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External heavy atom effects of 6-deoxy-6-iodo-α-cyclodextrin on the room-temperature phosphorescence of 6-bromo-2-naphthol and 3-bromoquinoline in aqueous solutions

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Abstract

6-Deoxy-6-iodo-α-cyclodextrin (α-CDI) has been found to form a 1:1 inclusion complex with 6-bromo-2-naphthol. A further association occurs between the 1:1 inclusion complex and an additional α-CDI molecule, leading to the formation of a 2:1 α-CDI–6-bromo-2-naphthol inclusion complex. The room-temperature phosphorescence of 6-bromo-2-naphthol is observed from the 2:1 α-CDI–6-bromo-2-naphthol inclusion complex, whereas the 1:1 inclusion complex does not emit it. The room-temperature phosphorescence intensity for the 2:1 α-CDI–6-bromo-2-naphthol inclusion complex is reduced by about 18% relative to that for the 2:1 inclusion complex composed of the parent α-CD, indicating the external heavy atom effects of α-CDI on the bound guest. The external heavy atom effects of α-CDI have also been examined on the room-temperature phosphorescence intensity of 3-bromoquinoline buried within the α-CDI cavity. At the same CD concentrations (2.0×10^{-3} mol dm^{-3}), the room-temperature phosphorescence for α-CDI has been decreased by about 10% relative to that for α-CD.

Keywords: Room-temperature phosphorescence; Inclusion complexes; 6-Deoxy-6-iodo-α-cyclodextrin; 6-Bromo-2-naphthol; 3-Bromoquinoline

1. Introduction

Cyclodextrins (CDs) are torus-shaped, cyclic oligosaccharides composed of six, seven, and eight D-glucose residues, which are called α-, β-, and γ-CD, respectively. Because CDs have a cavity in the molecular center, organic compounds can be incorporated into their cavities to form inclusion complexes in aqueous solutions.

It is usually very difficult to observe the room-temperature phosphorescence of aromatic compounds in solutions, although there are several reports on the observation of room-temperature phosphorescence [1,2]. Cyclodextrins often induce room-temperature phosphorescence of organic substances in aqueous solutions. Turro et al. [3] have found that the room-temperature phosphorescence of 1-bromonaphthalene and 1-chloronaphthalene is readily observable in N_2-purged aqueous solutions containing β-CD. They have also studied the emission behavior of 4-bromo-1-naphthoyl derivatives in CD solutions [4]. Accommodation of 4-bromo-1-naphthoyl derivatives in the γ-CD cavity protects them from an oxygen attack. As a consequence, the room-temperature phosphorescences of the guests are observed even under 1 atm of oxygen.

Ponce et al. [5] revealed that the intense room-temperature phosphorescence of 1-bromonaphthalene appears when alcohols are introduced to aqueous solutions containing 1-bromonaphthalene and glucosyl-β-CD. A ternary inclusion complex of glucosyl-β-CD, alcohol, and 1-bromonaphthalene is responsible for the room-temperature phosphorescence. Scypinski and Cline Love [6,7] have reported the room-temperature phosphorescence from non-halogenated phosphorophores included in the CD cavities. The intense room-temperature phosphorescence is due to the formation of a ternary inclusion complex made up of CD, bromoalkane such as 1,2-dibromomethane, and a non-halogenated phosphorophore. The addition of bromoalkanes, however, produces turbid sample solutions. To avoid the turbidity of the solutions and to investigate the room-temperature phosphorescence from an inclusion complex dissolved in solution, Hamai [8] employed bromoalcohols as additional heavy-atom perturbers, which keep the sample solutions containing CD and a phosphorophore transparent. As in the case of 1,2-dibromomethane, 2-bromoethanol forms a ternary inclusion complex with β-CD and acenaphthene to induce the room-

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temperature phosphorescence of acenaphthene in aqueous solutions. These additional brominated compounds exert external heavy atom effects on the phosphorescent guests co-incorporated into the CD cavity, thereby enhancing the intersystem crossing to the triplet state and the radiative transition from the triplet state.

