Room-temperature Phosphorescence of 6-Bromo-2-naphthol Included by α-Cyclodextrin in Aqueous Solution

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In aerated aqueous solutions, room-temperature phosphorescence of 6-bromo-2-naphthol is observed with an inclusion complex composed of one 6-bromo-2-naphthol (BN) and two α-cyclodextrin (α-CD) molecules, whereas a 1 : 1 α-CD–BN inclusion complex does not phosphoresce at room temperature.

Cyclodextrins (CDs) are cyclic oligosaccharides composed of 6, 7, and 8 glucopyranose units, α-, β-, and γ-CD, respectively, with hydrophobic cavities.[1,2] Guest molecules in the excited state are protected from quenching by iodide, for instance. Consequently, quenching rate constants for guests are reduced.[3,4] For ternary inclusion complexes that contain two different guests, a more profound protection effect toward a quencher is observed.[3,4]

Halogenated guests often exhibit room-temperature phosphorescence because of this protection.[5–7] For ternary inclusion complexes including both a halogenated guest (phosphorophore) and an additional guest having no heavy atom, room-temperature phosphorescence has been observed.[6,7] When ternary inclusion complexes contain a non-halogenated phosphorophore and a second guest having a heavy atom, the external heavy atom effect exerted by a second guest effectively generates the triplet state of the phosphorophore. The room-temperature phosphorescence can thus be observed.[8,9] Similarly, brominated CD efficiently produces the triplet state of a guest.[10] Only one CD molecule is associated with the phosphorophore in these instances, and only β- and γ-CDs (or their derivatives) are known to act in this way in solution.

We report the room-temperature phosphorescence of a 2 : 1 complex of α-CD and 6-bromo-2-naphthol.

Absorption spectra were recorded on a Shimadzu 260 spectrophotometer. Fluorescence and phosphorescence spectra were obtained with a Shimadzu RF-501 spectrofluorometer. Emission spectra were corrected for the spectral response of the spectrofluorometer. 6-Bromo-2-naphthol (Tokyo Kasei Kogyo, Ltd.) was twice recrystallized from benzene. α-CD (Nacalai Tesque, Inc.) was used as received. Concentrations of 6-bromo-2-naphthol were *ca.* 9×10^{-5} mol dm^{-3}. Measurements were made for aerated sample solutions at 25 °C.

Fig. 1 shows absorption spectra of 6-bromo-2-naphthol in aqueous solution in the absence and presence of α-CD. Because a pK_a value of 6-bromo-2-naphthol was found to be 9.2, 6-bromo-2-naphthol in aqueous solution is in neutral form. As the α-CD concentration is increased, absorption maxima at 323 and 337 nm are red-shifted with an enhancement of the absorption band intensity. In the low α-CD concentration range, isosbestic points at 287, 300, and 321 nm are observed. Over the α-CD concentration range examined, however, no isosbestic points appear, indicating that an inclusion complex other than a 1 : 1 α-CD–BN inclusion complex is also involved in the equilibria of the α-CD–BN system. Experimental data in absorbance did not fit a usual double reciprocal plot of 1/(Abs–Abs$_0$) against 1/[α-CD]$_0$, where Abs, Abs$_0$, and [α-CD]$_0$ are the absorbance of an aqueous 6-bromo-2-naphthol solution with α-CD, that without α-CD, and the initial α-CD concentration, respectively. This provides additional evidence for the existence of an inclusion complex other than a 1 : 1 α-CD–BN inclusion complex. Because the α-CD cavity is too less to accommodate a full part of 6-bromo-2-naphthol, it is most likely that an additional α-CD molecule tends to associate with the other end of 6-bromo-2-naphthol of which part is already accommodated into the α-CD cavity. Thus, we analysed the α-CD concentration effect on the absorbance of 6-bromo-2-naphthol under the assumption that in the α-CD–BN system there are two equilibria, eqns. (1) and (2),

$$\alpha\text{-CD} + \text{BN} \xrightleftharpoons{K_1} \alpha\text{-CD–BN} \qquad (1)$$

$$\alpha\text{-CD–BN} + \alpha\text{-CD} \xrightleftharpoons{K_2} (\alpha\text{-CD})_2\text{–BN} \qquad (2)$$

where K_1 and K_2 represent equilibrium constants for the formation of α-CD–BN and (α-CD)$_2$–BN, respectively. Under the conditions that the concentration of α-CD is significantly greater than that of 6-bromo-2-naphthol, the absorbance of 6-bromo-2-naphthol, A, is expressed as in eqn. (3),

