphorescence spectra for BN in PVA films were performed at 25 ± 2 °C.

3. Results and discussion

3.1. Absorption spectra of BN in PVA films containing CDs

In aqueous solution (25 ± 0.1 °C), the equilibrium constants for the formation of 1:1 inclusion complexes of BN with β-CD and TM-β-CD were evaluated to be 1900 ± 100 and 670 ± 10 mol^{-1} dm^{3}, respectively, from the absorption spectral change of BN. The methyl substituents in TM-β-CD somewhat prohibits the incorporation of BN into the TM-β-CD cavity, resulting in the equilibrium constant less than that for β-CD.

Since PVA does not form inclusion complexes with α-, β-, and γ-CD [20], the inclusional interactions do not take place between PVA and CDs. Fig. 1 shows absorption spectra of BN (1.25×10^{-8} mol kg^{-1}) in PVA films in the absence and presence of TM-β-CD (1.33×10^{-7} mol kg^{-1}) and α-CD (1.33×10^{-7} mol kg^{-1}). In the presence of TM-β-CD, the absorption peaks are slightly shifted to longer wavelengths. A 1:1 inclusion complex of TM-β-CD with BN is most likely formed in a PVA film as well as in aqueous solution. The absorption spectral change for α-CD is similar to that in aqueous α-CD solution of BN [11,12], although the absorption spectra of BN in PVA films are slightly blurred compared to those in aqueous solutions. With a 2:1 host–guest stoichiometry, α-CD forms an inclusion complex with BN in aqueous solution [11,12]. Therefore, the 2:1 α-CD–BN inclusion complex is most likely formed even in PVA films.

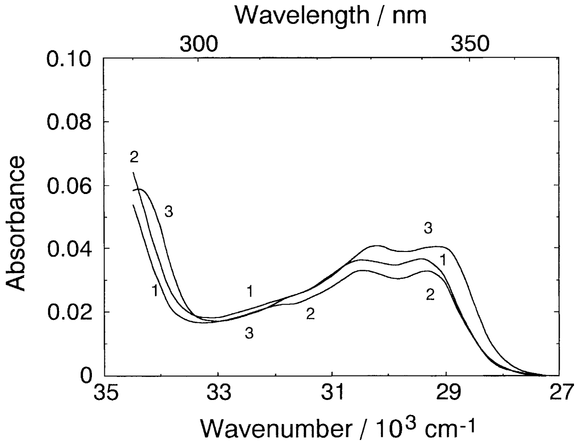


Fig. 1. Absorption spectra of BN (1.25×10^{-8} mol kg^{-1}) in PVA films in the absence (spectrum 1) and presence of TM-β-CD (1.33×10^{-7} mol kg^{-1}) (spectrum 2) and α-CD (1.33×10^{-7} mol kg^{-1}) (spectrum 3).

In PVA films, the absorption spectral change of BN is little upon the addition of β- and γ-CD. Therefore, we cannot decide here whether or not BN forms inclusion complexes with β- and γ-CDs.

3.2. Room-temperature (RT) phosphorescence of BN in PVA films containing TM-β-CD

The RT phosphorescence of BN was observed for PVA films with and without TM-β-CD (Fig. 2). As no RT phosphorescence can be observed in aqueous solution with and without TM-β-CD, the rigid environment of the PVA film induces the RT phosphorescence.

As will be mentioned below (Section 3.3), the RT phosphorescence intensity in the PVA film containing TM-β-CD increases after an induction period, and then attains the maximum intensity (I_p^∞). The RT phosphorescence intensity (I_p (induction)) during the induction period is one-third of that in the PVA film without CD. It is noted that I_p^∞ is about seven times greater than the RT phosphorescence intensity in the PVA film without CD.

Fig. 3 exhibits the dependence of I_p^∞ on the TM-β-CD concentration in a PVA film; I_p^∞ remains constant up to about 8.0×10^{-8} mol kg^{-1} and then increases. When the TM-β-CD concentration is raised, the crystalline phase of a PVA film may partly be changed to the amorphous phase. This phase change likely promotes the inclusion of BN into the TM-β-CD cavity, because the inclusion complex is considered to be formed in the amorphous region. The formation of the TM-β-CD–BN inclusion complex is responsible for the enhancement of the RT phosphorescence intensity. The appearance of a critical concentration (8.0×10^{-7} mol kg^{-1}) of TM-β-CD for the enhancement of the RT phosphorescence intensity is due to the phase change from the crystalline to amorphous phases of a PVA film. At the critical concentration, the molar ratio of TM-β-CD to PVA is estimated to be about 0.02, which seems to be reasonable. For PVA (completely hydrolyzed, 400–600 (polymerization degree)) containing TM-β-CD, a similar induction period and a similar enhancement of the RT phosphorescence have been obtained.