Besides the additional heavy-atom perturbers in the ternary inclusion complexes, a CD possessing a halogen atom(s) can exert the external heavy atom effects on a guest incorporated into its cavity. Femia and Cline Love [9] have reported that heptakis(6-bromo-6-deoxy)-β-CD enhances the room-temperature phosphorescence of a guest bound to the cavity. They used water–*N*,*N*-dimethylformamide mixtures as solvents, because heptakis(6-bromo-6-deoxy)-β-CD is insoluble in neat water. As previously stated, when an additional organic compound such as alcohol is added, ternary inclusion complexes may be formed among the CD, an additional organic compound, and a luminophore. To avoid this possibility, Hamai and Mononobe [10] have employed 6-deoxy-6-iodo-β-CD (β-CDI) as a host CD in neat water and have revealed that, upon the formation of an inclusion complex between β-CDI and 2-chloronaphthalene, its room-temperature phosphorescence efficiency is increased by at least 1.2 times compared to an inclusion complex with the parent β-CD.

In aqueous solutions, 6-bromo-2-naphthol forms a 1:1 inclusion complex with α-CD [11,12]. The 1:1 inclusion complex further associates with an additional α-CD molecule to form a 2:1 α-CD-6-bromo-2-naphthol inclusion complex [11,12]. The room-temperature phosphorescence of 6-bromo-2-naphthol has been observed from the 2:1 inclusion complex in even aerated aqueous solutions, whereas the 1:1 inclusion complex does not emit the room-temperature phosphorescence. A single α-CD molecule in the 1:1 inclusion complex is insufficient to protect a triplet-state guest from the attacks of oxygen and impurities. However, two α-CD molecules fully guard a guest bound to the cavities from the quenchers and effectively prohibit the radiationless transition of the triplet state of a guest because of the reduced degree of freedom of the guest. For 2-chloronaphthalene, room-temperature phosphorescence has been detected from a 2:1 α-CD-2-chloronaphthalene inclusion complex in aqueous D-glucose solutions, although it has not been observed in aqueous solutions without D-glucose [13].

We have been interested in whether or not, in such 2:1 α-CD-guest inclusion complexes, halogenation of α-CD influences the emission properties of the guest. Thus, we examined the external heavy atom effects of 6-deoxy-6-iodo-α-CD (α-CDI) on the emission properties of 6-bromo-2-naphthol in aqueous solutions. In this article, we report the formation of a 2:1 α-CDI–6-bromo-2-naphthol inclusion complex and its reduced room-temperature phosphorescence efficiency compared to a 2:1 α-CD–6-bromo-2-naphthol inclusion complex. In addition, we have investigated the α-CDI effect on the emission properties of 3-bromoquinoline in aqueous solutions.

2. Experimental

2.1. Synthesis of 6-deoxy-6-iodo-α-cyclodextrin (α-CDI)

According to the method of Melton and Slessor [14], α-CDI was synthesized from 6-*O*-toluenesulfonyl-α-CD and sodium iodide. α-CDI thus obtained was twice recrystallized from water. Analysis: calculated for $C_{36}H_{60}O_{30}\cdot 5H_2O$: C, 36.87; H, 5.93; I, 10.82; found: C, 36.40; H, 5.83; I, 11.28.

2.2. Materials

α-CD purchased from Nakalai Tesque, was used as received. 6-Bromo-2-naphthol purchased from Tokyo Kasei Kogyo was twice recrystallized from benzene. 3-Bromoquinoline from Tokyo Kasei Kogyo was purified by percolation through a silica gel column.

Sample solutions of 3-bromoquinoline were degassed using a conventional freeze–pump–thaw cycle technique. Because the solubility of α-CDI in water is not great compared to α-CD, the highest concentrations of α-CDI were 3.0×10^{-3} and 2.0×10^{-3} mol dm^{-3} for the experiments of 6-bromo-2-naphthol and 3-bromoquinoline, respectively.

