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The room-temperature phosphorescence of 2-chloronaphthalene induced by inclusion complexation with 6-iodo-6-deoxy-β-cyclodextrin and the excimer fluorescence of a β-cyclodextrin–2-chloronaphthalene inclusion complex in aqueous solution

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Abstract

In aqueous solution, 6-iodo-6-deoxy-β-cyclodextrin (β-CDI) forms a 1:1 inclusion complex with 2-chloronaphthalene (2CN), with a formation constant of 1400 ± 300 mol^{-1} dm^3. The fluorescence of 2CN is quenched by the formation of the inclusion complex with β-CDI. In addition, in deaerated aqueous solution, the room-temperature phosphorescence of 2CN is observed from the inclusion complex. Although parent β-cyclodextrin (β-CD) also induces the room-temperature phosphorescence of 2CN on formation of an inclusion complex with this compound, β-CDI as a heavy atom perturber is more than 1.2 times as effective in enhancing the room-temperature phosphorescence than β-CD. β-CD forms an inclusion complex with 2CN, from which the excimer fluorescence of 2CN is observed. It is probable that the excimer fluorescence is due to a 2:2 β-CD–2CN inclusion complex.

Keywords: Room temperature phosphorescence; 2-Chloronaphthalene; Inclusion complexes; Excimer fluorescence

1. Introduction

Cyclodextrins (CDs) are cyclic oligomers composed of D-glucopyranose residues which are joined by α-(1-4) glycosidic linkages. CDs possessing six, seven and eight D-glucopyranose residues are named α-, β- and γ-CDs respectively. Because these CDs are torus shaped with a relatively hydrophobic cavity, guest molecules of appropriate size can be incorporated into the CD cavity [1]. The inclusion of a fluorescent guest in the CD cavity usually leads to an enhancement of the guest fluorescence intensity with a slight sharpening of the fluorescence bands [2–6]. In the presence of a quencher, such as iodide, the wall of the CD cavity protects an incorporated guest from the quencher, so that the fluorescence quenching is considerably reduced compared with that of a free, unincorporated guest [3,5]. Since CDs also guard a triplet state guest bound in the CD cavity, the room-temperature phosphorescence, which cannot usually be detected in liquid media, is often observed in aqueous solutions [7–9].

Two 1:1 inclusion complexes self-associate to form a 2:2 inclusion complex [3,10–12]. In addition, CDs form inclusion complexes with the same or different kinds of guests [3,6,13–16]. The presence of an additional guest within the cavity further sterically inhibits the approach of a quencher to a fluorescent guest in the cavity, resulting in a further reduction in fluorescence quenching [3,5]. Similarly, the formation of ternary inclusion complexes effectively enhances the room-temperature phosphorescence in aqueous solutions [17–20].

Room-temperature phosphorescence has been observed from CD inclusion complexes of halogenated guests (phosphorophore), ternary inclusion complexes of a halogenated phosphorophore and an additional non-halogenated guest and ternary inclusion complexes of a non-halogenated phosphorophore and an additional halogenated guest, with the exception of inclusion complexes of heptakis(6-bromo-6-deoxy)-β-CD with polynuclear aromatic hydrocarbons [21]. The host heptakis(6-bromo-6-deoxy)-β-CD acts as an external heavy atom perturber towards non-halogenated guests. In a mixture of *N,N*-dimethylformamide and water, appreciable room-temperature phosphorescence of the aromatics occurs when they are included within the heptakis(6-bromo-6-deoxy)-β-CD cavity.

