Fluorescence and Phosphorescence Properties of Naphthalene in Aqueous D-Glucose Solutions Containing 6-Deoxy-6-iodo-β-cyclodextrin at Room Temperature

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In aqueous solutions, 6-deoxy-6-iodo-β-cyclodextrin (β-CDI) forms a 1 : 1 inclusion complex with naphthalene. The naphthalene fluorescence is quenched upon the formation of the inclusion complex with β-CDI. The room-temperature phosphorescence of naphthalene has been observed from aqueous naphthalene solutions containing both D-glucose and β-CDI. Although the room-temperature phosphorescence has also been observed from aqueous naphthalene solutions containing both D-glucose (5.0 g/5.0 mL) and β-cyclodextrin (1.0×10^{-2} mol dm^{-3}), its intensity amounts to at most 9% of that containing D-glucose (5.0 g/5.0 mL) and β-CDI (1.0×10^{-3} mol dm^{-3}). In addition to the high viscosities of D-glucose solutions, the external heavy atom effects of β-CDI cause the appearance of the room-temperature phosphorescence. The room-temperature phosphorescence quantum yield of naphthalene in D-glucose (5.0 g/5.0 mL) solution containing β-CDI (1.0×10^{-3} mol dm^{-3}) has been estimated to be 2.2×10^{-3}, which is around 1.8% of the intrinsic phosphorescence quantum yield of naphthalene in ethanol at 77 K.

Cyclodextrins (CDs), which have a hydrophobic cavity in the molecular center, are cyclic oligosaccharides composed of more than five D-glucose units.[1] CDs having six, seven, and eight D-glucose units are called α-, β-, and γ-CD, respectively. In aqueous solutions, CDs and their derivatives accommodate various kinds of aromatic compounds into their cavities to form inclusion complexes. Due to the formation of the inclusion complexes of CDs with guest molecules, spectroscopic properties, such as electronic absorption, fluorescence, and phosphorescence, of guest molecules are varied to some extent.[2—10] Fluorescence intensities of guests are usually increased when the guests are incorporated into the CD cavities. The CD cavities offer more hydrophobic environments to the guests than the bulk water environment. In addition, a guest molecule incorporated into the CD cavity is protected from quenchers such as oxygen, thereby having smaller quenching efficiency and even showing the room-temperature phosphorescence of a guest.[6,10a,10d,11—16]

It is known that the heavy atom effects accelerate spin-forbidden transitions such as intersystem crossing between the excited singlet state and the triplet state. In ternary inclusion complexes, an additional heavy atom perturber, such as bromo-substituted alcohol, which is co-included in the CD cavity, has heavy atom effects on a non-halogenated phosphorophore bound to the cavity, leading to the observation of room-temperature phosphorescence.[10d,13] The heavy atom perturber is not limited to an additional guest molecule. Femia and Cline Love have found that heptakis(6-bromo-6-deoxy)-β-CD in *N*,*N*-dimethylformamide–water mixtures acts on a bound guest as a heavy atom perturber.[14] In neat water, it has been found that upon the formation of an inclusion complex, 6-deoxy-6-iodo-β-CD (β-CDI) increases the room-temperature phosphorescence of 2-chloronaphthalene compared to native β-CD.[16c]

Until recently, room-temperature phosphorescence in solutions has been observed only from inclusion complexes of β- and γ-CD (derivatives). Furthermore, these inclusion complexes, which emit room-temperature phosphorescence, contain a single CD molecule. However, it has been found that an inclusion complex between α-CD and 6-bromo-2-naphthol also shows the room-temperature phosphorescence of a guest in aerated aqueous solutions.[16a,16b] In this 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 emit it. For 2-chloronaphthalene, inclusion complexes with α-CD do not have the room-temperature phosphorescence even in deaerated aqueous solutions. In aqueous solutions containing D-glucose, however, the 2 : 1 α-CD–2-chloronaphthalene inclusion complex emits the room-temperature phosphorescence of 2-chloronaphthalene.[16d] As in the case of 6-bromo-2-naphthol, the room-temperature phosphorescence of 2-chloronaphthalene has not been observed from a 1 : 1 inclusion complex in D-glucose solutions, although the high viscosities of the D-glucose solutions facilitate the emission of the room-temperature phosphorescence.