2.3. Apparatus

Absorption spectra were recorded on a Shimadzu UV-260 spectrophotometer. Fluorescence and phosphorescence spectra were taken with a Shimadzu RF-540 spectrofluorometer. These emission spectra were corrected for the spectral response of the fluorometer. Spectroscopic measurements were made from about 30 min after the preparation of the sample solutions at 25 ± 0.1°C.

3. Results and discussion

3.1. Absorption spectra of 6-bromo-2-naphthol

Fig. 1 shows the absorption spectra of 6-bromo-2-naphthol (1.4×10^{-4} mol dm^{-3}) in aqueous solutions containing several concentrations of α-CDI. When α-CDI is added, the absorption maxima are shifted to longer wavelengths. Although isosbestic points appear at 283 and 310 nm, these absorption spectra do not show isosbestic points at around 270, 287, and 298 nm, indicating that there are at least two inclusion complexes of α-CDI with 6-bromo-2-naphthol. The spectral changes are similar to those observed for the system of α-CD–6-bromo-2-naphthol in which 1:1 and 2:1 α-CD–6-bromo-2-naphthol inclusion complexes are formed [11,12]. Consequently, in aqueous solutions containing both α-CDI and 6-bromo-2-naphthol, there are two equilibria:

$$\alpha\text{-CDI} + 6\text{BN} \overset{K_1}{\rightleftharpoons} \alpha\text{-CDI}\cdot 6\text{BN}, \quad (1)$$

$$\alpha\text{-CDI} + \alpha\text{-CDI}\cdot 6\text{BN} \overset{K_2}{\rightleftharpoons} (\alpha\text{-CDI})_2\cdot 6\text{BN}, \quad (2)$$

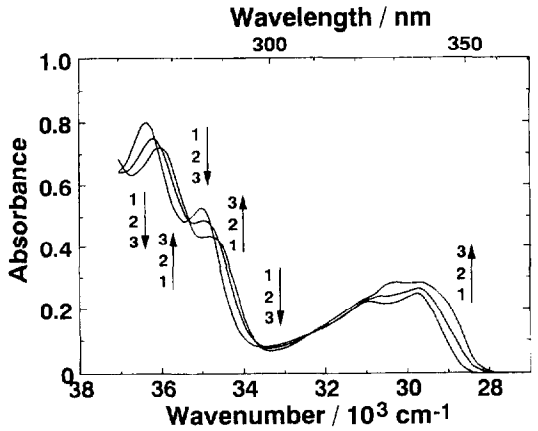

Fig. 1. Absorption spectra of 6-bromo-2-naphthol (1.4×10^{-4} mol dm^{-3}) in aqueous solutions containing several concentrations of α-CDI. Concentration of α-CDI: (1) 0, (2) 1.0×10^{-3}, and (3) 3.0×10^{-3} mol dm^{-3}.

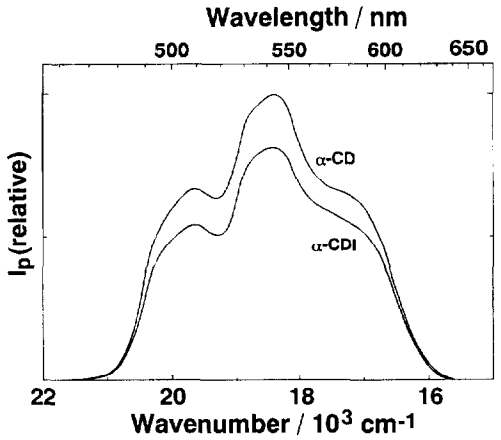

Fig. 2. Room-temperature phosphorescence of 6-bromo-2-naphthol (2.1×10^{-4} mol dm^{-3}) in aqueous solutions containing α-CD (3.0×10^{-3} mol dm^{-3}) and α-CDI (3.0×10^{-3} mol dm^{-3}). $\lambda_{ex}=310$ nm.

where 6BN, α-CDI·6BN, and (α-CDI)$_2$·6BN represent free 6-bromo-2-naphthol, the 1:1 α-CDI–6-bromo-2-naphthol inclusion complex, and the 2:1 α-CDI–6-bromo-2-naphthol inclusion complex, respectively, and K_1 and K_2 are the equilibrium constants for the formation of the 1:1 and 2:1 inclusion complexes, respectively.