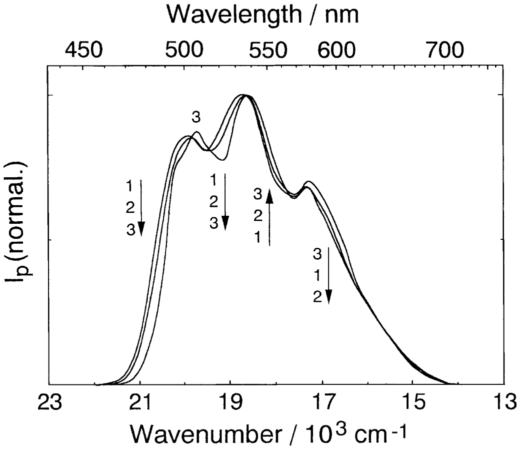


Fig. 2. RT phosphorescence spectrum of BN (1.25×10^{-8} mol kg^{-1}) in a PVA film without CD (spectrum 1), that with TM-β-CD of 1.33×10^{-7} mol kg^{-1} (spectrum 2), and that with α-CD of 1.33×10^{-7} mol kg^{-1} (spectrum 3). $\lambda_{ex} = 287$ nm.

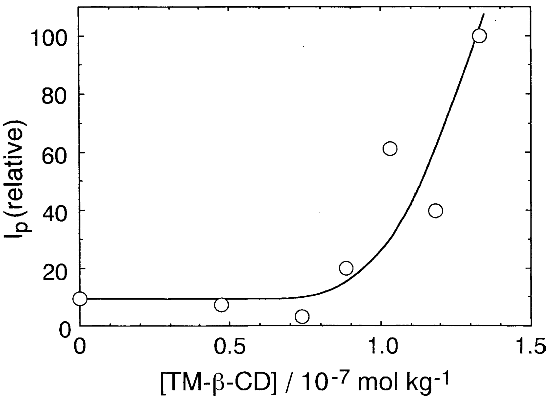


Fig. 3. Dependence of the maximal RT phosphorescence intensity of BN (1.25×10^{-8} mol kg^{-1}) in a PVA film containing TM-β-CD on the amount of TM-β-CD. $\lambda_{ex} = 87$ nm, $\lambda_{obs} = 500$ nm.

3.3. Irradiation-time effects on the RT phosphorescence of BN in a PVA film containing TM-β-CD

Fig. 4 shows the irradiation-time dependence of the RT phosphorescence intensity in a PVA film containing TM-β-CD. Such time-dependent behavior of the RT phosphorescence has not been observed for α-, β-, and γ-CD. The growth of the RT phosphorescence intensity is observed after an induction period of several minutes, whereas the weak RT phosphorescence (I_p (induction)) is observed immediately after the excitation. The same RT phosphorescence behavior has been again observed after standing the PVA film in the dark for about 2 days, indicating that the appearance of the induction period and the subsequent growth

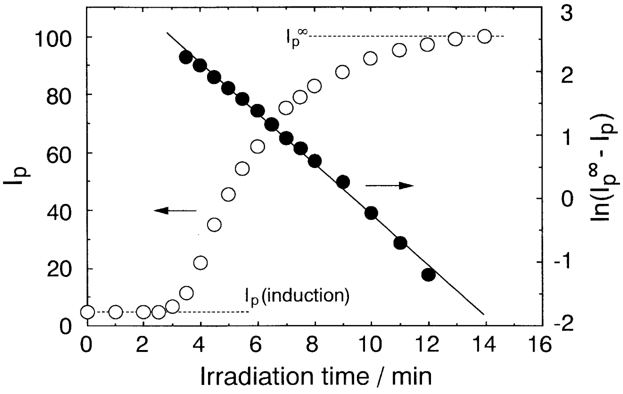


Fig. 4. Plots of RT phosphorescence intensity (○) and $\ln(I_p^\infty - I_p)$ (●) against irradiation time. The RT phosphorescence intensities at 510 nm were observed for BN (1.25×10^{-8} mol kg^{-1}) in a PVA film containing TM-β-CD (1.33×10^{-7} mol kg^{-1}), $\lambda_{ex} = 287$ nm.