As stated previously, the room-temperature phosphorescence of 2-chloronaphthalene in aqueous solution without D-glucose has been observed from a 1 : 1 inclusion complex with β-CDI.[16c] However, 2-chloronaphthalene has a chlorine substituent which potentially exerts internal heavy atom effects. Consequently, naphthalene, which has no such heavy atom, is more appropriate for examining the external heavy atom effects of β-CDI on the emission properties of a guest incorporated into the cavity. For the exciplex fluorescence of the anthracene–*N*,*N*-dimethylaniline system, it has been reported that the number of internal heavy atoms affects the exciplex fluorescence quantum yield.[17] From the viewpoint of the effects of the number of heavy atoms in inclusion complexes, an examination of the properties of room-temperature phosphorescence is interesting, since, in contrast to the β-CDI–2-chloronaphthalene system, only one heavy atom is involved in the β-CDI–naphthalene system. Despite several reports on the observation of room-temperature phosphorescence from CD inclusion complexes, there is so far little data concerning room-temperature phosphorescence quantum yield.[15,16d] To better understand the external heavy atom effects of β-CDI, therefore, it is very important to evaluate the room-temperature phosphorescence quantum yield of a guest incorporated into the β-CDI cavity. In addition to these unresolved points, the viscosity effects on the room-temperature phosphorescence from inclusion complexes in solution have not been examined except for the α-CD–2-chloronaphthalene system.[16d] Thus, we investigated the emission properties of naphthalene in aqueous (D-glucose) solutions containing β-CDI.

Experimental

The synthesis of β-CDI has been described elsewhere.[16c] β-CD obtained from Nacalai Tesque, Inc. was recrystallized twice from water. Naphthalene purchased from Nacalai Tesque, Inc. was recrystallized twice from ethanol. D-Glucose from Wako Pure Chemical Industries, Ltd. was used without further purification. Aqueous solutions of naphthalene were prepared by plunging purified naphthalene crystals into water in the dark for several days. Aqueous D-glucose solutions of naphthalene were prepared using a method similar to those of 2-chloronaphthalene.[16d] With respect to the aqueous D-glucose solutions, 5.0 mL of solutions contained 5.0 g of D-glucose unless otherwise stated. Concentrations of naphthalene were about 3.9×10^{-5} mol dm^{-3}. The viscosities of the D-glucose (5.0 g/5.0 mL) solutions were 600 mPa s at 25 °C.

Absorption spectra were recorded on a Shimadzu UV-260 spectrophotometer. Fluorescence spectra were taken with a Shimadzu RF-501 spectrofluorometer equipped with a cooled Hamamatsu R-943 photomultiplier. Room-temperature phosphorescence spectra were recorded on the fluorometer provided with a cylindrical chopper. Fluorescence and phosphorescence spectra were corrected for the spectral response of the fluorometer. Phosphorescence decay curves were obtained with a conventional flash photolysis apparatus.[18] Spectroscopic measurements were made at 25±0.1°C, except for the low-temperature phosphorescence spectrum and phosphorescence decay measurements, which were done at 77 K and at room temperature, respectively.

Results and Discussion

Fluorescence Properties of Naphthalene in Aqueous Solutions Containing D-Glucose. Figure 1 shows absorption spectra of naphthalene in aqueous solutions in the absence and presence of D-glucose. When D-glucose is added to aqueous naphthalene solution, the absorption peaks of naphthalene are shifted to longer wavelengths. An increase in the absorbance of the naphthalene absorption bands over the wavelength range examined is probably due to a slightly poor match in absorbance between sample and reference solutions. Figure 2 shows normalized fluorescence spectra of naphthalene in aqueous solutions in the absence and presence of D-glucose. As in the case of the absorption spectra shown in Fig. 1, the fluorescence spectrum of naphthalene in the presence of D-glucose is shifted to slightly longer wavelengths relative to that in the absence of D-glucose.