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Iodine in 6-iodo-6-deoxy-β-CD (β-CDI) is anticipated to exert an external heavy atom effect on an excited guest molecule bound within the β-CDI cavity, thereby inducing room-temperature phosphorescence of the guest. In addition, it is expected that β-CDI will be fairly soluble in water compared with heptakis(6-bromo-6-deoxy)-β-CD, since β-CDI has only one heavy atom (iodine) in a single molecule in contrast with heptakis(6-bromo-6-deoxy)-β-CD which bears seven bromine atoms per molecule. As mentioned previously, in the presence of small organic solvent molecules, CDs often form ternary inclusion complexes with a solute molecule and an additional organic solvent molecule(s). Since in neat aqueous solutions, no additional guest enters into the CD cavity, the formation of a binary inclusion complex alone is expected. Therefore, in neat aqueous solutions, the interactions between a single guest and a host CD molecule i.e. the external heavy atom effect produced by β-CDI can be examined in comparison with the behaviour of an inclusion complex of β-CD which has no heavy atom.

Thus, using absorption and emission spectroscopy, we investigated the photophysical behaviour of an inclusion complex between β-CDI and 2-chloronaphthalene (2CN) in aqueous solution in addition to that between parent β-CD and 2CN. In this report, we demonstrate excimer formation in the β-CD–2CN system, and describe the room-temperature phosphorescence of 2CN in deaerated aqueous solutions containing both 2CN and β-CDI.

2. Experimental details

2.1. Synthesis of β-CDI

According to a modified Melton–Slessor method, a mixture of 6-O-*p*-toluenesulphonyl-β-CD (5.2 g) and sodium iodide (5.0 g) in dimethylformamide was heated at 85 °C for 24 h [22]. Acetone was poured into the reaction mixture, and the precipitate was collected. The product was recrystallized from a mixture of 1-butanol, ethanol and water (5:4:3), with a yield of 85% (4.4 g). Analysis: calculated for $C_{42}H_{69}IO_{34} \cdot 4H_2O$: C, 38.31; H, 5.87; I, 9.64; found: C, 38.83; H, 5.90; I, 9.14.

2.2. Materials

β-CD (Nakarai Tesque, Inc.) was recrystallized twice from water. 2CN (Tokyo Kasei Kogyo, Ltd.) was purified by column chromatography. Sample solutions of 2CN were prepared from an aqueous solution in which purified crystals of 2CN were plunged for several days in the dark. The concentrations of 2CN in the sample solutions with β-CD were $(3–4) \times 10^{-5}$ mol dm^{-3}, with the exception of room-temperature phosphorescence measurements for which the 2CN concentrations were approximately 3×10^{-6} mol dm^{-3}. In solutions with β-CDI, the 2CN concentrations were approximately 3×10^{-6} mol dm^{-3} for both fluorescence and room-temperature phosphorescence measurements. To detect the room-temperature phosphorescence, sample solutions were degassed using a conventional freeze–pump–thaw cycle procedure.

2.3. Apparatus

Absorption spectra were run on a Shimadzu UV-260 spectrophotometer. Fluorescence and phosphorescence spectra were obtained with a Shimadzu RF-540 spectrofluorometer, with the exception of the measurement of the phosphorescence spectrum of 2CN at 77 K, for which a Shimadzu RF-501 spectrofluorometer was used. The fluorescence and phosphorescence spectra were corrected for the spectral responses of the fluorometers. Spectroscopic measurements were performed at 25 ± 0.1 °C, except for the measurement of the phosphorescence spectrum of 2CN at 77 K.

3. Results and discussion

3.1. Absorption and fluorescence spectra of 2CN in aqueous solutions containing β-CD

Figs. 1(a) and 1(b) show the absorption spectra of 2CN in aqueous solutions containing various concentrations of β-CD. Below a β-CD concentration of about 8.5×10^{-4} mol dm^{-3}, the absorption maxima are red shifted, accompanied by the appearance of isosbestic points at 248 and 277 nm, indicating the formation of a 1:1 inclusion complex between β-CD and 2CN. However, in the β-CD concentration range above about 8.5×10^{-4} mol dm^{-3}, no isosbestic points are observed, and as the concentration is further raised above about 4.26×10^{-3} mol dm^{-3}, the absorption intensities are enhanced over the absorption wavelength range examined. These findings indicate the formation of an inclusion complex other than the 1:1 β-CD–2CN inclusion complex.

