# Inclusion of 2-Chloronaphthalene by α-Cyclodextrin and Room-Temperature Phosphorescence of 2-Chloronaphthalene in Aqueous D-Glucose Solutions Containing α-Cyclodextrin

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In aqueous solutions, α-cyclodextrin (α-CD) forms a 1:1 inclusion complex with 2-chloronaphthalene (2-CN), and further associates with the 1:1 inclusion complex to form a 2:1 α-CD−2-CN inclusion complex. In aqueous D-glucose solutions, α-CD also forms the 1:1 and 2:1 inclusion complexes with 2-CN. Equilibrium constants for the formation of the 1:1 and 2:1 inclusion complexes have been evaluated from simulations of the observed fluorescence intensities of 2-CN in aqueous solutions with and without D-glucose. For 2-CN solutions containing both D-glucose and α-CD, the room-temperature phosphorescence of 2-CN has been observed. The 2:1 α-CD−2-CN inclusion complex is responsible for the room-temperature phosphorescence. The quantum yield ($\phi_p$) of the room-temperature phosphorescence from the 2:1 inclusion complex has been determined to be at least 0.029, which is 19% of a $\phi_p$ value of 2-CN in ethanol at 77 K. When KI is added to D-glucose solutions containing α-CD, the room-temperature phosphorescence intensity is initially enhanced, but it is decreased with a further increase in the KI concentration. The initial enhancement of the room-temperature phosphorescence intensity is due to the formation of an α-CD−2-CN−$I^-$ inclusion complex, and the intensity reduction at higher concentrations of KI seems to be due to the formation of a nonphosphorescent ternary inclusion complex containing two $I^-$ ions.

## Introduction

Cyclodextrins (CDs) are composed of D-glucose residues joined by α(1→4) linkages. α-, *β*-, and *γ*-CDs, which are made up of six, seven, and eight D-glucose residues, are the most common members of a CD family. These CDs are shaped like a truncated cone with a hollow, hydrophobic cavity in which a hydrophobic guest can be incorporated.

In aqueous solutions, inclusion of a guest molecule by CD frequently induces room-temperature phosphorescence of a guest molecule, which cannot be observed usually in solutions without CD.[1−3] It is known that ternary inclusion complexes are formed among CD(s) and two different kinds of guest molecules.[4−7] When a halogenated guest and another guest carrying no heavy atom are simultaneously incorporated into the same CD cavity, room-temperature phosphorescence of a halogenated guest has been observed.[8−10] Simultaneous accommodation of a non-halogenated guest and an additional guest carrying a heavy atom also induces the room-temperature phosphorescence of a non-halogenated guest.[11−14] The external heavy atom effect of the additional guest accelerates the intersystem crossing from the excited singlet state to the triplet state of the non-halogenated guest. Bromine atoms (or an iodine atom) substituted on the primary hydroxyl-group side of the CD cavity exert the external heavy atom effect on an incorporated guest molecule, resulting in the observation of the room-temperature phosphorescence of the guest molecule.[15,16]

In these inclusion complexes exhibiting room-temperature phosphorescence, *β*- and *γ*-CDs are used as a host. In addition, only one *β*- or *γ*-CD molecule is included in the inclusion complexes emitting room-temperature phosphorescence. On the other hand, α-CD has been found to form a 2:1 α-CD−6-bromo-2-naphthol inclusion complex from which the room-temperature phosphorescence of 6-bromo-2-naphthol is observed.[17,18] A 1:1 α-CD−6-bromo-2-naphthol inclusion complex does not phosphoresce at room temperature. The different emission behavior of the two inclusion complexes suggests that 6-bromo-2-naphthol within the 2:1 α-CD−6-bromo-2-naphthol inclusion complex is in a fairly rigid environment, whereas the degree of freedom of 6-bromo-2-naphthol within the 1:1 inclusion complex is high compared to the 2:1 inclusion complex. Therefore, 2:1 α-CD−guest inclusion complexes may have the unique property that emits room-temperature phosphorescence in aqueous solutions.

Thus, we investigated the emission behavior of 2-chloronaphthalene (2-CN) in aqueous solutions and D-glucose solutions in the presence of α-CD. For 2-CN solutions containing both D-glucose and α-CD, the room-temperature phosphorescence of 2-CN was observed, although it was not detected for 2-CN solutions containing only α-CD. We also examined the concentration effects of KI on the 2-CN room-temperature phosphorescence intensity.

## Experimental Section

2-Chloronaphthalene (2-CN) purchased from Tokyo Kasei Kogyo, Co. Ltd. was purified by use of silica-gel column chromatography. α-Cyclodextrin (α-CD) purchased from Nacalai Tesque, Inc., was used as received. *β*-CD obtained from Nacalai Tesque, Inc., was recrystallized two times from water. D-Glucose obtained from Wako Pure Chemical Industries, Ltd., was used without further purification. Aqueous solutions of 2-CN were prepared by plunging purified 2-CN crystals into water in the dark for several days. Aqueous D-glucose solutions of 2-CN were prepared as follows. A 1.7 mL volume of aqueous 2-CN solution was added to 5.0 g of D-glucose in a small glassware, with or without α-CD (e.g., 54.1 mg ($1.0 \times 10^{-2}$ mol $dm^{-3}$)). The mixture was heated to about 110 °C to make it transparent. To obtain reproducible experimental data, the sample solution thus prepared was transferred to a quartz cell under nitrogen atmosphere in a glovebox. The viscosities