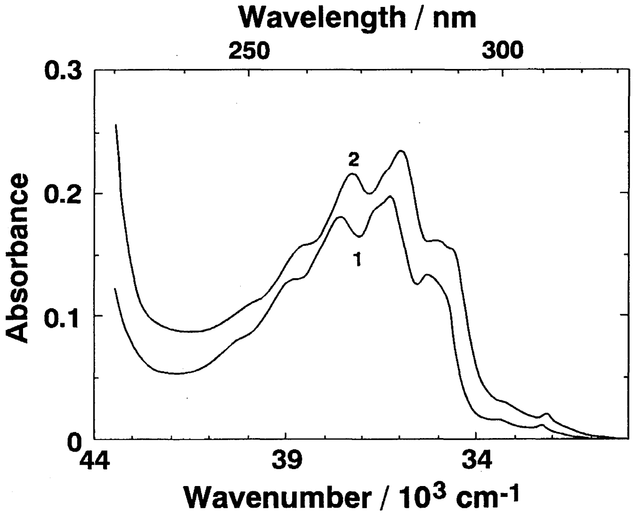

Fig. 1. Absorption spectra of naphthalene (3.9×10^{-5} mol dm^{-3}) in aqueous solutions in the absence (spectrum 1) and presence (spectrum 2) of D-glucose (5.0 g/5.0 mL).

The fluorescence quantum yield (ϕ_f) of naphthalene in aqueous solution was evaluated to be 0.086 on the basis of a ϕ_f value (0.546) of quinine sulfate in 1 mol dm^{-3} H_2SO_4 solution.[19] Next, a ϕ_f value of naphthalene in D-glucose (5.0 g/5.0 mL) solution was measured as 0.17 by using an aqueous naphthalene solution as a secondary standard. This ϕ_f value

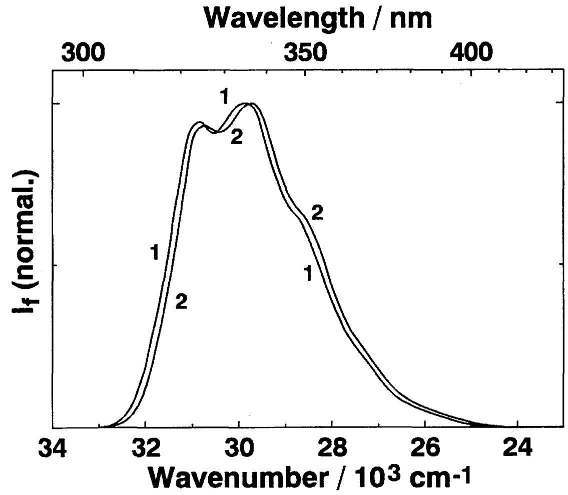

Fig. 2. Normalized fluorescence spectra of naphthalene (3.9×10^{-5} mol dm^{-3}) in aqueous solutions in the absence (spectrum 1) and presence (spectrum 2) of D-glucose (5.0 g/5.0 mL). $\lambda_{ex}=285$ nm.

for D-glucose solution is about two times greater than that for an aqueous solution without D-glucose. The greater ϕ_f value is due to the increased viscosity of D-glucose solution.

Inclusion Complexes of β-CD with Naphthalene in Aqueous D-Glucose Solutions. Figure 3 illustrates normalized fluorescence spectra of naphthalene in D-glucose solutions with and without β-CD. Upon the addition of β-CD (1.0×10^{-2} mol dm^{-3}), the naphthalene monomer fluorescence is very slightly increased, and a new, broad longer-wavelength emission appears, which is ascribed to the naphthalene excimer fluorescence. Furthermore, in the presence of β-CD, the vibrational structures of the monomer fluorescence are much sharper than that in the absence of β-CD. In aqueous solutions without D-glucose, similar spectral changes have already been observed for the naphthalene fluorescence.[10a)] As in the case of aqueous naphthalene solutions without D-glucose, the spectral and intensity changes in the naphthalene monomer fluorescence for D-glucose solution is most likely due to the formation of a 1 : 1 β-CD–naphthalene inclusion complex:

$$\beta\text{-CD} + \text{N} \overset{K_1}{\rightleftarrows} \beta\text{-CD}\cdot\text{N} \qquad (1)$$

Here, N and β-CD·N represent naphthalene and the 1 : 1 inclusion complex between β-CD and naphthalene, respectively, and K_1 is the equilibrium constant for the formation of the 1 : 1 inclusion complex. Addition of β-CD to aqueous naphthalene solution without D-glucose results in the appearance of the naphthalene excimer fluorescence, which arises from a 2 : 2 β-CD–naphthalene inclusion complex.[10a)] Since the presence of D-glucose does not essentially alter the inclusion modes of CD,[16d)] the 2 : 2 β-CD–naphthalene inclusion complex, which is responsible for the naphthalene excimer fluorescence, is most likely formed in aqueous solution containing D-glucose:

$$\beta\text{-CD}\cdot\text{N} + \beta\text{-CD}\cdot\text{N} \overset{K_2}{\rightleftarrows} (\beta\text{-CD}\cdot\text{N})_2 \qquad (2)$$