Fig. 2 illustrates the fluorescence spectra of 2CN in aqueous solutions containing various concentrations of β-CD. As the β-CD concentration is increased, the monomer fluorescence of 2CN is reduced in intensity, accompanied by the emergence of a new longer wavelength emission peaking at approximately 420 nm. The longer wavelength emission can be ascribed to the excimer fluorescence of 2CN. For the β-CD–naphthalene and β-CD–1-cyanonaphthalene systems, the excimer fluorescence of naphthalene and 1-cyanonaphthalene has been found [3,5]. The naphthalene (1-cyanonaphthalene) excimer fluorescence is due to a 2:2 β-CD–naphthalene (β-CD–1-cyanonaphthalene) inclusion complex formed by the self-association of two 1:1 β-CD–naphthalene (β-CD–1-cyanonaphthalene) inclusion complexes. Because 2CN is bulkier than naphthalene, it is unlikely that two 2CN molecules are accommodated into a single β-CD cavity. Like naphthalene, therefore, the excimer fluorescence is probably due to a 2:2 inclusion complex

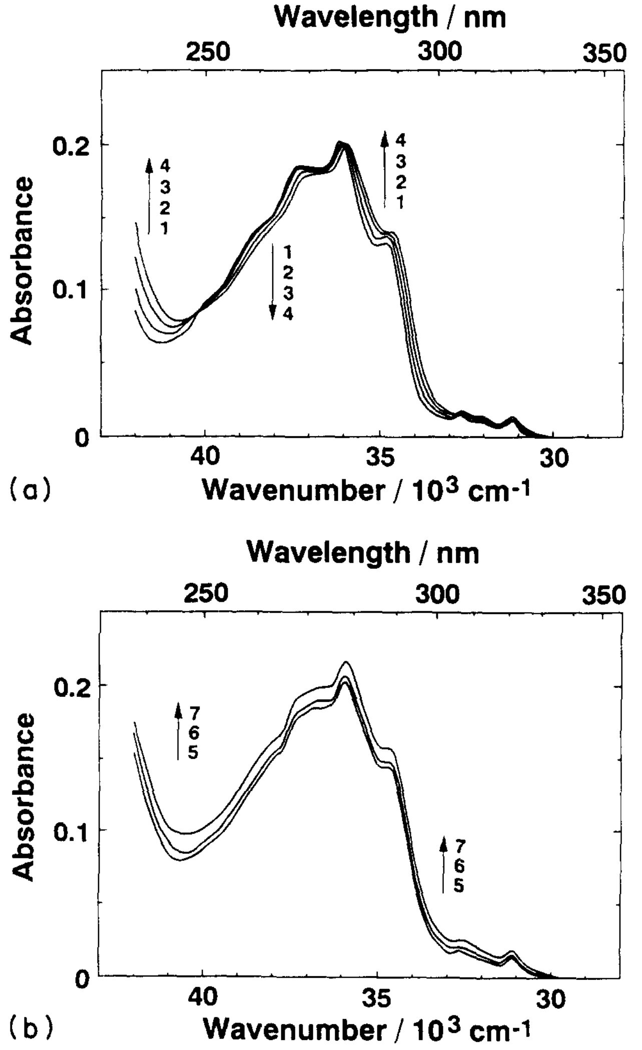

Fig. 1. Absorption spectra of 2CN (4.1×10^{-5} mol dm^{-3}) in aqueous solution containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 2.55×10^{-4}, (3) 8.51×10^{-4}, (4) 2.55×10^{-3}, (5) 4.26×10^{-3}, (6) 5.96×10^{-3} and (7) 8.51×10^{-3} mol dm^{-3}.

formed by the self-association of the 1:1 β-CD–2CN inclusion complex.