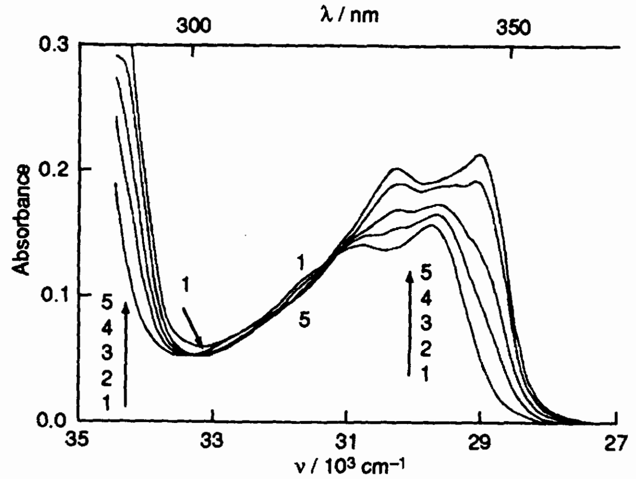

Fig. 1 Absorption spectra of 6-bromo-2-naphthol in aqueous solutions containing varying concentratons of α-CD. Concentration of α-CD: (1) 0, (2) 1.0×10^{-3}, (3) 2.0×10^{-3}, (4) 5.0×10^{-3}, and (5) 1.0×10^{-2} mol dm^{-3}.

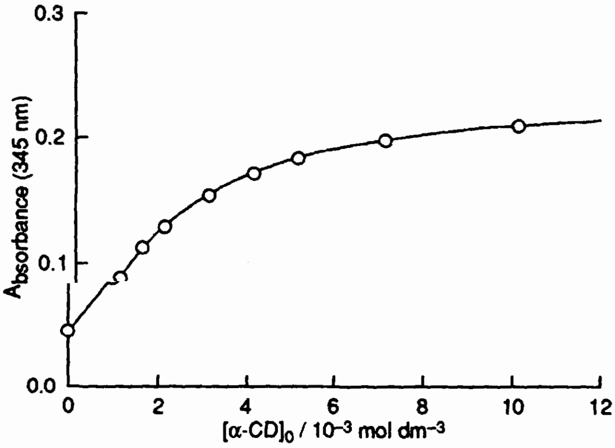

Fig. 2 α-CD concentration dependence of the absorbance at 345 nm. Circles represent experimental points. The best-fit curve was calculated with K_1 = 560 mol^{-1} dm^3, K_2 = 530 mol^{-1} dm^3, ε_1 = 930 mol^{-1} dm^3 cm^{-1}, and ε_2 = 2730 mol^{-1} dm^3 cm^{-1}.

$$A = \frac{[\mathrm{BN}]_0(\varepsilon_0 + \varepsilon_1 K_1[\alpha\text{-CD}]_0 + \varepsilon_2 K_1 K_2[\alpha\text{-CD}]_0{}^2)}{(1 + K_1[\alpha\text{-CD}]_0 + K_1 K_2[\alpha\text{-CD}]_0{}^2)} \quad (3)$$

where ε_0, ε_1, and ε_2 are molar absorption coefficients of free 6-bromo-2-naphthol, α-CD–BN, and (α-CD)$_2$–BN, respectively. Fig. 2 depicts the observed α-CD concentration dependence of the absorbance at 345 nm together with the best-fit curve that was calculated using a known ε_0 (345 nm) value (500 mol^{-1} dm^3 cm^{-1}) and assumed values K_1 = 560 mol^{-1} dm^3, K_2 = 530 mol^{-1} dm^3, ε_1 (345 nm) = 930 mol^{-1} dm^3 cm^{-1}, and ε_2 (345 nm) = 2730 mol^{-1} dm^3 cm^{-1}. The best-fit curve for the absorbance change excellently fits the experimental data, indicating that the second inclusion complex is assigned to (α-CD)$_2$–BN.

Fig. 3 illustrates emission spectra of 6-bromo-2-naphthol in aqueous solution containing varying concentrations of α-CD.