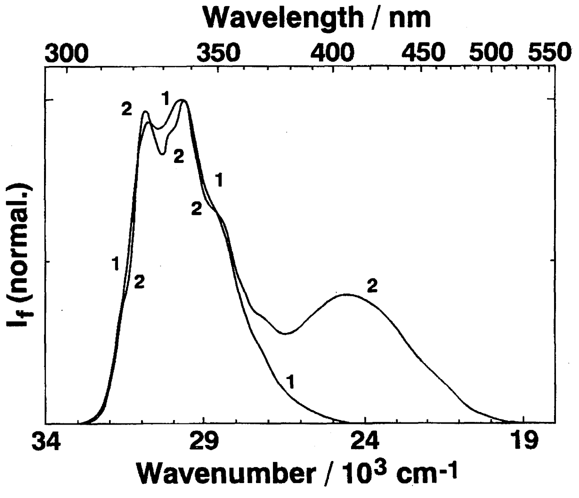

Fig. 3. Normalized fluorescence spectra of naphthalene (3.9×10^{-5} mol dm^{-3}) in aqueous D-glucose (5.0 g/5.0 mL) solutions in the absence and presence of β-CD (1.0×10^{-2} mol dm^{-3}). $\lambda_{ex} = 285$ nm.

Here, $(\beta\text{-CD}\cdot\text{N})_2$ stands for the 2 : 2 β-CD–naphthalene inclusion complex, and K_2 is the equilibrium constant for the formation of the 2 : 2 inclusion complex.

Inclusion Complex of β-CDI with Naphthalene in Aqueous and Aqueous D-Glucose Solutions. When β-CDI (1.0×10^{-3} mol dm^{-3}) was added to aqueous solution of naphthalene, the monomer fluorescence of naphthalene was reduced in intensity, indicating the formation of a 1 : 1 β-CDI–naphthalene inclusion complex. In contrast to naphthalene solutions containing β-CD, the new longer-wavelength emission band did not appear, probably because the β-CDI concentration was about one-tenth of the β-CD concentration owing to the much lower solubility of β-CDI in water. At low concentrations of β-CDI, self-association of 1 : 1 inclusion complexes, which causes the formation of the naphthalene excimer, would not occur, because of the low concentration of a 1 : 1 inclusion complex. From a double reciprocal plot for the naphthalene monomer fluorescence,[10a)] the K_1 for β-CDI has been estimated to be 330±90 mol^{-1} dm^3 (Fig. 4). This K_1 is about half those (685 and 630±40 mol^{-1} dm^3) for the parent β-CD.[10a,20)]

A naphthalene molecule incorporated into the β-CDI cavity is protected from attack by a quencher. Figure 5 shows the result of the quenching experiment using KI in aqueous solutions with β-CDI (1.0×10^{-3} mol dm^{-3}). From the Stern–Volmer plot in Fig. 5, an apparent Stern–Volmer constant for a naphthalene solution containing β-CDI (1.0×10^{-3} mol dm^{-3}) is estimated to be 211 mol^{-1} dm^3, which is slightly smaller than that (240 mol^{-1} dm^3) for naphthalene solution without β-CDI.[10a)] This finding provides additional evidence for the formation of the inclusion complex between β-CDI and naphthalene. The fluorescence quenching by KI also indicates that the fluorescence of naphthalene bound to the β-CDI cavity is not completely quenched by β-CDI.

The absorption spectrum of naphthalene in aqueous D-glucose solution with β-CDI (1.0×10^{-3} mol dm^{-3}) was nearly the same as that without β-CDI, because the β-CDI concentration was low. The monomer fluorescence of naphthalene in aqueous D-glucose solution was quenched by β-CDI, indi-