of the RT phosphorescence are the reversible processes. The RT phosphorescence band shape does not change during the irradiation. In Fig. 4, a plot of $\ln(I_p^\infty - I_p)$ versus irradiation time is also shown, where I_p is the RT phosphorescence intensity at a given time. The plot exhibits a straight line, indicating a first-order reaction with a rate constant (k) of $6.7 \times 10^{-3}\,s^{-1}$.

It is unlikely that the induction period is due to a shift in an equilibrium between free BN and the TM-β-CD–BN inclusion complex, because the absorption spectrum of BN does not change during the irradiation. One might suppose that the local heating of a PVA film caused by the excitation light is responsible for the growth of the RT phosphorescence intensity after the induction period. However, it is not probable, because the RT phosphorescence intensity is reduced upon the raise of temperature of the sample.

3.4. Oxygen and nitrogen effects on the RT phosphorescence intensity of BN in a PVA film containing TM-β-CD

To examine the effect of oxygen molecules involved in a PVA film, we placed a PVA sample containing TM-β-CD in a sealed container filled with oxygen or nitrogen gas for 2 days. Immediately after taking the PVA sample out of the container, the RT phosphorescence was measured in an aerated atmosphere. Fig. 5 illustrates the oxygen and nitrogen gas effects on the irradiation-time dependence of the RT phosphorescence intensity. Oxygen gas definitely lengthens the induction period and reduces the k value down to $1.2 \times 10^{-3}\,s^{-1}$. In contrast, nitrogen gas gets rid of the induction period and increases the k value up to $9.4 \times 10^{-3}\,s^{-1}$. Such significant effects of oxygen and nitrogen gases indicate that oxygen molecules in the PVA film are responsible for the irradiation-time dependence of the RT phosphorescence intensity. The slight intensity rise of the RT phosphorescence observed for the sample placed in nitrogen atmosphere may be attributed to residual O_2 in the PVA film.

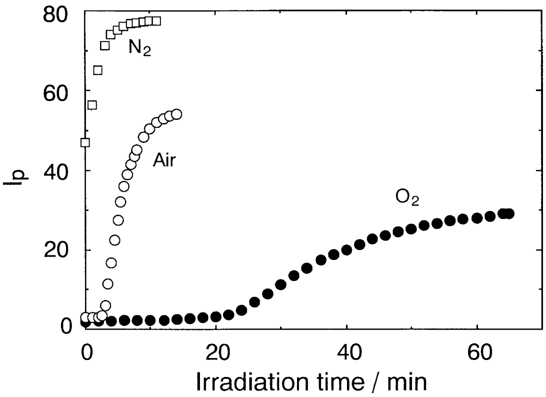


Fig. 5. Oxygen and nitrogen effects on the RT phosphorescence intensity of BN ($1.25 \times 10^{-8}\,mol\,kg^{-1}$) in PVA films containing TM-β-CD ($1.33 \times 10^{-7}\,mol\,kg^{-1}$). Data for PVA samples, which were treated under the atmosphere of air, oxygen, and nitrogen, were represented by open circles, closed circles, and squares, respectively. The PVA sample, which was treated with oxygen or nitrogen, was placed under the atmosphere of oxygen or nitrogen for 2 days. Under the aerobic atmosphere, the RT phosphorescence intensity of the PVA sample was measured immediately after taking it out from a container filled with oxygen or nitrogen.

The O_2 molecules in the PVA film may quench the RT phosphorescence. Consequently, the growth of the RT phosphorescence intensity after the induction period suggests that the O_2 molecules around BN are consumed by a first-order reaction with a rate constant of k upon the steady light irradiation. The RT phosphorescence intensity in the PVA film without TM-β-CD is not changed by a prolonged irradiation. Therefore, as the O_2 consumption reaction, we can suppose the oxygenation reaction of TM-β-CD by singlet oxygen, which may be generated by the energy transfer from triplet BN to O_2.