3.2. Room-temperature phosphorescence of 6-bromo-2-naphthol

Fig. 2 exhibits the room-temperature phosphorescence of 6-bromo-2-naphthol in aerated aqueous 6-bromo-2-naphthol solution containing α-CDI (3.0×10^{-3} mol dm^{-3}), together with that containing α-CD (3.0×10^{-3} mol dm^{-3}). As in the case of α-CD, the fluorescence intensity of 6-bromo-2-naphthol was slightly varied with time in the presence of α-CDI. Photochemical reactions such as debromination from 6-bromo-2-naphthol may occur under the light illumination. On the other hand, the room-temperature phosphorescence intensity of 6-bromo-2-naphthol was not varied with time. Thus, we focused on the room-temperature phosphorescence of 6-bromo-2-naphthol in aqueous solutions. In the system of α-CD–6-bromo-2-naphthol, the room-temperature phosphorescence arises from a 2:1 α-CD–6-bromo-2-naphthol inclusion complex [11,12]. In contrast to the 2:1 inclusion complex, a 1:1 α-CD–6-bromo-2-naphthol inclusion complex does not exhibit room-temperature phosphorescence. Thus, we have tried to identify a species exhibiting room-temperature phosphorescence in the 6-bromo-2-naphthol solution containing α-CDI. Under our experimental conditions, the room-temperature phosphorescence intensity is proportional to the concentration of an emitting species. Consequently, as a function of the α-CDI concentration, we have compared concentration curves calculated for the 1:1 and 2:1 α-CDI–6-bromo-2-naphthol inclusion complexes with the observed room-temperature phosphorescence intensities. When the 2:1 inclusion complex is responsible for the room-temperature phosphorescence, the room-temperature phosphorescence intensity, I_p, is expressed by:

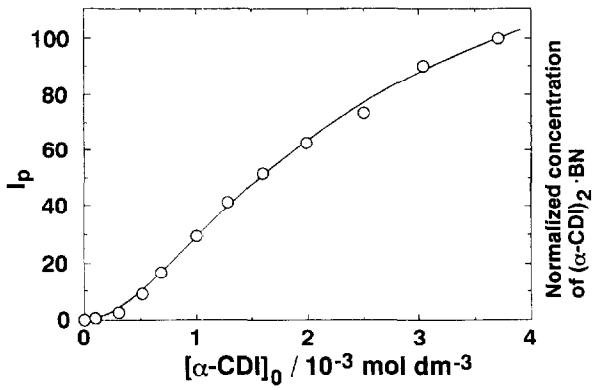

Fig. 3. The best fit concentration curve for the 2:1 α-CDI–6-bromo-2-naphthol inclusion complex, which has been calculated with $K_1=637$ and $K_2=511$ mol^{-1} dm^3. The room-temperature phosphorescence intensity data points are also plotted as a function of α-CDI concentration. The concentrations of 6-bromo-2-naphthol were 2.0×10^{-4} mol dm^{-3}. $\lambda_{ex}=310$ nm.

$$I_p = aK_1K_2[\alpha\text{-CDI}]_0^2[6BN]_0/(1+K_1[\alpha\text{-CDI}]_0 + K_1K_2[\alpha\text{-CDI}]_0^2), \quad (3)$$