When the 2CN concentration in aqueous solution containing β-CD is reduced to about one-tenth (4.6×10^{-6} mol dm^{-3}) of its original value, excimer fluorescence is not observed. In addition, the monomer fluorescence intensity of 2CN is enhanced in contrast to the fluorescence behaviour of a concentrated (approximately 4×10^{-5} mol dm^{-3}) 2CN solution, indicating that excimer formation is responsible for the reduction in the monomer fluorescence intensity. This finding seems to suggest that a 1:1 β-CD–2CN inclusion complex alone is formed in dilute 2CN aqueous solution containing β-CD. Thus, using dilute 2CN solutions, we attempted to estimate the equilibrium constant ($K(\beta\text{-CD})$) for the formation of a 1:1 β-CD–2CN inclusion complex. $K(\beta\text{-CD})$ can be evaluated based on the following equation [3]

$$\frac{1}{I_f - I_f^0} = \frac{1}{a} + \frac{1}{aK(\beta\text{-CD})}\,\frac{1}{[\beta\text{-CD}]_0} \qquad (1)$$

where I_f, I_f^0, a and $[\beta\text{-CD}]_0$ are the monomer fluorescence intensity in the presence of β-CD, that in the absence of β-CD, a constant and the initial concentration of β-CD respectively. Fig. 3 shows a plot of $1/(I_f - I_f^0)$ against $1/[\beta\text{-CD}]_0$ for 2CN. From the intercept/slope value of this plot, $K(\beta\text{-CD})$ is evaluated to be 85 ± 20 mol^{-1} dm^3. On the other hand, the $K(\beta\text{-CD})$ values for the formation of a 1:1 β-CD inclusion complex are 685, 630, 590 ± 50, 581 ± 6 and 560 ± 110 mol^{-1} dm^3 for naphthalene, 2-methoxynaphthalene, 2-naphthol, 2-acetylnaphthalene and 2-naphthyloxyacetic acid respectively [3,23–25]. Since $K(\beta\text{-CD})$ for 2CN is significantly less than those for naphthalene, etc., it does not seem to represent the equilibrium constant for the formation of a 1:1 β-CD–2CN inclusion complex. In the low β-

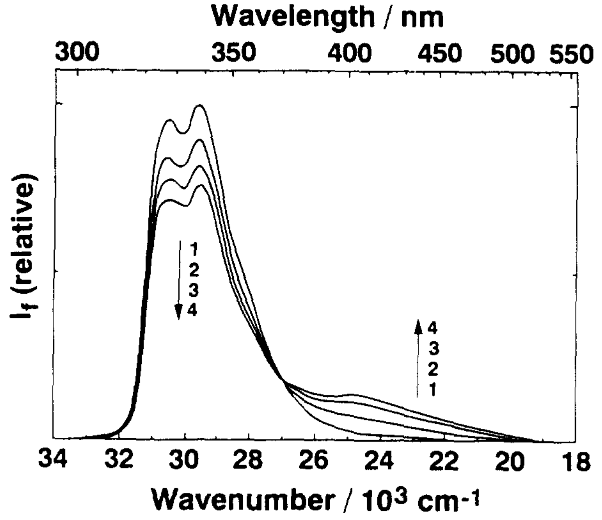

Fig. 2. Fluorescence spectra of 2CN (3.4×10^{-5} mol dm^{-3}) in aqueous solution containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 8.51×10^{-4}, (3) 2.55×10^{-3} and (4) 8.51×10^{-3} mol dm^{-3}. $\lambda_{ex} = 278$ nm.

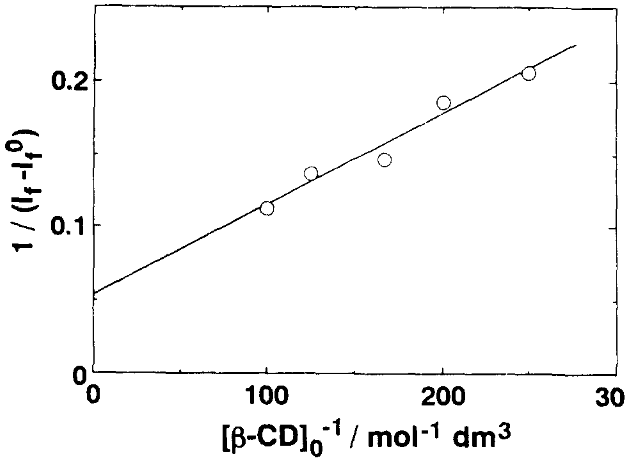

Fig. 3. Plot of $1/(I_f - I_f^0)$ against $1/[\beta\text{-CD}]_0$ for 2CN (4.6×10^{-6} mol dm^{-3}). $\lambda_{ob} = 330$ nm.