In a rigid PVA film, the migration of solute molecules is very slow. It is true for O_2. Indeed, we need about 2 days for the recovery of the irradiation-time dependence of the RT phosphorescence intensity in the PVA film containing TM-β-CD. Therefore, it may be assumed that the penetration of O_2 into the PVA films from surrounding atmosphere is negligible during the measurement of the RT phosphorescence.

Although the migration of O_2 is slow in the PVA film, the RT phosphorescence intensity rapidly rises after the induction period as shown in Fig. 4. The energy transfer from triplet BN to O_2 has to take place within the triplet lifetime of BN and the subsequent oxygenation reaction within the lifetime of singlet oxygen. The triplet lifetime is 7.4 ms at most (see Table 1) and the lifetime of singlet oxygen is considered to be less than about 1 μs [21,22]. In a rigid PVA film, these lifetimes are too short for triplet BN and singlet oxygen to migrate far away. Therefore, both the energy transfer and the oxygenation reaction must occur in the vicinity of TM-β-CD, i.e. in the TM-β-CD–BN inclusion complex.

For the kinetic analysis of the irradiation-time dependence of the RT phosphorescence intensity shown in Figs. 4 and 5, we assume simply two kinds of species as the inclusion complexes: first is a phosphorescent TM-β-CD–BN inclusion complex (TM-β-CD · BN), in which O_2 is not involved. Second is a non-phosphorescent TM-β-CD–BN–O_2 inclusion complex (TM-β-CD · BN/O_2), in which O_2 quenches triplet BN to yield singlet oxygen. There arises the induction period when all of the species remains as the second one. The RT phosphorescence observed during the induction period is attributed to the RT phosphorescence of free BN in bulk PVA, and hence, its intensity does not change during the irradiation. The RT phosphorescence intensity begins to grow when the second species are turned into the first species upon the irradiation. In this period, O_2 is consumed by the oxygenation reaction of TM-β-CD with singlet oxygen. The oxygenation reaction would take place during the induction period. However, the growth of the RT phosphorescence intensity does not begin until all of the O_2 molecules in the

Table 1
The τ_T and A values of the triplet decays and the relative intensities (I_p (relative)) of the RT phosphorescence of BN in a PVA film without CD and those in PVA films containing α-, β-, γ-CD, and TM-β-CD

Cd[a]	τ_T(fast) (ms)	τ_T(slow) (ms)	A_f (%)	A_s (%)	I_p (relative)[b] (calc.)	I_p (relative)[c] (exp.)
None	0.26	1.5	41.9	58.1	1.0	1.0
α-CD	0.43	4.2	26.2	73.8	3.3	20
β-CD	0.35	2.3	26.8	73.2	1.8	2.3
γ-CD	0.34	3.4	26.4	73.6	2.6	2.5
TM-β-CD[d]	0.11	0.67	73.3	26.7	0.26	0.3
TM-β-CD[e]	1.6	7.4	41.1	58.9	5.1	7

[a] The concentrations of BN and CDs in PVA films were 1.25×10^{-8} and 1.33×10^{-7} mol kg^{-1}, respectively.
[b] The relative RT phosphorescence intensities of BN were calculated according to Eq. (9).
[c] The relative RT phosphorescence intensities of BN were obtained from the experiments.
[d] Data during the induction period.
[e] Data after the growth of the RT phosphorescence intensity.

neighborhood of BN incorporated into the TM-β-CD cavity is consumed.

We represent the concentration of TM-β-CD · BN, which is responsible for the increased intensity of the RT phosphorescence at time t after the induction period, as [TM-β-CD · BN](t). Because the absorbance of BN dissolved in a PVA film is less than 0.1 and the highly phosphorescent species is only TM-β-CD · BN, the intensity $I_p(t)$ of the RT phosphorescence at time t is represented by

$$I_p(t) - I_p(\text{induction}) = \frac{\alpha \Phi_p I_{abs}^0 [\text{TM-}\beta\text{-CD} \cdot \text{BN}](t)}{[\text{BN}]_0} \quad (1)$$

