12t were observed in the region from ca. δ 6.8 to 2.3.

Sensitized Photolysis of Dimethylenebicyclobutane (3). A ca. 1 mM solution of diazene **2** in CH_2Cl_2 (which had been placed under vacuum) was irradiated with light from the Hg(Xe) arc lamp, directed through filter combination no. 1 (Table II), at −95 °C until no diazene remained, as indicated by UV spectroscopy. The vessel was then pressurized with nitrogen, and the solution was quickly cannulated through 30-gauge Teflon tubing with ca. 400 μL being delivered to each of eight N_2-purged sample tubes. To each tube had been added the requisite amount of sensitizer to make a ca. 0.04 M solution (due to its large ϵ and low solubility, enough methylene blue was used to make a ca. 0.01 M solution). The sensitizers used and their triplet energies, E_T, are listed in Table V. The samples were immediately placed in liquid N_2 and later evacuated and sealed with a flame. Each sample, in turn, was thawed carefully, submerged in a CO_2/Me_2CO bath, withdrawn briefly, and shaken to dissolve all or most of the sensitizer, irradiated at −78 °C for 1 min with filter combination no. 3 (Table II), and finally warmed to room temperature. The methylene blue sample was irradiated instead for 2 min with filter combination no. 6. The solutions were analyzed by GC, and the fraction of total dimers constituted by **13t** is reported in Table V for each sensitizer used. In addition, a small, unidentified peak at retention time 7.37 min (relative to those reported above) was observed in each of the last five samples (the peak was quite large in the benzil sample). Control experiments demonstrated that this species is produced upon sensitized photolysis of a mixture of **11** and **12t**. Control experiments also established that the source of the **13t** observed was neither diazene **2** nor the dimers (**11** and **12t**).

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Room-Temperature Phosphorescence from 1:1:1 Inclusion Compounds of β-Cyclodextrin with Brominated Alcohols and Acenaphthene

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Abstract: Acenaphthene (AN) has been found to form a 1:1:1 inclusion compound by complexing with a 1:1 inclusion compound of β-cyclodextrin (CDx) and alcohol. Of the primary alcohols examined, 1-propanol most easily associates with a 1:1 inclusion compound of CDx and AN. When brominated alcohol is included in the 1:1:1 inclusion compound, a room-temperature phosphorescence of AN is induced by a heavy-atom effect. From experiments on the AN phosphorescence quenching by $NaNO_2$, we have estimated a rate constant (k_3) for the association of AN with CDx, which already accommodates a 2-bromoethanol (BE) molecule, to be 1×10^{10} mol^{-1} dm^3 s^{-1} and a rate constant (k_4) for the dissociation of AN from the 1:1:1 inclusion compound including BE to be 8×10^4 s^{-1}. In the CDx–BE–AN system, k_3 is 2 orders of magnitude larger than the rate constant (k_1) for the association with free CDx into which BE is not incorporated, whereas k_4 is 1 order of magnitude smaller than the rate constant (k_2) for the dissociation from the 1:1 inclusion compound of CDx with AN. These findings indicate that a guest molecule (BE) inside the CDx cavity accelerates the association rate of AN with CDx and conversely decelerates the dissociation rate of AN from the 1:1:1 inclusion compound.

Room temperature phosphorescences of polynuclear aromatic hydrocarbons such as acenaphthene (AN), naphthalene, and pyrene are observed not only in micellar solutions containing Tl^+ as a heavy-atom perturber[1-4] but also in cyclodextrin solutions containing 1,2-dibromoethane.[4,5] As a phosphorescence-inducing mechanism in cyclodextrin solutions, Scypinsky and Cline Love have proposed the formation of a trimolecular complex among a luminophor, cyclodextrin, and 1,2-dibromoethane.[5] Using their technique with cyclodextrin, one can obtain reproducible, good-quality room-temperature phosphorescence spectra.

In a previous paper,[6] we have reported that a self-association occurs between two 1:1 inclusion compounds of β-cyclodextrin (CDx) with naphthalene. Subsequently, it has been found that a 1:1 inclusion compound of CDx with pyrene further associates with a primary or cyclic alcohol molecule to produce a 1:1:1 inclusion compound.[7] Because pyrene does not deeply enter the CDx cavity owing to the steric hindrance, the additional alcohol molecule can be incorporated into the void interior of the cavity which already accommodates pyrene. Since AN as well as pyrene is relatively bulky for the CDx cavity, it is expected that AN is shallowly bound to the CDx cavity and then complexes with an additional alcohol molecule to form a 1:1:1 inclusion compound. Thus, we studied the behavior of the inclusion compounds of AN. Since we found that brominated alcohol induces the room temperature phosphorescence of AN, we tried to determine a rate constant for the association of AN with a 1:1 inclusion compound of CDx–2-bromoethanol and a rate constant for the dissociation of AN from the 1:1:1 inclusion compound of CDx–2-bromoethanol–AN.