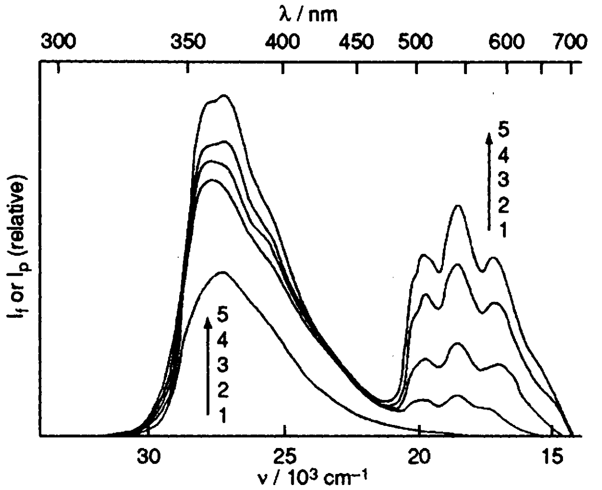

Fig 3 Corrected emission spectra of 6-bromo-2-naphthol in aqueous solutions containing varying concentrations of α-CD. Concentration of α-CD: (1) 0, (2) 1.0 × 10^{-3}, (3) 2.0 × 10^{-3}, (4) 5.0 × 10^{-3}, and (5) 1.0 × 10^{-2} mol dm^{-3}. λ_{ex} = 287 nm.

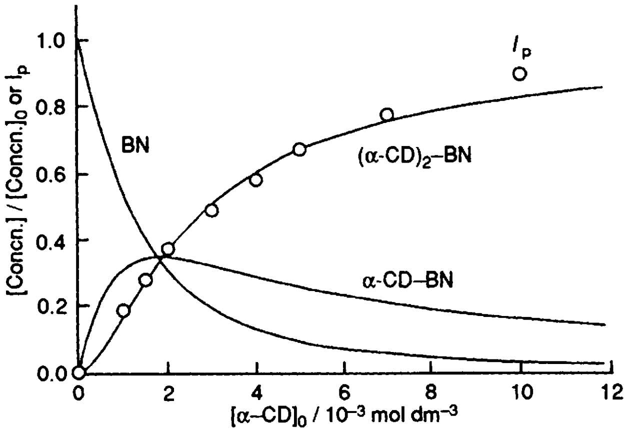

Fig. 4 α-CD concentration dependence of the observec room-temperature phosphorescence intensity at 535 nm (I_p), the coicentration of free BN, that of α-CD–BN, and that of (α-CD)$_2$–3N. The concentrations of these species were calculated using K_1 and K_2 determined in this study, and were normalized as [BN]$_0$ = 10.

In the absence of α-CD, the fluorescence of 6-bromo-2-naphthol is alone observed. Upon the addition of α-CD, the fluorescence intensity is increased accompanied by an appearance of vibrational structures. At the same time, a new emission band appears in the wavelength range from 480 to 700 nm, which can be assigned to the room-temperature phosphorescence of 6-bromo-2-naphthol from a similarity with the phosphorescence spectrum of 6-bromo-2-naphthol in methanol–ethanol (1:1) at 77 K. For 1-bromonaphthalene derivatives bearing an amino group, the pH-dependent phosphorescence has been reported.[11] In alkaline solutions containing α-CD, the room-temperature phosphorescence from 6-bromo-2-naphthol could not be detected. The triplet state of 6-bromo-2-naphthol, which is generated by the internal heavy atom effect and is guarded by bound α-CD, emits the room-temperature phosphorescence. To clarify which inclusion complex is a phosphorescent species, a comparison between the concentration of α-CD–BN or (α-CD)$_2$–BN and the room-temperature phosphorescence intensity was made. The concentrations of free BN, α-CD–BN, and (α-CD)$_2$–BN are respectively represented by eqns. (4)–(6).

$$[\mathrm{BN}] = \frac{[\mathrm{BN}]_0}{(1 + K_1[\alpha\text{-CD}]_0 + K_1 K_2[\alpha\text{-CD}]_0{}^2)} \quad (4)$$

$$[\alpha\text{-CD–BN}] = \frac{K_1[\mathrm{BN}]_0[\alpha\text{-CD}]_0}{(1 + K_1[\alpha\text{-CD}]_0 + K_1 K_2[\alpha\text{-CD}]_0{}^2)} \quad (5)$$

$$[(\alpha\text{-CD})_2\text{–BN}] = \frac{K_1 K_2[\mathrm{BN}]_0[\alpha\text{-CD}]_0{}^2}{(1 + K_1[\alpha\text{-CD}]_0 + K_1 K_2[\alpha\text{-CD}]_0{}^2)} \quad (6)$$

As a function of α-CD concentration, Fig. 4 shows the observed room-temperature phosphorescence intensities together with concentration curves simulated for free 6-bromo-2-naphthol, α-CD–BN, and (α-CD)$_2$–BN. These concentration curves were calculated using the K_1 and K_2 values which were previously evaluated from the α-CD concentration dependence of the absorbance. The excellent fit of the calculated (α-CD)$_2$–BN concentration curve to the observed intensity of the room-temperature phosphorescence at 535 nm provides evidence that 6-bromo-2-naphthol located within the 2:1 inclusion complex (α-CD)$_2$–BN emits room-temperature phosphorescence.

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