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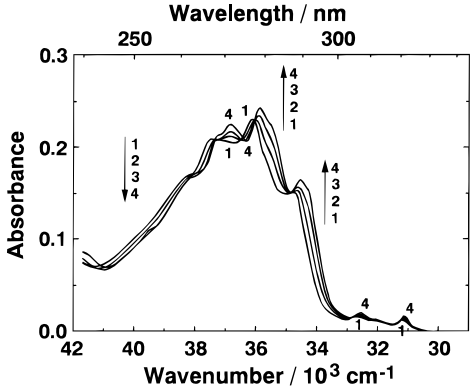


**Figure 1.** Absorption spectra of 2-CN ($4.6 \times 10^{-5}$ mol dm$^{-3}$) in aqueous solutions containing varying concentrations of α-CD. Concentration of α-CD: (1) 0, (2) $2.0 \times 10^{-3}$, (3) $5.0 \times 10^{-3}$, and (4) $1.0 \times 10^{-2}$ mol dm$^{-3}$.

of D-glucose solutions with and without α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$) were evaluated to be 600 and 850 cP, respectively, at 25 °C.

Concentrations of 2CN in aqueous solutions were about $4.6 \times 10^{-5}$ mol dm$^{-3}$ for absorption and induced circular dichroism (icd) spectral measurements, and they were about $2.3 \times 10^{-5}$ mol dm$^{-3}$ for fluorescence and phosphorescence measurements. The 2-CN concentrations of D-glucose solutions were about $1.6 \times 10^{-5}$ mol dm$^{-3}$ for all the spectroscopic measurements.

Absorption spectra were recorded on a Shimadzu UV-260 spectrophotometer. Fluorescence and phosphorescence spectra were taken with a Shimadzu RF-501 spectrofluorometer equipped with a cooled Hamamatsu R-943 photomultiplier. Fluorescence and phosphorescence spectra were corrected for the spectral response of the fluorometer. Fluorescence and phosphorescence quantum yields of 2-CN in D-glucose solutions were corrected for the refractive indices of D-glucose solutions. Icd spectra were measured with a JASCO J-600 spectropolarimeter.

In fluorescence lifetime experiments, light pulses for excitation were second harmonics (300 nm) of the output of a Coherent OPA 9400 optical parametric amplifier (200 kHz), which was seeded from a Coherent Mira 900 Ti:sapphire oscillator (76 MHz). Both the amplifier and the oscillator were pumped with a Coherent Innova 400 CW argon ion laser. Fluorescence decays were measured employing a Hamamatsu C4334 streak scope. Phosphorescence decay curves were obtained with a conventional flash photolysis apparatus.[19]

Spectroscopic measurements were made at 25 ± 0.1 °C except for icd, fluorescence lifetime, and phosphorescence lifetime studies which were made at room temperature.

## Results and Discussion

**Absorption Spectra of 2-CN in Aqueous Solutions.** Figure 1 shows absorption spectra of 2-CN in aqueous solutions containing varying concentrations of α-CD. Although the absorption spectra show isosbestic points at 267.5 and 278 nm, they are not observed at around 245 and 275 nm. This finding indicates that there is more than one inclusion complex of 2-CN with α-CD. A usual double reciprocal plot of $1/(A - A_0)$ against $1/[\alpha\text{-CD}]_0$ exhibited an upward concave curve (not shown), where $A$ and $A_0$ are the absorbances of 2-CN in the presence and absence of α-CD, and $[\alpha\text{-CD}]_0$ is the initial concentration of α-CD, providing further evidence for the existence of at least two kinds of inclusion complexes. Because the cavity of α-CD is smaller than that of $\beta$-CD, part of a 2-CN molecule in a 1:1 inclusion complex with α-CD is still located in a bulk water environment. Consequently, another α-CD molecule is most likely to accommodate the protruded part of 2-CN in the 1:1 inclusion complex, leading to the formation of a 2:1 α-CD−2-CN inclusion complex:

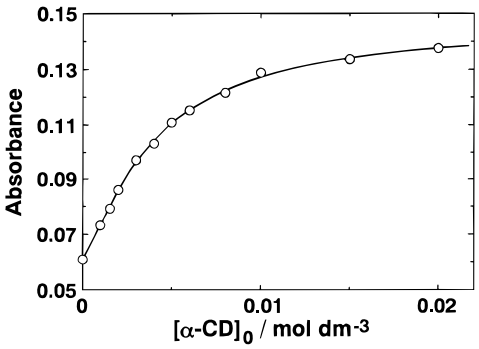


**Figure 2.** α-CD concentration dependence of the 2-CN absorbance in aqueous solution. Circles represent experimental points. The best fit curve was calculated with $K_1 = 292$ mol$^{-1}$ dm$^3$, $K_2 = 246$ mol$^{-1}$ dm$^3$, $\epsilon_0 = 1330$ mol$^{-1}$ dm$^3$ cm$^{-1}$, $\epsilon_1 = 2130$ mol$^{-1}$ dm$^3$ cm$^{-1}$, and $\epsilon_2 = 3240$ mol$^{-1}$ dm$^3$ cm$^{-1}$. $\lambda_{obs} = 293$ nm.