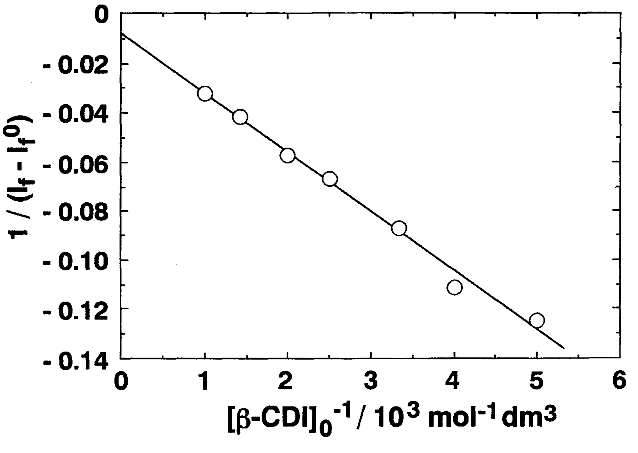

Fig. 4. Double reciprocal plot for the naphthalene monomer fluorescence intensity in the β-CDI–naphthalene (3.9×10^{-5} mol dm^{-3}) system. λ_{ex}=285 nm. λ_{obsd}=335 nm.

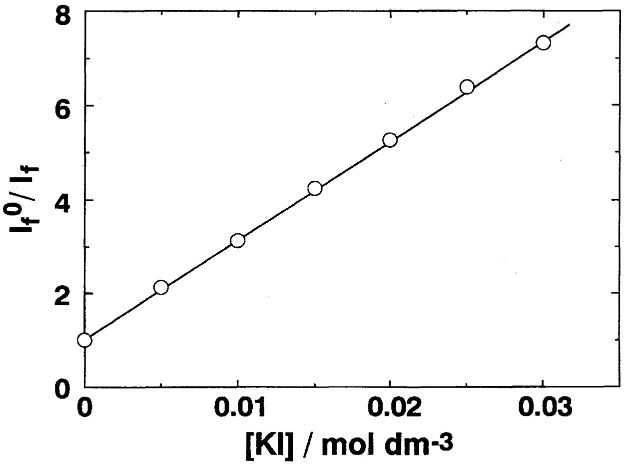

Fig. 5. Stern–Volmer plot for the naphthalene monomer fluorescence in aqueous β-CDI (1.0×10^{-3} mol dm^{-3}) solution containing KI. λ_{ex}=285 nm. λ_{obsd}=335.5 nm.

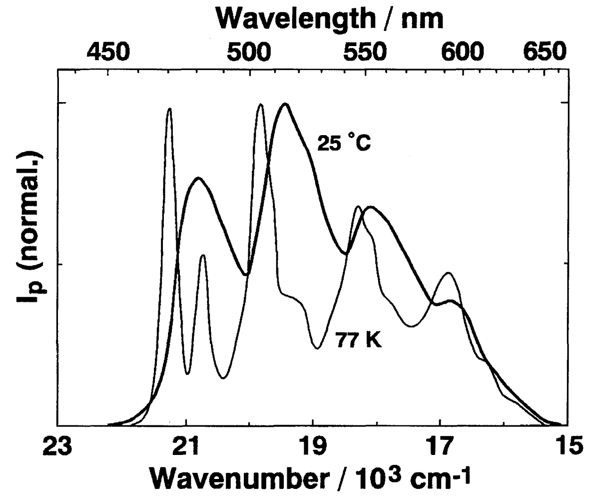

Fig. 6. Normalized phosphorescence spectrum of naphthalene (3.9×10^{-5} mol dm^{-3}) in aqueous solution containing D-glucose (5.0 g/5.0 mL) and β-CDI (1.0×10^{-3} mol dm^{-3}) at 25 °C and that in ethanol at 77 K.

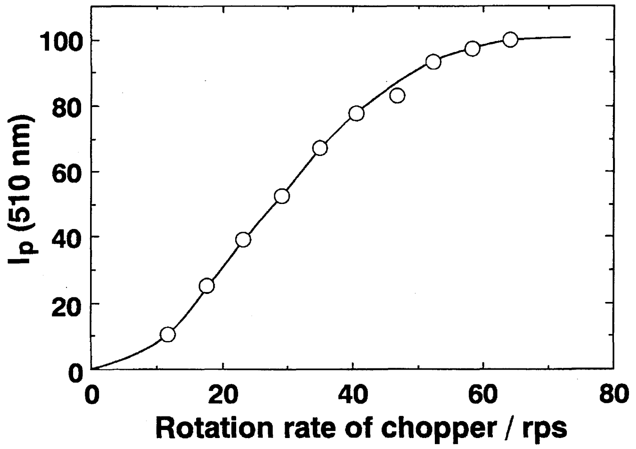

Fig. 7. Dependence of the room-temperature phosphorescence intensity of naphthalene (3.9×10^{-5} mol dm^{-3}) in aqueous D-glucose (5.0 g/5.0 mL) solutions containing β-CDI (1.0×10^{-3} mol dm^{-3}) on the rotation rate of a chopper. λ_{ex} = 285 nm. λ_{obsd} = 510 nm.