where a is a constant including the phosphorescence quantum yield of 6-bromo-2-naphthol which is incorporated into the two α-CDI cavities, and $[\alpha\text{-CDI}]_0$ and $[6BN]_0$ are the initial concentrations of α-CDI and 6-bromo-2-naphthol, respectively. As a function of the α-CDI concentration, Fig. 3 illustrates the best fit concentration curve of the 2:1 α-CDI–6-bromo-2-naphthol inclusion complex, along with the observed room-temperature phosphorescence intensity data. The quality of the fit is excellent, definitely indicating that the room-temperature phosphorescence is due to the 2:1 inclusion complex. From this simulation, the K_1 and K_2 values are evaluated to be 637 and 511 mol^{-1} dm^3,[1] respectively, which are similar to those ($K_1=560$ and $K_2=530$ mol^{-1} dm^3) for α-CD [11,12]. On the other hand, the concentration curves simulated for the 1:1 inclusion complex could not reproduce the observed room-temperature phosphorescence

[1] The errors of K_1 and K_2 values were estimated to be less than 10%.

intensities, providing additional evidence for our conclusion that the 2:1 α-CDI–6-bromo-2-naphthol inclusion complex is responsible for the room-temperature phosphorescence.

As shown in Fig. 2, the room-temperature phosphorescence intensity of 6-bromo-2-naphthol in solution containing α-CDI is rather reduced compared to the solution containing α-CD. At 3.0×10^{-3} mol dm^{-3} of α-CD and α-CDI, the concentrations of the 2:1 inclusion complexes of α-CD and α-CDI are accidentally identical to each other; calculations using the K_1 and K_2 values for α-CD and α-CDI indicate that 49.8% of the 6-bromo-2-naphthol exists as the relevant 2:1 inclusion complexes.[2] Consequently, the apparent intensity ratio (0.82) of the room-temperature phosphorescence for α-CDI to that for α-CD is equal to the intrinsic intensity ratio.[3] The external heavy atom effects of α-CDI cause an 18% decrease in the room-temperature phosphorescence intensity compared to α-CD. This finding is in contrast to the result of the β-CDI–2-chloronaphthalene system, in which the external heavy atom effects of β-CDI enhance the room-temperature phosphorescence intensity of 2-chloronaphthalene relative to β-CD.

Because the spin-orbit coupling interaction responsible for the heavy atom effects is approximately proportional to the fourth power of the effective nuclear charge, a bromine atom exerts significantly stronger heavy atom effects than a chlorine atom does. Therefore, the emission properties of 6-bromo-2-naphthol are already perturbed to a significant degree by the internal heavy atom effects of a bromine atom, whereas those of 2-chloronaphthalene are weakly perturbed by the internal heavy atom effects of a chlorine atom. An iodine atom in β-CDI exerts the additional heavy atom effects on the intersystem crossing in 2-chloronaphthalene. Because the cavity size of β-CDI used in the system of 2-chloronaphthalene is different from that of α-CDI in the system of 6-bromo-2-naphthol, the distances between the guest and iodine substituted on the CD may be different from each other. However, the results for the β-CDI–2-chloronaphthalene system are useful in understanding the external heavy atom effects of iodine-substituted CDs.

In the case of the α-CDI–6-bromo-2-naphthol system, the additional heavy atom effects of α-CDI seems to preferentially accelerate the deactivation processes from the triplet state of 6-bromo-2-naphthol rather than the intersystem crossing to the triplet state and/or the radiative transition from the triplet state. Although the external heavy atom effects of α-CDI surely accelerate the intersystem crossing to the triplet state to some extent, this process is already to a large extent accelerated by the internal heavy atom effects of an intramolecular bromine atom. Consequently, the external heavy atom effects of α-CDI on the intersystem crossing may not appear prominently. For 2-chloronaphthalene, the internal heavy atom effects of an intramolecular chlorine atom do not fully increase the intersystem crossing rate, so that β-CDI promotes the intersystem crossing. For these reasons, α-CDI rather reduces the room-temperature phosphorescence intensity of 6-bromo-2-naphthol upon the formation of the 2:1 inclusion complex, whereas β-CDI enhances the room-temperature phosphorescence intensity of 2-chloronaphthalene upon the formation of the 1:1 inclusion complex.