$$\alpha\text{-CD} + 2\text{-CN} \overset{K_1}{\rightleftharpoons} \alpha\text{-CD}\cdot 2\text{-CN} \quad (1)$$

$$\alpha\text{-CD} + \alpha\text{-CD}\cdot 2\text{-CN} \overset{K_2}{\rightleftharpoons} (\alpha\text{-CD})_2\cdot 2\text{-CN} \quad (2)$$

Here, α-CD·2-CN and $(\alpha\text{-CD})_2$·2-CN are the 1:1 and 2:1 α-CD−2-CN inclusion complexes, respectively, and $K_1$ and $K_2$ are the equilibrium constants for the formation of α-CD·2CN and $(\alpha\text{-CD})_2$·2CN, respectively.

The absorbance for α-CD solution in a 1 cm pass length cell is represented as a sum of the absorbances of free 2CN, α-CD·2CN, and $(\alpha\text{-CD})_2$·2CN:

$$A = \epsilon_0[2\text{-CN}] + \epsilon_1[\alpha\text{-CD}\cdot 2\text{-CN}] + \epsilon_2[(\alpha\text{-CD})_2\cdot 2\text{-CN}] \quad (3)$$

where $\epsilon_0$, $\epsilon_1$, and $\epsilon_2$ are the molar absorption coefficients of free 2-CN, α-CD·2-CN, and $(\alpha\text{-CD})_2$·2-CN, respectively, and square brackets stand for the concentration. In the α-CD−2-CN system where the concentration of 2-CN is negligible relative to that of α-CD, the concentrations of these species are expressed by

$$[2\text{-CN}] = [2\text{-CN}]_0/(1 + K_1[\alpha\text{-CD}]_0 + K_1K_2[\alpha\text{-CD}]_0^2) \quad (4)$$

$$[\alpha\text{-CD}\cdot 2\text{-CN}] = K_1[2\text{-CN}]_0[\alpha\text{-CD}]_0/(1 + K_1[\alpha\text{-CD}]_0 + K_1K_2[\alpha\text{-CD}]_0^2) \quad (5)$$

$$[(\alpha\text{-CD})_2\cdot 2\text{-CN}] = K_1K_2[2\text{-CN}]_0[\alpha\text{-CD}]_0^2/(1 + K_1[\alpha\text{-CD}]_0 + K_1K_2[\alpha\text{-CD}]_0^2) \quad (6)$$

Here, suffixes 0 stand for the initial concentration. We used an $\epsilon_0$ value (1330 mol$^{-1}$ dm$^3$ cm$^{-1}$) at 293 nm determined from the absorption spectrum of 2-CN in ethanol. Thus, the absorbance could be calculated employing $\epsilon_1$, $\epsilon_2$, $K_1$, and $K_2$ values as parameters. Figure 2 exhibits the observed α-CD concentration dependence of the absorbance, together with the best fit curve calculated with $\epsilon_1 = 2130$ mol$^{-1}$ dm$^3$ cm$^{-1}$, $\epsilon_2 = 3240$ mol$^{-1}$ dm$^3$ cm$^{-1}$, $K_1 = 292$ mol$^{-1}$ dm$^3$, and $K_2 = 246$ mol$^{-1}$ dm$^3$.[20] The $K_2$ value is slightly less than the $K_1$ value. Although a $K_2$ value (35 ± 5 mol$^{-1}$ dm$^3$) significantly less than a $K_1$ value (250 ± 50 mol$^{-1}$ dm$^3$) has been obtained for 2-naphthol,[21] nearly the same or a greater $K_2$ value has been estimated for 6-bromo-2-naphthol and 2-methylnaphthalene, compared to a $K_1$ value.[18,22]

**Fluorescence Spectra of 2-CN in Aqueous Solutions.** Figure 3 shows fluorescence spectra of 2-CN in aqueous

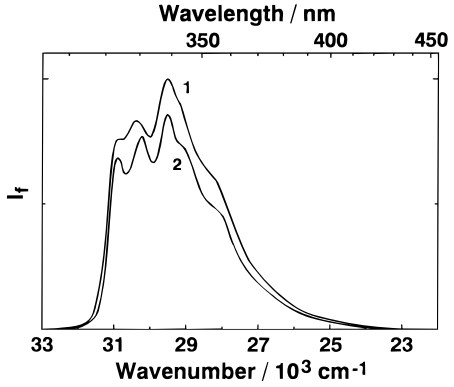


**Figure 3.** Fluorescence spectra of 2-CN ($2.3 \times 10^{-5}$ mol dm$^{-3}$) in aqueous solutions in the absence (spectrum 1) and presence (spectrum 2) of α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$). $\lambda_{ex} = 267.5$ nm.