cating the formation of an inclusion complex between β-CDI and naphthalene. The locations of the spectral peaks and the shape of the naphthalene monomer fluorescence were not varied by the addition of β-CDI. As in the case of the naphthalene solution without D-glucose, β-CDI (1.0×10^{-3} mol dm^{-3}) did not induce the naphthalene excimer fluorescence, probably because the concentration of the 1 : 1 inclusion complex is very low owing to the low concentration of β-CDI.

Room-Temperature Phosphorescence of Naphthalene in D-Glucose Solutions Containing β-CDI. Even when aqueous naphthalene solution containing β-CDI was degassed, the room-temperature phosphorescence of naphthalene was not detected. However, the room-temperature phosphorescence of naphthalene was observed from aqueous naphthalene solutions containing both β-CDI (1.0×10^{-3} mol dm^{-3}) and D-glucose (5.0 g/5.0 mL), although a mechanical chopper had to be used to remove the intense naphthalene fluorescence from the naphthalene emissions. This indicates that the high viscosity of D-glucose solution as well as the presence of β-CDI induces the room-temperature phosphorescence of naphthalene. Figure 6 depicts the room-temperature phosphorescence of naphthalene in aqueous D-glucose solution containing β-CDI, together with the phosphorescence spectrum of naphthalene in ethanol at 77 K. The room-temperature phosphorescence is shifted to longer wavelengths by around 10 nm, with blurred vibrational structures, compared to the low-temperature phosphorescence.

Figure 7 illustrates the dependence of the room-temperature phosphorescence intensity of naphthalene in D-glucose solution containing β-CDI (1.0×10^{-3} mol dm^{-3}) on the rotation rate of a chopper. At about 60 rps, the room-temperature phosphorescence intensity reaches a plateau. Thus, we tried to estimate the room-temperature phosphorescence quantum yield (ϕ_p) using the fluorescence (ϕ_f = 0.086) of an aqueous naphthalene solution as a standard. By use of our apparatus, the apparent ϕ_p value of naphthalene in D-glucose (5.0 g/5.0 mL) solution containing β-CDI (1.0×10^{-3} mol dm^{-3}) was found to be 2.1×10^{-4}. In our phosphorometer, however, a cylindrical chopper cuts off the illumination time of the excitation light by 11/18, so that the integrated excitation light intensity is reduced to 7/18 irrespective of the rotation rate of the chopper. Therefore, the apparent ϕ_p value has to be multiplied by 18/7, giving 5.4×10^{-4} as a corrected ϕ_p value. Furthermore, not all naphthalene molecules associate with β-CDI, since the β-CDI concentration is relatively low. Under the assumption that the K_1 for D-glucose solution is the same as that for a solution without D-glucose and that the absorption spectra of solutions with and without β-CDI are identical, the corrected ϕ_p above obtained should be further multiplied by $(1+K_1[\beta\text{-CDI}])/K_1[\beta\text{-CDI}]$ (=4.03) as a correction factor. Consequently, the finally corrected ϕ_p value for D-glucose solution containing β-CDI is 2.2×10^{-3}.

Although the room-temperature phosphorescence emissions of naphthalene were observed from D-glucose solutions with and without β-CD (1.0×10^{-2} mol dm^{-3}), these intensities were less than 9% of that for D-glucose solution containing β-CDI of 1.0×10^{-3} mol dm^{-3}. This finding indicates that the inclusion of naphthalene into the β-CD cavity causes little or no increase of the room-temperature phosphorescence, although the association of the 1 : 1 β-CD–naphthalene inclusion complexes, which induces the naphthalene excimer, may reduce the room-temperature phosphorescence intensity of naphthalene. From these results, the external heavy atom effects of β-CDI on the naphthalene emission properties are definitely confirmed.