3.3. Absorption spectra of 3-bromoquinoline

Fig. 4 shows the absorption spectra of 3-bromoquinoline (3.2×10^{-4} mol dm^{-3}) in aqueous solutions containing varying concentrations of α-CD. Below around 3.0×10^{-3} mol dm^{-3} of α-CD, isosbestic points are observed at 250, 283, 308.5, 320, and 323 nm. However, at high α-CD concentrations, there are no isosbestic points as seen in Fig. 4, indicating that at least two inclusion complexes are formed between α-CD and 3-bromoquinoline. As in the case of 6-bromo-2-naphthol, these inclusion complexes are most likely assigned to the 1:1 and 2:1 α-CD–3-bromoquinoline inclusion complexes. The absorbance A is expressed by the sum of the contribution from uncomplexed 3-bromoquinoline, the 1:1 inclusion complex, and the 2:1 inclusion complex:

$$A=\varepsilon_0[3BQ]d+\varepsilon_1[\alpha\text{-CD}\cdot3BQ]d+\varepsilon_2[(\alpha\text{-CD})_2\cdot3BQ]d, \quad (4)$$

where ε_0, ε_1, ε_2, and d are the molar absorption coefficients of free 3-bromoquinoline, the 1:1 α-CD–3-bromoquinoline inclusion complex, the 2:1 α-CD–3-bromoquinoline inclusion complex, and the path length (1.0 cm) of a quartz cell, respectively, and 3BQ, α-CD·3BQ, and (α-CD)$_2$·3BQ rep-

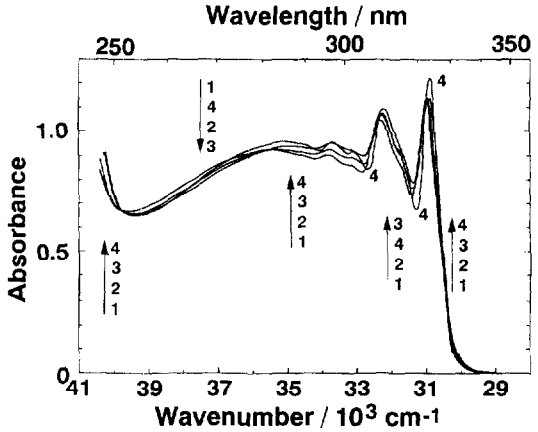

Fig. 4. Absorption spectra of 3-bromoquinoline (3.2×10^{-4} mol dm^{-3}) in aqueous solutions containing varying concentrations of α-CD. Concentration of α-CD: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 3.0×10^{-2} mol dm^{-3}.

[2] The errors for the concentrations of the 2:1 inclusion complexes were estimated to be less than 7%.

[3] At 3.0×10^{-3} mol dm^{-3} of α-CDI and α-CD, the ratio of the constant a in Eq. (3) for α-CDI to that for α-CD reflects the apparent intensity ratio, because the concentrations of the 2:1 inclusion complexes of α-CDI and α-CD are the same.

resent free 3-bromoquinoline, the 1:1 inclusion complex, and the 2:1 inclusion complex, respectively. The concentrations of free 3-bromoquinoline, the 1:1 inclusion complex and the 2:1 inclusion complex are respectively given by:

$$[3BQ]=[3BQ]_0/(1+K_1[\alpha\text{-CD}]_0+K_1K_2\times[\alpha\text{-CD}]_0^2), \quad (5)$$

$$[\alpha\text{-CD}\cdot 3BQ]=K_1[3BQ]_0[\alpha\text{-CD}]_0/(1+K_1\times[\alpha\text{-CD}]_0+K_1K_2[\alpha\text{-CD}]_0^2), \quad (6)$$

$$[(\alpha\text{-CD})_2\cdot 3BQ]=K_1K_2[3BQ]_0[\alpha\text{-CD}]_0^2/\times(1+K_1[\alpha\text{-CD}]_0+K_1K_2[\alpha\text{-CD}]_0^2). \quad (7)$$