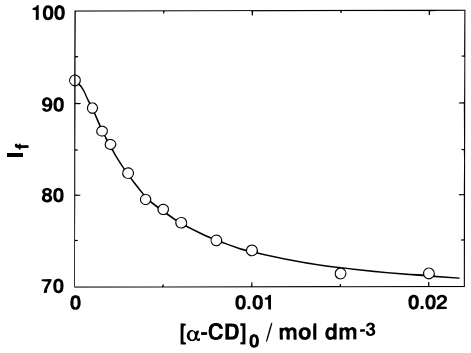


**Figure 4.** α-CD concentration dependence of the fluorescence intensity of 2-CN in aqueous solution. Circles represent experimental points. The best fit curve was calculated with $K_1 = 486$ mol$^{-1}$ dm$^3$, $K_2 = 364$ mol$^{-1}$ dm$^3$, $b = 0.979$, and $c = 0.737$. $\lambda_{obs} = 338$ nm.

solutions in the absence and presence of α-CD. Upon the addition of α-CD, vibrational structures of the 2-CN fluorescence are sharpened with a slightly weak intensity, indicating a relatively nonpolar environment around a 2-CN molecule within the inclusion complexes.

As in the case of the absorbance change, $K_1$ and $K_2$ can be estimated from the α-CD concentration dependence of the fluorescence intensity ($I_f$):

$$I_f = a([\text{2-CN}] + b[\text{α-CD·2-CN}] + c[(\text{α-CD})_2\text{·2-CN}]) \quad (7)$$

where $a$, $b$, and $c$ are constants including the fluorescence quantum yield of each species. The concentration of each species in eq 7 is represented by eqs 4−6. In Figure 4, the best fit curve for the fluorescence intensity change is illustrated together with the observed fluorescence intensities. From this simulation, 486 and 364 mol$^{-1}$ dm$^3$ are obtained as $K_1$ and $K_2$ values, respectively.[23] The corresponding $K$ values obtained from the fluorescence method are comparable with those from the absorbance method. In addition, the same relationship between $K_1$ and $K_2$, $K_1 > K_2$, holds for both results. These findings seem to suggest that these $K$ values are reliable. Since the absorbance change shown in Figure 2 is small, the $K$ values estimated from the absorbance change seem to be less reliable compared to those estimated from the fluorescence intensity change.

**Induced Circular Dichroism Spectra of 2-CN in Aqueous Solutions.** Figure 5 depicts induced circular dichroism (icd) spectra of 2-CN in aqueous solutions containing α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$) and $\beta$-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$). For α-CD solution of 2-CN, the icd band of 285 nm exhibits a positive signal, whereas the 240 nm band exhibits a negative signal. The reverse signs are observed for a $\beta$-CD solution of 2-CN, indicating that an inclusion mode of $\beta$-CD is different from that

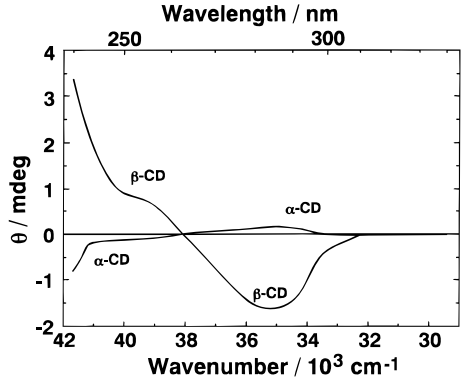


**Figure 5.** Icd spectra of 2-CN ($4.6 \times 10^{-5}$ mol dm$^{-3}$) in aqueous solutions containing α-CD and $\beta$-CD. Concentrations of CDs were $1.0 \times 10^{-2}$ mol dm$^{-3}$.

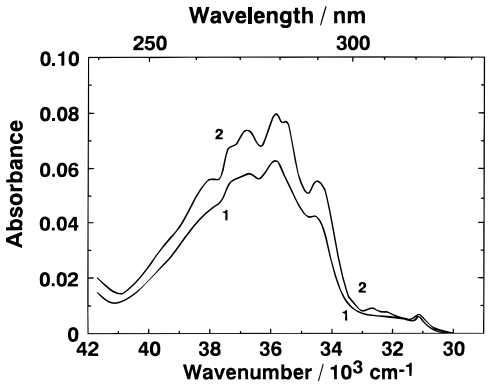


**Figure 6.** Absorption spectra of 2-CN ($1.6 \times 10^{-5}$ mol dm$^{-3}$) in D-glucose solutions in the absence (spectrum 1) and presence (spectrum 2) of α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$).

of α-CD. A naphthalene ring of 2-CN is expected to be axially encapsulated by $\beta$-CD. On the other hand, α-CD, whose cavity size is smaller than that of $\beta$-CD, is likely to first accommodate a 2-CN molecule from a chlorine-substituted side of a naphthalene ring, and then the second α-CD molecule binds to the nonsubstituted side to form a 2:1 α-CD−2-CN inclusion complex. Therefore, the molecular axis of α-CD is tilted about 30° relative to the longitudinal axis of a naphthalene ring of 2-CN. A similar inclusion mode has already been reported for a 2:1 α-CD−6-bromo-2-naphthol inclusion complex.[18]