Here, α, Φ_p, and I_{abs}^0 are an instrumental constant, the quantum yield for the RT phosphorescence of TM-β-CD · BN, and the rate of the excitation-light absorption by a sample, respectively. $[\text{BN}]_0$ is the total concentration of BN involved in the PVA film:

$$[\text{BN}]_0 = [\text{BN}]_{bulk} + \left[\frac{\text{TM-}\beta\text{-CD} \cdot \text{BN}}{\text{O}_2}\right](t) + [\text{TM-}\beta\text{-CD} \cdot \text{BN}](t) \quad (2)$$

The concentration ($[\text{BN}]_{bulk}$) of free BN in bulk PVA is kept constant during the irradiation, because the photo-degradation of BN in the PVA film without CD is negligible. Therefore, the sum of $[\text{TM-}\beta\text{-CD} \cdot \text{BN/O}_2]](t)$ and [TM-β-CD · BN](t) remains constant, C_0:

$$C_0 = \left[\frac{\text{TM-}\beta\text{-CD} \cdot \text{BN}}{\text{O}_2}\right](t) + [\text{TM-}\beta\text{-CD} \cdot \text{BN}](t) \quad (3)$$

By the prolonged irradiation, TM-β-CD · BN/O_2 is completely converted into TM-β-CD · BN, so that $I_p(t)$ attains the maximum phosphorescence intensity, I_p^∞:

$$I_p^\infty - I_p(\text{induction}) = \frac{\alpha \Phi_p I_{abs}^0 C_0}{[\text{BN}]_0} \quad (4)$$

From Eqs. (1) and (4), we derive the equation:

$$I_p^\infty - I_p(t) = \alpha \Phi_p I_{abs}^0 \frac{[\text{TM-}\beta\text{-CD} \cdot \text{BN/O}_2](t)}{[\text{BN}]_0} \quad (5)$$

The rate of decrease in [TM-β-CD · BN/O_2] due to the oxygenation reaction through the singlet-oxygen generation is considered to be proportional to the rate of light absorption by TM-β-CD · BN/O_2.

$$-\frac{d[\text{TM-}\beta\text{-CD} \cdot \text{BN/O}_2](t)}{dt} = \Phi_r I_{abs}^0 \frac{[\text{TM-}\beta\text{-CD} \cdot \text{BN/O}_2](t)}{[\text{BN}]_0} \quad (6)$$

Here, Φ_r is the quantum yield for photo-conversion of TM-β-CD · BN/O_2 into TM-β-CD · BN. Thus, we obtain

$$\left[\frac{\text{TM-}\beta\text{-CD} \cdot \text{BN}}{\text{O}_2}\right](t) = C_0 \exp(-kt) \quad (7)$$

Here,

$$k = \frac{\Phi_r I_{abs}^0}{[\text{BN}]_0}.$$

From Eqs. (5) and (7), we obtain

$$I_p^\infty - I_p(t) = \left(\frac{\alpha \Phi_p I_{abs}^0}{[\text{BN}]_0}\right) C_0 \exp(-kt) \quad (8)$$

Therefore, $I_p^\infty - I_p$ follows a first-order kinetics as shown in Fig. 4.

The lifetime of singlet oxygen is influenced by the presence of hydroxy groups in an environment; in protic solvents such as water and alcohol, the lifetime is shortened [21,22]. Since TM-β-CD does not have a hydroxy group in contrast to α-, β-, and γ-CDs, the lifetime of singlet oxygen located within the TM-β-CD cavity is expected to be longer than those within the cavities of α-, β-, and γ-CDs. Therefore, the oxygenation reaction due to singlet oxygen is facilitated within the TM-β-CD cavity. This will be one of the reasons why the induction period followed by the growth of the RT phosphorescence is observed for TM-β-CD alone.

We further examined the dependence of the k value on the TM-β-CD concentration in a PVA film (Fig. 6). The k value is decreased as the TM-β-CD concentration is increased. In PVA films, CDs are most likely hydrogen bonded to PVA.