In a simulation as a function of the α-CD initial concentration, the parameters are K_1, K_2, ε_1, and ε_2. Fig. 5 illustrates the best fit curve simulated for the absorbance observed at 270 nm, which has been calculated with $K_1=23.9$ mol^{-1} dm^3, $K_2=374$ mol^{-1} dm^3, $\varepsilon_1=468$ mol^{-1} dm^3 cm^{-1}, and $\varepsilon_2=2900$ mol^{-1} dm^3 cm^{-1}. The K_1 value is one order of magnitude less than the K_2 value. A similar trend concerning the magnitudes of K_1 and K_2 has been found for the α-CD–2-methylnaphthalene system, in which the K_1 and K_2 values are 44.6 and 376 mol^{-1} dm^3, respectively [15]. These results may imply that the two α-CD molecules in the 2:1 inclusion complex are hydrogen-bonded with each other, resulting in the greater K_2 value than the K_1 value. In the low-concentration ranges of α-CD and α-CDI, the absorption spectral changes in 3-bromoquinoline were similar to each other. The smaller K_1 value of 3-bromoquinoline than that of 6-bromo-2-naphthol is probably due to the greater solubility of 3-bromoquinoline in water compared to 6-bromo-2-naphthol. Because, as previously stated, α-CDI is not too soluble in water and because the relatively high concentration of α-CDI produced precipitates in solutions containing 3-bromoquinoline, we could not estimate the K_1 and K_2 values for α-CDI employing a simulation method analogous to that applied for α-CD.

3.4. Room-temperature phosphorescence of 3-bromoquinoline

3-Bromoquinoline exhibited room-temperature phosphorescence in deaerated aqueous solutions, although it did not exhibit phosphorescence in aerated aqueous solutions. The addition of α-CD (2.0×10^{-3} mol dm^{-3}) to the deaerated 3-bromoquinoline solution resulted in an about 10% increase in the fluorescence intensity and an about 16% increase in the room-temperature phosphorescence intensity. On the basis of calculations using the evaluated K_1 and K_2 values, at an α-CD concentration of 2.0×10^{-3} mol dm^{-3}, 92.3, 4.4, and 3.3% of the 3-bromoquinoline exist as a free species, the 1:1 inclusion complex, and the 2:1 inclusion complex, respectively. Consequently, about 8% of the 3-bromoquinoline buried within the inclusion complexes contributes to the enhancement of the fluorescence and room-temperature phosphorescence intensities, although the emission efficiencies of the fluorescence and phosphorescence may not be the same for the 1:1 and 2:1 inclusion complexes.

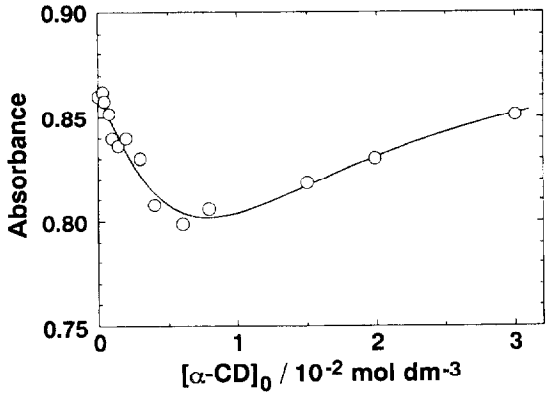

Fig. 5. The best fit curve simulated for the absorbance of 3-bromoquinoline (3.2×10^{-4} mol dm^{-3}) in aqueous solutions containing varying concentrations of α-CD, which has been calculated with $K_1=23.9$ mol^{-1} dm^3, $K_2=374$ mol^{-1} dm^3, $\varepsilon_1=468$ mol^{-1} dm^3 cm^{-1}, and $\varepsilon_2=2900$ mol^{-1} dm^3 cm^{-1}. The data points of the absorbance are also plotted as a function of α-CD concentration. $\lambda_{obs}=270$ nm.