The 285 and 240 nm bands of 2CN are assignable to the $^1L_b$ and $^1B_b$ transitions, respectively. The directions of these transition moments are varied to some extent from those in naphthalene by the chlorine-atom substitution. Signs in icd signals of CD inclusion complexes reflect the angle between the CD molecular axis and the direction of the electronic transition moment of an incorporated guest molecule. When the angle is from −54.44 to 54.44°, a positive signal is anticipated for icd spectra.[24] Applying this relation to the $^1L_b$ and $^1B_b$ transitions of 2-CN in solutions containing α-CD and $\beta$-CD, the angles between the transition moment and the longitudinal axis of 2-CN are estimated to be in the range of 54.44−84.44° and −24.44 to −54.44°, respectively. These values are the same as those for 2-methylnaphthalene, suggesting that the directions of the $^1L_b$ and $^1B_b$ transition moments of naphthalene are similarly perturbed by a chlorine and a methyl substituent.[22]

**Absorption spectra of 2-CN in Aqueous D-Glucose Solutions.** Figure 6 shows absorption spectra of 2-CN in aqueous D-glucose solutions in the absence and presence of α-CD. Addition of α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$) to a D-glucose solution of 2-CN results in an enhancement and sharpening of the absorption bands. The spectral change is similar to that for

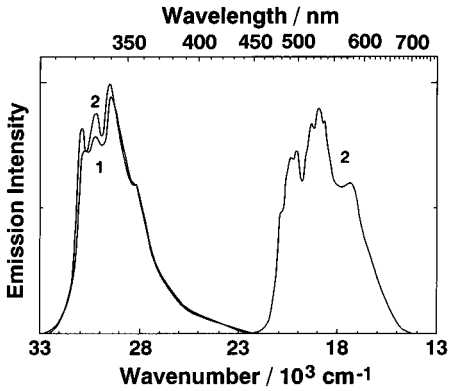


**Figure 7.** Emission spectra of 2-CN ($1.6 \times 10^{-5}$ mol dm$^{-3}$) in D-glucose solutions in the absence (spectrum 1) and presence (spectrum 2) of α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$). $\lambda_{ex} = 267.5$ nm.

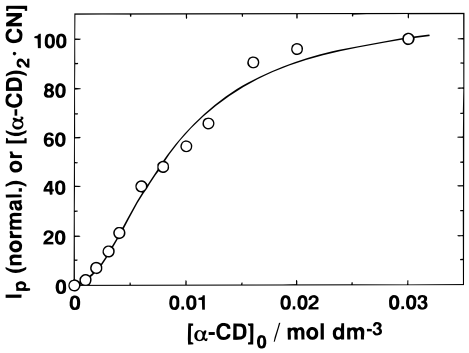


**Figure 8.** α-CD concentration dependence of the room-temperature phosphorescence intensity of 2-CN in D-glucose solution containing α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$). Circles represent experimental points. The best fit curve was calculated with $K_1 = 21.3$ mol$^{-1}$ dm$^3$ and $K_2 = 699$ mol$^{-1}$ dm$^3$. $\lambda_{ex} = 290$ nm. $\lambda_{obs} = 525$ nm.

aqueous 2-CN solution without D-glucose, in which both 1:1 and 2:1 α-CD−2-CN inclusion complexes exist, although the absorbance for the D-glucose solution is raised over the wavelength region of the absorption bands. Consequently, 1:1 and 2:1 α-CD−2-CN inclusion complexes seem to exist in D-glucose solution irrespective of the presence of D-glucose.

**Emission Behavior of 2-CN in D-Glucose Solutions.** Figure 7 illustrates emission spectra of 2-CN in aqueous D-glucose solution in the absence and presence of α-CD. In the absence of α-CD, the 2-CN fluorescence is predominantly observed. When α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$) is added to a D-glucose solution of 2-CN, vibrational structures of the fluorescence are sharpened accompanied by a slight enhancement of intensity, and a new emission with vibrational structures appears at longer wavelengths of 470−650 nm. From a similarity between the new emission and the phosphorescence of 2-CN in a methanol−ethanol (1:1) mixture at 77 K (not shown), the new emission can be assigned to the phosphorescence of 2-CN. It should be noted that the room-temperature phosphorescence of 2-CN shows the fairly sharp vibrational structures. This is attributed to the high viscosity of a D-glucose solution. At most 4% of the room-temperature phosphorescence intensity for D-glucose solution with α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$) was detected for D-glucose solutions without α-CD.

As shown in Figure 3, no room-temperature phosphorescence is seen for a 2-CN solution containing only α-CD. As with 2-CN, therefore, both D-glucose and α-CD are required to observe the room-temperature phosphorescence. Since D-glucose provides a rigid environment around an inclusion complex of 2-CN, the translational and rotational movements of α-CD in the inclusion complex are restricted. In addition, α-CD prevents the molecular motions of the included 2-CN molecule. Consequently, the radiationless transition from the triplet state of 2-CN is significantly depressed, resulting in the appearance of the room-temperature phosphorescence of 2-CN. Furthermore, the higher viscosity of a D-glucose solution with α-CD than that without α-CD may partially contribute to the enhancement of the room-temperature phosphorescence.