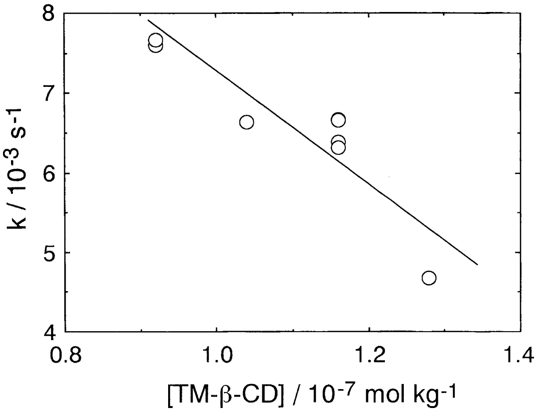


Fig. 6. TM-β-CD concentration dependence of k for BN (1.25×10^{-8} mol kg^{-1}) in PVA films containing TM-β-CD.

In the hydrogen bonding interaction between TM-β-CD and PVA, TM-β-CD acts as only a hydrogen acceptor towards PVA, while α-, β-, and γ-CDs act both as a hydrogen acceptor and a hydrogen donor. This implies that the interactions between TM-β-CD and PVA are weaker than those between the other CDs and PVA. When the TM-β-CD concentration is increased, the structure of the PVA film becomes loose compared to that without TM-β-CD, and hence, the mobility of O_2 increases with an increase of TM-β-CD concentration. If the O_2 molecules apart from TM-β-CD · BN can migrate to encounter with BN included in TM-β-CD · BN, the RT phosphorescence may be quenched by the O_2 molecules, too. Thus, the effective O_2 concentration for the quenching increases with the increase in the TM-β-CD concentration. The increase in the effective O_2 concentration reduces the k value. Such consideration is supported by the facts shown in Fig. 5 that the increase (or decrease) in the effective O_2 concentration by standing the PVA film in oxygen (or nitrogen) atmosphere decreases (or increases) the k value, and increases (or decreases) the induction period.

3.5. *RT phosphorescence of BN in a PVA film containing α-, β-, or γ-CD*

The RT phosphorescence spectrum for a PVA film containing β- or γ-CD is nearly the same as that for a PVA film containing TM-β-CD. In contrast, the RT phosphorescence spectrum for α-CD is slightly sharpened compared to those for the other CDs (Fig. 2) and it is similar to that observed for aqueous BN solution containing α-CD [11,12]. In aqueous solution, the 2:1 α-CD–BN inclusion complex is responsible for the RT phosphorescence. Even in PVA films, therefore, the 2:1 α-CD–BN inclusion complex is formed. The RT phosphorescence intensities in PVA films containing α-, β-, and γ-CD are about 20, 2.3, and 2.5 times greater than that in the absence of CD, respectively. The significantly enhanced RT phosphorescence in the PVA film containing α-CD provides additional evidence for the formation of the 2:1 α-CD–BN inclusion complex. In the cases of β- and γ-CDs, no evidence for the inclusion complex formation was obtained from the phosphorescence spectra as well as the absorption spectra. Consequently, the increase in the RT phosphorescence intensity may be attributed to the increased rigidity of a PVA film containing β- or γ-CD owing to the hydrogen bond formation between PVA and CD, although the change from the crystalline phase to the amorphous phase is partly induced by the presence of β- or γ-CD. It is noteworthy that the inclusion complex of β-CD with BN is formed in aqueous solution [12], but not in the PVA film.

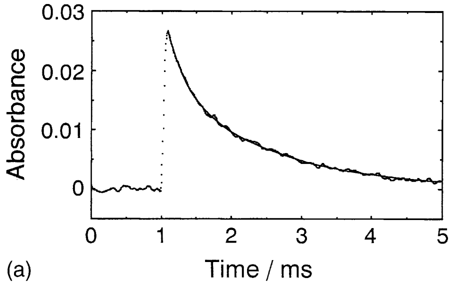
When PVA films with and without α-CD were maintained at 50 °C for 30 min and then were cooled at room temperature for 1 h, the RT phosphorescence from PVA films was enhanced in intensity by 1.3 to about two times. It is likely that the PVA films become hard through the further drying at 50 °C, because water molecules are removed from the PVA films to some extent. The increased hardness of the PVA films is responsible for the increase in the intensity of the RT phosphorescence. In addition, the decrease in the oxygen concentration in the PVA films through the drying at 50 °C may contribute to the increase in the RT phosphorescence intensity. When PVA of the polymerization degree of about 1500 has been used for the preparation of films, the phosphorescence spectrum and intensity have been similar to those from PVA films of the polymerization degree of about 500, indicating that the RT phosphorescence of BN is not affected by the polymerization degree of PVA.