The ratio of the room-temperature phosphorescence intensity of naphthalene in β-CDI (1.0×10^{-3} mol dm^{-3}) solution to that in β-CD (1.0×10^{-2} mol dm^{-3}) solution is estimated to be about 11. However, the concentration of the inclusion complex of β-CDI is much lower than that of β-CD, since the concentration of β-CDI is one-tenth of that of β-CD. Therefore, the intrinsic intensity ratio for the room-temperature phosphorescence of naphthalene is greater than 11. For the β-CDI–2-chloronaphthalene system in aqueous solutions without D-glucose, on the other hand, at least a 20% increase of the room-temperature phosphorescence has been observed compared to the β-CD–2-chloronaphthalene system.[16c)] The intensity ratio of the room-temperature phosphorescence is about 1.2 for 2-chloronaphthalene, although the iodine atom of β-CDI is a much stronger perturber than the chlorine atom of 2-chloronaphthalene. A comparison of the intensity ratios between naphthalene and 2-chloronaphthalene suggests that the second heavy atom (an iodine atom of β-CDI) in the inclusion complex makes a less effective contribution to the increase in the room-temperature phosphorescence quantum yield.

Langelaar et al. have measured the ϕ_p values of naphthalene in ethanol to be 2×10^{-5} and 0.12 at 20 °C and 77 K, respectively.[21)] Consequently, the ϕ_p value (2.2×10^{-3}) of naphthalene in D-glucose solution with β-CDI is two orders of magnitude greater than that in ethanol at 20 °C, and is 1.8% of the intrinsic ϕ_p value at 77 K. For the α-CD–2-chloronaphthalene system in D-glucose solution, the ϕ_p value of the room-temperature phosphorescence is at least 19% of the ϕ_p value at 77 K.[16d)] These results suggest that in the inclusion complexes the internal heavy atom effects may be more effective than the external heavy atom effects, although the inclusion modes of α-CD and β-CDI are different. The significantly small ϕ_p value of naphthalene compared to the ϕ_f value (0.17) for D-glucose solution is consistent with the fact that the intense naphthalene fluorescence obscures the room-temperature phosphorescence of naphthalene when a chopper is not used. The room-temperature phosphorescence lifetime of naphthalene in aqueous D-glucose solution containing β-CDI (1.0×10^{-3} mol dm^{-3}) has been found to be 0.40 ms, which is an order of magnitude less than that (3 ms)[22)] for naphthalene in ethanol at 20 °C. Using a relationship of $k_p=\phi_p/(\tau_p\phi_T)$, where k_p, τ_p, and ϕ_T are the rate constant for phosphorescence, the phosphorescence lifetime, and the triplet quantum yield, respectively, the ratio of a k_p value of naphthalene in aqueous D-glucose solutions containing β-CDI to that in ethanol is estimated to be 8.3×10^2 under the assumption that the ϕ_T value for aqueous D-glucose solutions with β-CDI is identical to that for ethanol. The ϕ_T value for ethanol solution at 20 °C is reported to be 0.71 or 0.80.[22,23)] Because the ϕ_T value for solution containing β-CDI is likely to be greater than that for solution without β-CDI owing to the external heavy atom effects of β-CDI, the estimated k_p ratio may be slightly overestimated. However, the error amounts to at most 30%, since the ϕ_T value is 0.71 (or 0.80) for ethanol. Consequently, the more than two orders of magnitude greater ratio of the k_p value definitely indicates external heavy atom effects of β-CDI on naphthalene bound to the β-CDI cavity; the increase in k_p greatly contributes to the increase of the room-temperature phosphorescence of naphthalene.

The ratio of the k_p value of naphthalene in a mixture of ethanol/methanol/propyl iodide (3.2 : 8 : 1) to that in a mixture of ethanol/methanol (4 : 1) has been reported to be 6.8.[24)] This value is much smaller than the k_p ratio (8.3×10^2) regarding solutions with and without β-CDI. At 77 K, the phosphorescence lifetimes of naphthalene in EPA (diethyl ether/2-methylbutane/ethanol = 5 : 5 : 2) and propyl iodide have been measured to be 2.6 and 0.076 s, respectively.[25)] Assuming that the nonradiative rate constant is negligible to k_p, the ratio of k_p in propyl iodide to that in EPA is calculated to be about 34. From the results that the ratio of k_p for β-CDI solution to that for solution without β-CDI is one or two orders of magnitude greater than the roughly estimated k_p ratio regarding neat solvents and the k_p ratio regarding mixed solvents, the external heavy atom effects of β-CDI on the k_p value of a guest molecule bound to the β-CDI cavity seem to be considerably greater than the external heavy atom effects due to solvent. This may imply the close contact of the guest molecule with an iodine atom of β-CDI compared to an iodine atom of a solvent molecule.