In the case of the α-CD−6-bromo-2-naphthol system, a 2:1 α-CD−6-bromo-2-naphthol inclusion complex emits the room-temperature phosphorescence, but a 1:1 inclusion complex does not.[17,18] So, identification of a phosphorescent species was tried for 2-CN solutions containing D-glucose and α-CD. Under our experimental conditions, the room-temperature phosphorescence intensity is proportional to the concentration of an emitting species. Thus, as a function of the α-CD concentration, we compared the room-temperature phosphorescence intensities with concentration curves of a 1:1 and a 2:1 α-CD−2-CN inclusion complex, which were calculated by assuming $K_1$ and $K_2$ values in eqs 4−6. In Figure 8, the best fit concentration curve of the 2:1 α-CD−2-CN inclusion complex is displayed along with data points of the observed room-temperature phosphorescence intensity. The quality of fit is excellent, evidently indicating that the 2:1 α-CD−2-CN inclusion complex is responsible for the room-temperature phosphorescence. The observed intensity data did not fit any simulation curves calculated for the 1:1 inclusion complex, supporting the conclusion regarding a species emitting the room-temperature phosphorescence. In the case of 2-CN as well as 6-bromo-2-naphthol, the phosphorescent species is a 2:1 α-CD−guest inclusion complex.

From the above simulation, $K_1$ and $K_2$ values are estimated to be 21.3 and 699 mol$^{-1}$ dm$^3$, respectively.[25] In contrast to the $K_1$ value for solutions without D-glucose, the $K_1$ value for D-glucose solutions is 1 order of magnitude less than the $K_2$ value for D-glucose solutions. The environment in D-glucose solution relatively resembles that inside the α-CD cavity compared to neat water. Consequently, hydrophobic interaction in the formation of an inclusion complex becomes weak in D-glucose solution, so that $K_1$ for D-glucose solution is significantly small compared to that for aqueous solution without D-glucose. On the other hand, the $K_2$ value for D-glucose solution is about 2 times greater than that for aqueous solution without D-glucose. The additional binding of α-CD to a 1:1 inclusion complex is accelerated in D-glucose solution compared to aqueous solution without D-glucose. The reason for the acceleration of the binding is unclear at present.

Since α-CD is not large enough to fully encapsulate a 2-CN molecule, the degree of freedom of the 2-CN molecular motions is still fairly high in a 1:1 inclusion complex. Consequently, the radiationless transition from the 2-CN triplet is not suppressed in a 1:1 inclusion complex, whereas, in a 2:1 α-CD−2-CN inclusion complex, it is suppressed owing to the restriction of the molecular motions of 2-CN buried within the two α-CD cavities, resulting in the appearance of the room-temperature phosphorescence from the 2:1 inclusion complex.

Because the absorbance of 2-CN was extremely low in D-glucose solutions as shown in Figure 6, icd spectra of 2-CN in D-glucose solutions with α-CD were not measured. However, the binding mode of α-CD with 2-CN in D-glucose solutions is most likely to be identical to that for aqueous solutions.

**Fluorescence and Room-Temperature Phosphorescence Quantum Yields of 2-CN in D-Glucose Solutions Containing α-CD.** Despite several works on room-temperature phosphorescence from CD inclusion complexes, there is so far no data concerning room-temperature phosphorescence quantum yields, except for the glucosyl-$\beta$-CD−alcohol−1-bromonaphthalene systems.[9] Thus, we tried to evaluate the room-temperature phosphorescence quantum yield of 2-CN. The environment

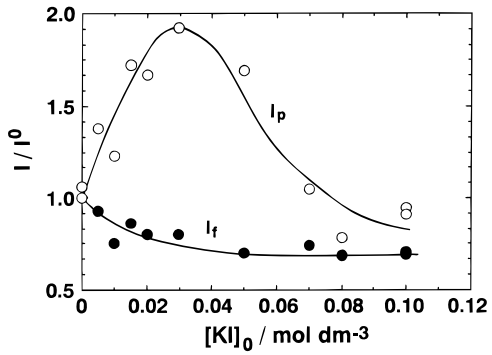


**Figure 9.** Concentration effects of KI on the fluorescence and room-temperature phosphorescence intensities of 2-CN in D-glucose solution containing α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$). $\lambda_{ex} = 290$ nm. $\lambda_{obs}$(fluor) = 339 nm. $\lambda_{obs}$(phosph) = 525 nm.

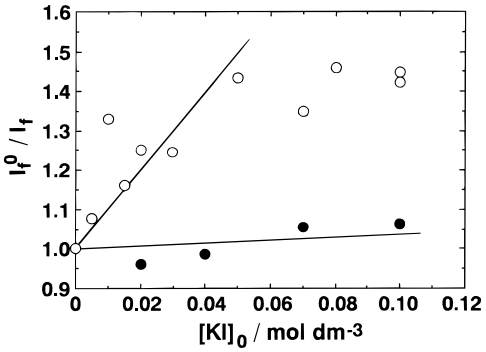


**Figure 10.** Stern−Volmer plots for the fluorescence of 2-CN in D-glucose solutions with (○) and without α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$) (●).