3.6. *Triplet lifetimes of BN in PVA films containing CDs*

To further characterize the properties of the RT phosphorescence, we measured the T–T absorption spectra of BN in PVA films with and without CDs. In cyclohexane, a peak of the T–T absorption band of BN is located at 450 nm, and a weak band peak is at 420 nm [23]. In PVA films with and without CDs, in contrast, the peak of the T–T absorption is located at 460 nm, and the weak peak (or shoulder) at 430 nm.

The decay curve of triplet BN in the PVA film without CD was apparently analyzed as a bi-exponential function (Fig. 7(a)). The triplet lifetimes (τ_T) obtained from the fast- and slow-decay components were 0.26 and 1.5 ms, respectively. The former amplitude ($A_f = 41.9\%$) was less than the latter ($A_s = 58.1\%$). The decay curves of triplet BN in PVA films containing CDs were also analyzed as a bi-exponential function (Fig. 7(b)) for α-CD). The τ_T and A values evaluated are summarized in Table 1.

The τ_T(fast) and τ_T(slow) values in the presence of α-, β-, or γ-CD are greater than those in the absence of CD, respectively, supporting the increase in the environment rigidity due to the hydrogen bond formation between the CDs and PVA. The τ_T(slow) value for α-CD slightly greater than those for β- and γ-CDs suggests that BN forms the inclusion complex with α-CD. Due to the hydrogen-bonding characteristics of TM-β-CD acting as only a hydrogen acceptor towards PVA, the rigidity of the amorphous phase of a PVA



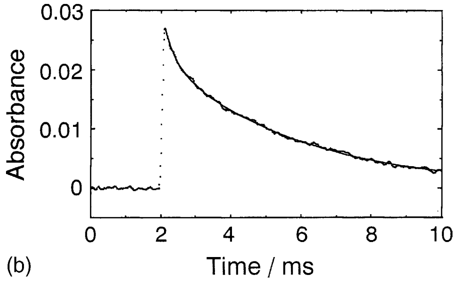


Fig. 7. (a) T–T absorption decay of BN (1.25×10^{-8} mol kg^{-1}) in a PVA film without CD: (···) observed decay; (—) decay curve calculated with $A_f = 0.0136$, $\tau_T(\text{fast}) = 0.26$ ms, $A_s = 0.0188$, and $\tau_T(\text{slow}) = 1.5$ ms. (b) T–T absorption decay of BN (1.25×10^{-8} mol kg^{-1}) in a PVA film containing α-CD (1.33×10^{-7} mol kg^{-1}): (···) observed decay; (—) decay curve calculated with $A_f = 0.00761$, $\tau_T(\text{fast}) = 0.43$ ms, $A_s = 0.0214$, and $\tau_T(\text{slow}) = 4.2$ ms, $\lambda_{obs} = 430$ nm.

film containing TM-β-CD is most likely lower than those of PVA films containing the other CDs. During the induction period, therefore, the effective O_2 concentration in the quenching of triplet BN is likely high compared to the PVA films with the other CDs. Consequently, both the τ_T(fast) and τ_T(slow) values for TM-β-CD are minimal, though a part of BN molecules forms the inclusion complexes. After the growth of the RT phosphorescence, on the other hand, the O_2 concentration is drastically reduced, and hence, both the τ_T(fast) and τ_T(slow) values for TM-β-CD are maximal. At any rate, the large τ_T values in the presence of CD are consistent with the enhancement of the RT phosphorescence in the PVA films.

When two components with different lifetimes such as τ_T(fast) and τ_T(slow) are responsible for the RT phosphorescence, the RT phosphorescence yield (Φ_p) is given by

$$\Phi_p = k_p \Phi_{isc}(A_f \tau_T(\text{fast}) + A_s \tau_T(\text{slow})) \quad (9)$$

Here, k_p and Φ_{isc} are the rate constant for phosphorescence and the quantum yield of intersystem crossing, respectively. The relative RT phosphorescence intensity is linear with respect to Φ_p. k_p is most likely a constant. Φ_{isc} can be assumed to be close to unity, because the intersystem crossing is significantly enhanced by the presence of a heavy atom such as Br. Therefore, the relative RT phosphorescence intensities for the PVA films can be calculated from Eq. (9), using the A and τ_T values in Table 1. The relative RT phosphorescence intensities calculated were listed in Table 1, together with those obtained from the experiments.