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References

1) M. L. Bender and M. Komiyama, "Cyclodextrin Chemistry," Springer-Verlag, New York (1978).

2) C. J. Seliskar and L. Brand, *Science*, **171**, 799 (1971).

3) K. Kano, S. Hashimoto, A. Imai, and T. Ogawa, *J. Inclusion Phenom.*, **2**, 737 (1984).

4) A. Ueno, F. Moriwaki, and T. Osa, *Tetrahedron*, **43**, 1571 (1987).

5) G. Patnay, K. Fowler, A. Shapira, G. Nelson, and I. M. Warner, *J. Inclusion Phenom.*, **5**, 717 (1987).

6) R. A. Agbaria, B. Uzan, and D. Gill, *J. Phys. Chem.*, **93**, 3855 (1989).

7) A. Nag and K. Bhattacharyya, *J. Chem. Soc., Faraday Trans.*, **86**, 53 (1990).

8) S. De Feyter, J. van Stam, N. Boens, and F. C. De Schryver, *Chem. Phys. Lett.*, **249**, 46 (1996).

9) H. Yang and C. Bohne, *J. Phys. Chem.*, **100**, 14533 (1996).

10) a) S. Hamai, *Bull. Chem. Soc. Jpn.*, **55**, 2721 (1982); b) S. Hamai, *J. Phys. Chem.*, **92**, 6140 (1988); c) S. Hamai, *Bull. Chem. Soc. Jpn.*, **62**, 2763 (1989); d) S. Hamai, *J. Am. Chem. Soc.*, **111**, 3954 (1989); e) S. Hamai, *J. Phys. Chem.*, **94**, 2595 (1990); f) S. Hamai, T. Ikeda, A. Nakamura, H. Ikeda, A. Ueno, and F. Toda, *J. Am. Chem. Soc.*, **114**, 6012 (1992).

11) N. J. Turro, J. D. Bolt, Y. Kuroda, and I. Tabushi, *Photochem. Photobiol.*, **35**, 69 (1982).

12) N. J. Turro, G. S. Cox, and S. Li, *Photochem. Photobiol.*, **37**, 149 (1983).

13) S. Scypinski and L. J. Cline Love, *Anal. Chem.*, **56**, 322 (1984).

14) R. A. Femia and L. J. Cline Love, *J. Phys. Chem.*, **89**, 1897 (1985).

15) A. Ponce, P. A. Wong, J. J. Way, and D. G. Nocera, *J. Phys. Chem.*, **97**, 11137 (1993).

16) a) S. Hamai, *J. Chem. Soc., Chem. Commun.*, **1994**, 2243; b) S. Hamai, *J. Phys. Chem.*, **99**, 12109 (1995); c) S. Hamai and N. Mononobe, *J. Photochem. Photobiol. A: Chem.*, **91**, 217 (1995); d) S. Hamai, *J. Phys. Chem. B*, **101**, 1707 (1997); e) S. Hamai, *Recent Res. Develop. Phys. Chem.*, **1**, 321 (1997).

17) S. Hamai, *Bull. Chem. Soc. Jpn.*, **57**, 2700 (1984).

18) K. Kikuchi, H. Kokubun, and H. Koizumu, *Bull. Chem. Soc. Jpn.*, **41**, 1545 (1968).

19) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

20) M. Fujiki, T. Deguchi, and I. Sanemasa, *Bull. Chem. Soc. Jpn.*, **61**, 1163 (1988).

21) J. Langelaar, R. P. Rettschnick, and G. J. Hoijtink, *J. Chem. Phys.*, **54**, 1 (1971).

22) C. A. Parker, "Photoluminescence of Solutions," Elsevier Publishing Co., Amsterdam (1968).

23) A. R. Horrocks and F. Wilkinson, *Proc. R. Soc., Ser. A*, **306**, 257 (1968).

24) S. P. McGlynn, F. J. Smith, and G. Clento, *Photochem. Photobiol.*, **3**, 269 (1964).

25) S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodoyleas, *J. Chem. Phys.*, **66**, 2499 (1962).