In the presence of α-CDI (2.0×10^{-3} mol dm^{-3}), the fluorescence and room-temperature phosphorescence of 3-bromoquinoline in the deaerated solution were decreased in intensity by about 5% and 10% relative to α-CD, respectively. Fig. 6 shows the emission spectrum of 3-bromoquinoline in aqueous solution containing α-CDI of 2.0×10^{-3} mol dm^{-3}. For α-CDI, as previously stated, we could not estimate the K_1 and K_2 values because α-CDI is not too soluble in water. Unfortunately, therefore, we could not make a quantitative estimation of the fluorescence and phosphorescence intensities for the α-CDI–3-bromoquinoline inclusion complexes. Nonetheless, the fluorescence quenching is interpreted as due to the enhancement of the intersystem crossing from the excited singlet state to the triplet state of 3-bromo-

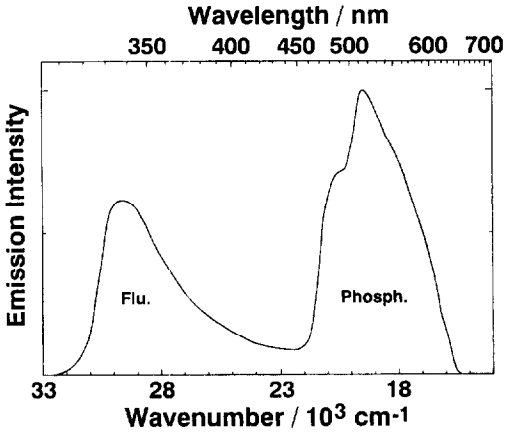

Fig. 6. Emission spectrum of 3-bromoquinoline (8.7×10^{-5} mol dm^{-3}) in aqueous solution containing α-CDI (2.0×10^{-3} mol dm^{-3}). $\lambda_{ex}=300$ nm.

quinoline by α-CDI. As in the case of 6-bromo-2-naphthol, the reduction in the room-temperature phosphorescence intensity of 3-bromoquinoline relative to α-CD is likely due to the acceleration of the nonradiative transition from the triplet state by α-CDI. Because the internal heavy atom effects of a bromine atom in 3-bromoquinoline increase the population of the triplet state to a fairly large degree, α-CDI may not remarkably enhance the triplet population through the external heavy atom effects, although fluorescence quenching is observed. Consequently, α-CDI apparently accelerates the nonradiative transition from the triplet state, resulting in the decrease in the room-temperature phosphorescence intensity of 3-bromoquinoline.

4. Concluding remarks

In aqueous solutions, α-CD forms 1:1 and 2:1 inclusion complexes with 3-bromoquinoline as well as 6-bromo-2-naphthol. α-CDI has been found to similarly behave as a host for 6-bromo-2-naphthol and 3-bromoquinoline, although a 2:1 α-CDI–3-bromoquinoline inclusion complex is not spectroscopically confirmed. The external heavy atom effects of α-CDI within the 2:1 α-CDI–6-bromo-2-naphthol inclusion complex reduce the room-temperature phosphorescence intensity of 6-bromo-2-naphthol compared to α-CD. This finding is in contrast to the result concerning a 1:1 β-CDI–2-chloronaphthalene inclusion complex, where the room-temperature phosphorescence intensity of 2-chloronaphthalene is enhanced by at least 20% relative to a 1:1 β-CD–2-chloronaphthalene inclusion complex. The external heavy atom effects of α-CDI seem to efficiently accelerate the nonradiative transition of the triplet state of the 6-bromo-2-naphthol located within the α-CDI cavities, although the heavy atom effects also enhance the intersystem crossing to the triplet state to some extent. The fluorescence and room-temperature phosphorescence intensities of 3-bromoquinoline have been decreased upon the addition of α-CDI compared to α-CD. Unfortunately, the K_1 and K_2 values for the α-CDI-3-bromoquinoline system could not be estimated so that the quantitative assessment remains unresolved at present. Nonetheless, the nonradiative transition from the triplet state is most likely to be significantly promoted by α-CDI compared to the intersystem crossing.

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