effects of D-glucose on the fluorescence ($\phi_f$) and phosphorescence quantum yields ($\phi_p$) were also investigated. We first determined a $\phi_f$ value of 2-CN in aqueous solution to be 0.014, employing quinine sulfate in 1 mol dm$^{-3}$ $H_2SO_4$ solution as a primary standard ($\phi_f = 0.546$).[26] Next, using the $\phi_f$ value for the aqueous 2-CN solution as a secondary standard, $\phi_f$ values of 2-CN in D-glucose solutions with and without α-CD ($3.0 \times 10^{-2}$ mol dm$^{-3}$) were evaluated to be 0.014 and 0.013, respectively. Within experimental errors, these $\phi_f$ values are identical to each other. Furthermore, these $\phi_f$ values are the same as that for aqueous solution without D-glucose, in spite of the high viscosity of the D-glucose solutions. The absorbances of the D-glucose solutions have been evaluated on the basis of the absorbance of aqueous 2-CN solutions that have been used for preparation of the D-glucose solutions. Since D-glucose solutions have been heated in the course of sample preparation, 2-CN has probably been evaporated and lost to a small extent. Consequently, the 2-CN concentrations in D-glucose solutions would be lower than those calculated. As a consequence, the true $\phi_f$ values for D-glucose solutions with and without α-CD ($3.0 \times 10^{-2}$ mol dm$^{-3}$) seem to be more than 0.014 and 0.013, respectively.

A $\phi_p$ value of the room-temperature phosphorescence of 2-CN in D-glucose solution containing α-CD ($3.0 \times 10^{-2}$ mol dm$^{-3}$) was determined to be 0.029, using the $\phi_f$ value of 2-CN in aqueous solution as a standard. For the same reason as the unexpectedly small $\phi_f$ values for D-glucose solutions, the $\phi_p$ value of 0.029 is slightly underestimated. At $3.0 \times 10^{-2}$ mol dm$^{-3}$ of α-CD, approximately 90% of 2-CN is converted to the 2:1 inclusion complex. From this view, the estimated $\phi_p$ value is further underestimated. To compare this $\phi_p$ value with a $\phi_p$ value at 77 K, a $\phi_p$ value of 2-CN in ethanol at 77 K was determined to be 0.15 by use of an ethanol solution of phenanthrene at 77 K as a standard ($\phi_p = 0.12$).[27] Consequently, the $\phi_p$ value of the room-temperature phosphorescence is at least 19% of the intrinsic $\phi_p$ value.

**Effects of KI on the Fluorescence and Room-Temperature Phosphorescence Intensities.** When KI is added to a 2-CN solution containing both D-glucose and α-CD, the fluorescence and the room-temperature phosphorescence of 2-CN are varied in intensity as a function of the KI concentration (Figure 9). As the KI concentration is increased, the fluorescence intensity is reduced and reaches a plateau above about 0.03 mol dm$^{-3}$. On the other hand, the intensity of the room-temperature phosphorescence initially increases with an increase of the KI concentration, reaches a maximum at a KI concentration of 0.03 mol dm$^{-3}$, and then decreases with a further increase of the KI concentration.

Figure 10 depicts Stern−Volmer plots for the fluorescence of 2-CN in D-glucose solutions with and without α-CD. In the absence of α-CD, a Stern−Volmer constant, $K_{SV}$, for KI is evaluated to be 0.42 mol$^{-1}$ dm$^3$, whereas it is evaluated to be 10 mol$^{-1}$ dm$^{-3}$ from the initial slope in the presence of α-CD. Since the viscosity of a D-glucose solution is very high, the $K_{SV}$ value for solutions without α-CD is considerably small owing to little collision leading to dynamic quenching by $I^-$. Irrespective of no dynamic quenching, however, the $K_{SV}$ value for a D-glucose solution containing α-CD is unusually large. Therefore, the fluorescence quenching in the presence of α-CD is due to the static quenching by $I^-$. It is most likely that a ternary inclusion complex among α-CD, 2-CN, and $I^-$ is responsible for the static quenching of the 2-CN fluorescence.

In the ternary inclusion complex of α-CD−2-CN−$I^-$, the intersystem crossing of 2-CN from the excited singlet state to the triplet state is promoted by the external heavy atom effect of $I^-$, resulting in the 1.9 times increase of the room-temperature phosphorescence intensity, which is seen at a KI concentration of 0.03 mol dm$^{-3}$ in Figure 9. Iodine-substituted $\beta$-CD (6-deoxy-6-iodo-$\beta$-CD) has been found to enhance the room-temperature phosphorescence intensity of 2-CN in aqueous solutions.[16] In this case, the external heavy atom effect of an iodine atom substituted on the $\beta$-CD rim causes a 2.5 times enhancement of the room-temperature phosphorescence of guest 2-CN. Nearly the same efficiency in enhancement of the room-temperature phosphorescence of 2-CN in the α-CD−2CN−$I^-$ ternary inclusion complex may imply that a distance between $I^-$ and included 2-CN in the ternary inclusion complex is nearly the same as the distance between included 2-CN and an iodine atom substituted on the $\beta$-CD rim of 6-deoxy-6-iodo-$\beta$-CD. Consequently, an $I^-$ ion seems to exist near the α-CD mouth of the 2:1 α-CD−2-CN inclusion complex.