If it is taken into account that I_p strongly depends on the geometrical arrangement of the PVA film, the agreement of the calculated and the experimental values are good in the cases of β-, γ-, and TM-β-CD (I_p (induction)), but not in the cases of α-CD and TM-β-CD (I_p^∞).

In the cases of the PVA films with and without β- or γ-CD, the inclusion complex is not formed, as stated previously. Consequently, all of triplet BN is equivalently dispersed in the bulk PVA film, and hence, Eq. (9) can be used for the calculation of the relative RT phosphorescence intensity.

In the cases of the PVA films with α-CD or TM-β-CD, there are two kinds of triplet BN: one is located in bulk PVA and the other is in the inclusion complex. The triplet BN in the inclusion complexes (the α-CD–BN inclusion complex and TM-β-CD · BN) is highly phosphorescent, but not the triplet BN in bulk PVA. Consequently, the former lifetime should be remarkably longer than the latter ones (τ_T(fast) and τ_T(slow) in Table 1). However, such an extraordinary long-lived triplet BN was not detected by the flash photolysis even in the PVA film with α-CD or TM-β-CD. Therefore, the population of triplet BN with an extraordinary long-lifetime is considered to be quite low.

The apparent discrepancy in the relative phosphorescence intensity between the calculated and the experimental ones may be interpreted as follows: in the measurement of the T–T absorption decay, all the triplet molecules located in both bulk PVA and the inclusion complex are equivalently counted. In the measurement of the RT phosphorescence by using a chopper, in contrast, there is a tendency that the triplet BN molecules with an extraordinary long-lifetime are selectively counted. As the contribution of the extraordinary long-lived triplet molecules is not taken into account in Eq. (9), Eq. (9) cannot be used to evaluate the RT phosphorescence intensity in the PVA film with α-CD or TM-β-CD (I_p^∞). In other words, the discrepancy of the relative phosphorescence intensity between the calculated and the experimental ones may provide evidence for the inclusion complex formation, even if the extraordinary slow decay component cannot be detected by the flash photolysis. If there is no discrepancy, it presents evidence for the lack of the inclusion complex formation.

4. Concluding remarks

BN was found to form inclusion complexes with α-CD and TM-β-CD in PVA films. The RT phosphorescence of BN was enhanced by the α-CD–BN and TM-β-CD–BN inclusion complex formation, although the weak RT phosphorescence was detected for BN in a PVA film without CD. At relatively high concentrations of CDs, part of the crystalline phase of a PVA film is most likely changed to the amorphous phase. The enhanced RT phosphorescence of BN in PVA films containing β- and γ-CD is due to the increased rigidity around BN in the amorphous phase, because CD can be hydrogen bonded to PVA. The strongest

RT phosphorescence of BN was observed for the α-CD–BN inclusion complex, whose stoichiometry has been most likely 2:1 from the similarity between the absorption spectrum of BN in a PVA film and that in aqueous solution.

In a PVA film containing TM-β-CD, the induction period was observed for the enhancement of the RT phosphorescence of BN, although the weak RT phosphorescence immediately appeared upon the excitation. A large amount of oxygen dissolved in a PVA film lengthens the induction period and retards the rate of the rising of the RT phosphorescence intensity, whereas nitrogen exerts the reverse effects on the induction period and the rising rate of the RT phosphorescence. During the irradiation of the excitation light, the O_2 molecules in the vicinity of a BN molecule, which is incorporated into the TM-β-CD cavity, is most likely consumed through the oxygenation reaction, resulting in the enhancement of the RT phosphorescence after the induction period.

The τ_T(slow) and τ_T(fast) values for PVA films containing CDs are respectively greater than those for a PVA film without CD, except for those for a PVA film containing TM-β-CD during the induction period. The small τ_T values for TM-β-CD during the induction period may be attributed to the increase in the effective concentration of O_2 due to the soft environment of a PVA film containing TM-β-CD. On the other hand, the τ_T values for TM-β-CD after the attainment of the maximal RT phosphorescence intensity are the greatest of all the values examined, suggesting the consumption of oxygen in a PVA film until the attainment of the maximal RT phosphorescence intensity.

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