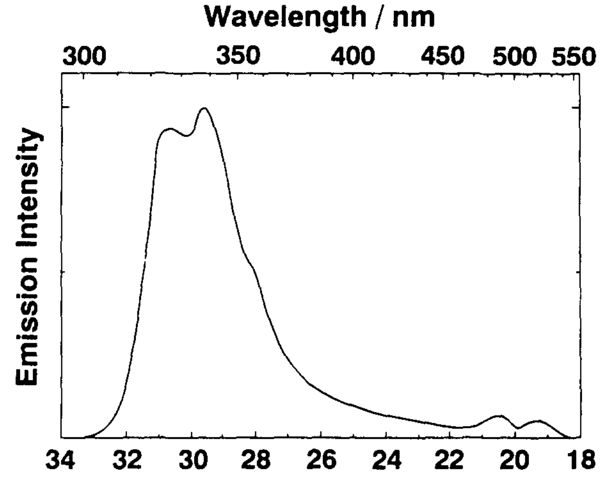

Fig. 4. Emission spectrum of 2CN (3.0×10^{-6} mol dm^{-3}) in deaerated aqueous solution containing β-CDI (1.0×10^{-3} mol dm^{-3}). $\lambda_{ex}=285$ nm.

CD concentration range, 2CN carrying a hydrophobic chlorine atom may be already encapsulated by β-CD to form a 1:1 inclusion complex. Consequently, there is the possibility that K(β-CD) obtained for 2CN can be assigned to the equilibrium constant for the formation of 2:1 β-CD–2CN from β-CD and a 1:1 inclusion complex because the β-CD concentrations in Fig. 3 are relatively high (4.0×10^{-3} to 1.0×10^{-2} mol dm^{-3}).

3.2. *Absorption and fluorescence spectra of 2CN in aqueous solutions containing β-CDI*

Although a weak absorption band of β-CDI is slightly superimposed on the 2CN absorption band, the absorption peak of 2CN at 276 nm is red shifted by the addition of β-CDI (not shown), indicating the formation of an inclusion complex between β-CDI and 2CN.

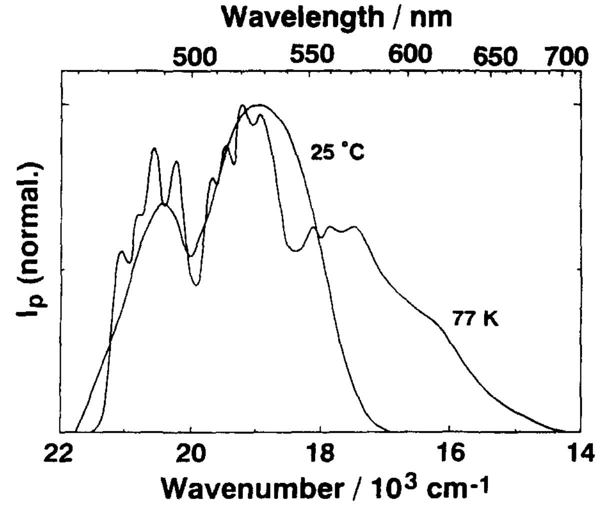

Fig. 5. Comparison of the longer wavelength emission of 2CN (3.0×10^{-6} mol dm^{-3}) in deaerated aqueous solution containing β-CDI (1.0×10^{-3} mol dm^{-3}) at 25 °C with the phosphorescence spectrum of 2CN (1.3×10^{-4} mol dm^{-3}) in methanol–ethanol (1:1) at 77 K. $\lambda_{ex}=285$ nm.