As shown in Figure 9, the room-temperature phosphorescence is decreased in intensity at KI concentrations higher than about 0.03 mol dm$^{-3}$. One possible explanation for the decrease is that the ternary inclusion complex of α-CD−2CN−$I^-$ further associates with $I^-$; in this inclusion complex containing two $I^-$ ions, the radiationless transition of 2-CN from the triplet state to the ground state is accelerated by the external heavy atom effects of two $I^-$ ions, leading to the reduction in the room-temperature phosphorescence intensity.

**Fluorescence Lifetimes of 2-CN in D-Glucose Solutions.** Fluorescence decays of 2-CN in D-glucose solution containing α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$) and KI could be analyzed as a sum of two exponential functions (not shown). Figure 11 illustrates fluorescence lifetimes of 2-CN as a function of the KI concentration. The two decay components (0.56 and 2.7 ns) remain constant over the KI concentration range examined, although there is somewhat of a scatter for the longer-lifetime component. The concentrations of free 2-CN, the 1:1 inclusion complex, and the 2:1 α-CD−2-CN inclusion complex can be calculated using the $K_1$ and $K_2$ values previously evaluated. At

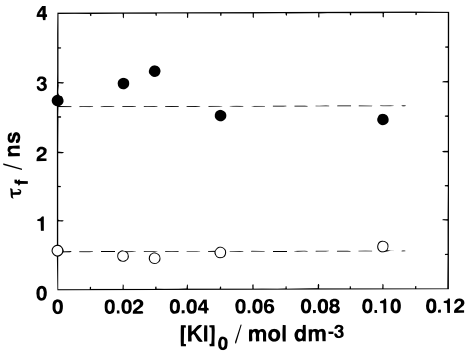


**Figure 11.** Concentration effects of KI on the fluorescence lifetimes of 2-CN in D-glucose solution containing α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$).

an α-CD concentration of $1.0 \times 10^{-2}$ mol dm$^{-3}$, the concentration of the 1:1 inclusion complex amounts to at most several percent of the initial 2-CN concentration. Consequently, the contribution from the 1:1 inclusion complex to the fluorescence would be negligible. Hence, the shorter-lifetime and longer-lifetime components are likely to be due to free 2-CN and the 2:1 α-CD−2-CN inclusion complex, respectively. No effect of KI on the fluorescence lifetimes provides further evidence for the static quenching by $I^-$ and the formation of a ternary inclusion complex among α-CD, 2-CN, and $I^-$.

**Room-Temperature Phosphorescence Lifetimes of 2-CN in D-Glucose Solutions Containing α-CD.** In D-glucose solutions containing α-CD ($1.0 \times 10^{-2}$ mol dm$^{-3}$), the room-temperature phosphorescence decays could be deconvoluted as a single exponential (not shown), although the decay at a zero KI concentration has a fast-decay component with a very small weight. The fast-decay component may be due to free 2-CN in D-glucose solution, which emits the room-temperature phosphorescence with a significantly small intensity. The room-temperature phosphorescence lifetimes of 2-CN were determined to be 18, 21, 22, and 21 ms at KI concentrations of 0, 0.02, 0.03, and 0.1 mol dm$^{-3}$, respectively. In our scheme, the phosphorescent species are a 2:1 α-CD−2CN inclusion complex and a 2:1:1 α-CD−2CN−$I^-$ inclusion complex. The reason why the room-temperature phosphorescence decays do not have two components in D-glucose solutions containing both α-CD and KI is due probably to the close phosphorescence lifetimes of the two species, so that the decay components may not be separated under our experimental conditions. The room-temperature phosphorescence lifetimes are invariant over the KI concentration range examined, except for that at zero KI concentration. Consequently, this finding is consistent with our conclusion that the ternary inclusion complex containing two $I^-$ ions, which is nonphosphorescent, is formed at high KI concentrations.

## Conclusions

α-CD forms both a 1:1 and a 2:1 inclusion complex with 2-CN in aqueous solutions and aqueous D-glucose solutions. The equilibrium constants, $K_1$ and $K_2$, for the formation of the 1:1 and 2:1 α-CD−2-CN inclusion complexes were evaluated on the basis of simulation procedures. For aqueous solutions without D-glucose, the $K_1$ value is slightly greater than the $K_2$ value, whereas, in the case of D-glucose solutions, the $K_1$ value is 1 order of magnitude less than the $K_2$ value. The room-temperature phosphorescence of 2-CN is observed for aqueous D-glucose solutions containing α-CD. From the simulation concerning the room-temperature phosphorescence intensity, it is concluded that not the 1:1 inclusion complex but the 2:1 α-CD−2-CN inclusion complex emits the room-temperature phosphorescence of 2-CN. The high viscosity of D-glucose solutions as well as the inclusion of 2-CN by two α-CD molecules causes the deceleration of the radiationless transition of the 2-CN triplet state. Addition of KI (below 0.03 mol dm$^{-3}$) to a D-glucose solution containing α-CD results in the enhancement of the room-temperature phosphorescence intensity of 2-CN. The enhancement is due to the formation of a ternary inclusion complex among α-CD, 2-CN, and $I^-$. Upon further addition of KI, the intensity of the room-temperature phosphorescence is reduced. The formation of an α-CD−2CN−$I^-$ ternary inclusion complex containing two $I^-$ ions seems to be responsible for the reduction in the room-temperature phosphorescence.

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