The addition of β-CDI to a 2CN aqueous solution results in the quenching of 2CN fluorescence, without a spectral shape change. Because of the low concentrations of 2CN (3.0×10^{-6} mol dm^{-3}) and β-CDI (less than 1.0×10^{-3} mol dm^{-3}), no excimer fluorescence is observed for the β-CDI–2CN system. From a plot of $1/(I_f-I_f^0)$ against $1/[\beta\text{-CDI}]_0$ in the β-CDI concentration range 2.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} (not shown), K(β-CDI) for 2CN is evaluated to be 1400 ± 300 mol^{-1} dm^3. A good linearity of the plot suggests the formation of a 1:1 β-CDI–2CN inclusion complex. The K(β-CDI) value is about 16-fold greater than K(β-CD) for 2CN, and about twofold greater than the K(β-CD) values (600–700 mol^{-1} dm^3) for naphthalene and naphthalene derivatives previously described. Since the iodine atom substituted on C-6 is relatively far from the cavity interior, it is unlikely to affect the inclusion behaviour of the β-CD moiety. Indeed, from an analysis based on the fluorescence quenching of 2-methoxynaphthalene by complexation with β-CDI, K(β-CDI) for 2-methoxynaphthalene was found to be 510 ± 100 mol^{-1} dm^3. This value is similar to K(β-CD) (630 mol^{-1} dm^3) for inclusion complexation between β-CD and 2-methoxynaphthalene [3]. So, the greater K(β-CDI) value for 2CN is due predominantly to the presence of the hydrophobic chlorine atom in the guest rather than the substituent iodine atom in the host β-CDI. Furthermore, the greater K(β-CDI) value indicates that K(β-CD) determined for 2CN cannot be assigned to the equilibrium constant for the formation of a 1:1 β-CD–2CN inclusion complex since, in the case of 2-methoxynaphthalene, K(β-CD) is similar to K(β-CDI).

3.3. *Room-temperature phosphorescence of 2CN incorporated into the β-CDI cavity*

When a 2CN (3.0×10^{-6} mol dm^{-3}) aqueous solution containing β-CDI (1.0×10^{-3} mol dm^{-3}) is deaerated, a new longer wavelength emission appears with maxima at approximately 490 and 530 nm (Fig. 4). Fig. 5 depicts a comparison between the new longer wavelength emission at 25 °C and the phosphorescence spectrum of 2CN in methanol–ethanol (1:1) at 77 K. From the similarity between the two spectra, the new emission can be assigned to the room-temperature phosphorescence of 2CN accommodated in the β-CDI cavity. Although the room-temperature phosphorescence is also observed for a solution with β-CD (1.0×10^{-2} mol dm^{-3}) (Fig. 6), the apparent room-temperature phosphorescence intensity (I_p) is reduced to 65% of that for β-CDI (1.0×10^{-3} mol dm^{-3}). To estimate the intrinsic I_p values, a correction must be made for the different concentrations of the inclusion complexes of β-CD and β-CDI. Under the assumption that the K(β-CD) value previously evaluated for 2CN is the equilibrium constant for the formation of a 1 : 1 inclusion complex, the intrinsic I_p values for β-CD and β-CDI can be calculated employing K(β-CD) and

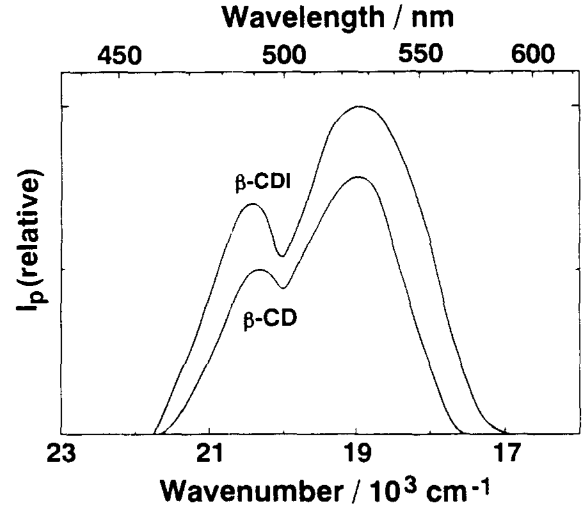

Fig. 6. Room-temperature phosphorescence spectra of 2CN (3.0×10^{-6} mol dm^{-3}) in aqueous solutions containing β-CDI (1.0×10^{-3} mol dm^{-3}) and β-CD (1.0×10^{-2} mol dm^{-3}). $\lambda_{ex}=285$ nm.

K(β-CDI). In this case, the ratio of the intrinsic I_p value for β-CDI to that for β-CD is evaluated to be 1.2. As stated previously, however, K(β-CD) for 2CN is unlikely to be the equilibrium constant for the formation of a 1:1 inclusion complex. Thus, assuming that K(β-CD) is the same as K(β-CDI), the intrinsic I_p(β-CDI)/I_p(β-CD) value is increased to 2.5. The larger intrinsic I_p(β-CDI) value compared with the intrinsic I_p(β-CD) value is due to the external heavy atom effect exerted by the iodine atom substituted on β-CD.

As previously indicated, β-CDI causes the emergence of the room-temperature phosphorescence and the fluorescence quenching of 2CN. Thus, using the apparent I_p(β-CDI) and I_f(β-CDI) values at a β-CDI concentration of 1.0×10^{-3} mol dm^{-3} and the apparent I_p(β-CD) and I_f(β-CD) values at a β-CD concentration of 1.0×10^{-2} mol dm^{-3}, the apparent ratio of I_p(β-CDI)/I_f(β-CDI) to I_p(β-CD)/I_f(β-CD) is estimated to be 3.2. At these β-CDI and β-CD concentrations, free and complexed 2CN coexist in aqueous solution. Consequently, the estimated value of 3.2 is not the intrinsic ratio value. As the concentrations of the inclusion complexes of β-CD and β-CDI are increased, I_p(β-CDI) and I_p(β-CD) are increased, whereas I_f(β-CDI) is decreased but I_f(β-CD) is expected to remain nearly constant or be slightly enhanced. As a result, the intrinsic value of I_p(β-CDI)I_f(β-CD)/I_f(β-CDI)I_p(β-CD) will be significantly greater than 3.2. Such a value exceeding unity provides additional evidence for the external heavy atom effect of β-CDI on a guest entering into the β-CDI cavity. Taking account of the I_p(β-CDI)I_f(β-CD)/I_f(β-CDI)I_p(β-CD) and I_p(β-CDI)/I_p(β-CD) values, the external heavy atom effect of β-CDI produces both intersystem crossing from the excited singlet state to the triplet state and radiative transition from the triplet state of 2CN. In addition, β-CDI may promote the radiationless transition from the triplet state to the ground state because the I_p(β-CDI) value is not much larger than I_p(β-CD).

4. Concluding remarks

In aqueous solutions, in addition to the formation of a 1:1 β-CD–2CN inclusion complex, β-CD forms a 2:2 inclusion complex with 2CN, which emits the excimer fluorescence of 2CN. It is found that β-CDI forms a 1:1 inclusion complex with 2CN. The equilibrium constant for the formation of the 1:1 β-CDI–2CN inclusion complex is estimated to be 1400 ± 300 mol^{-1} dm^3, which is about twofold greater than that for 2-substituted naphthalenes, such as 2-methoxynaphthalene, suggesting that a hydrophobic chlorine atom accelerates the complexation with β-CDI. β-CDI effectively quenches the fluorescence of 2CN located within the β-CDI cavity. In addition, the external heavy atom effect exerted by β-CDI promotes the triplet production of the guest, resulting in a slight enhancement of the room-temperature phosphorescence of the guest 2CN.

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