Experimental Section

Acenaphthene purchased from Tokyo Kasei and β-cyclodextrin from Nakarai were recrystallized three times from ethanol and water, respectively. Primary alcohols from methanol to 1-hexanol were purified by distillation under atmospheric or reduced pressure. 2-Bromoethanol (BE) and 2,3-dibromo-1-propanol were distilled under reduced pressure. Aqueous solutions of AN were prepared by using the same method as that for pyrene aqueous solutions.[7] Concentrations of AN were about 1.5×10^{-5} mol dm^{-3}. Aerated sample solutions were used except for measurements of the room-temperature phosphorescence, for which so-

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(1) Kalyanasundaram, K.; Grieser, F.; Thomas, J. K. *Chem. Phys. Lett.* **1977**, *51*, 501.

(2) Skrilec, M.; Cline Love, L. J. *Anal. Chem.* **1980**, *52*, 1559.

(3) Cline Love, L. J.; Habarta, J. G.; Dorsey, J. G. *Anal. Chem.* **1984**, *56*, 1132A.

(4) Cline Love, L. J.; Weinberger, R. *Spectrochim. Acta, Part B*, **1983**, *38*, 1421.

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

(6) Hamai, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2721.

(7) Hamai, S. *J. Phys. Chem.* **1989**, *93*, 2074.

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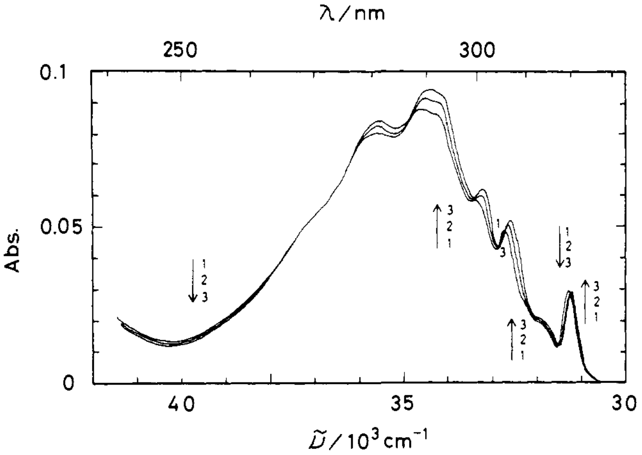

Figure 1. Absorption spectra of AN aqueous solutions containing varying amounts of CDx: (1) 0 mol dm^{-3} CDx; (2) 4.2 × 10^{-3} mol dm^{-3} CDx; (3) 8.4 × 10^{-3} mol dm^{-3} CDx.

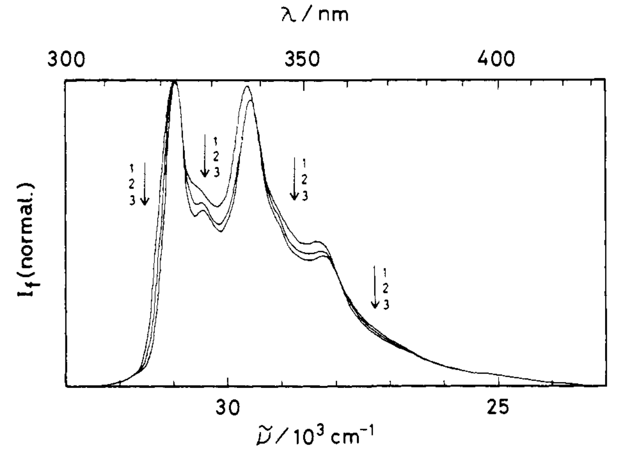

Figure 2. Normalized fluorescence spectra of AN: (1) in aqueous solution; (2) in aqueous solution containing 8.4 × 10^{-3} mol dm^{-3} CDx; (3) in aqueous solution containing both CDx (8.4 × 10^{-3} mol dm^{-3}) and 1-propanol (1.34 × 10^{-3} mol dm^{-3}). λ_{ex} = 287 nm.

lutions were degassed by repeated freeze–pump–thaw cycles. Absorption spectra were obtained with a Shimadzu UV-260 spectrophotometer by using a procedure in which a spectral data accumulation was repeated 10 times. Fluorescence and phosphorescence spectra were taken on a Shimadzu RF-501 spectrofluorometer. Phosphorescence lifetimes were obtained from photographed oscilloscope traces. Emission spectra were corrected for the wavelength-dependent sensitivity of the fluorometer. Unless otherwise stated, spectroscopic measurements were made at 25 ± 0.1 °C.

Results and Discussion

1:1 Inclusion Compound of CDx with AN. Figure 1 shows the absorption spectra of aqueous AN solutions with varying amounts of CDx. As the CDx concentration is increased, absorption maxima are red-shifted. Isosbestic points appearing at 304, 306, 317, and 320 nm indicate the formation of a 1:1 inclusion compound (AC) of AN with CDx:

$$\mathrm{AN} + \mathrm{CDx} \overset{K_1}{\rightleftharpoons} \mathrm{AC} \tag{1}$$

where K_1 is an equilibrium constant for the formation of AC. The fluorescence spectrum of an AN aqueous solution containing CDx is displayed in Figure 2. On adding CDx, the fluorescence peaks are slightly shifted to longer wavelengths. From the intensity change in the AN fluorescence,[6] K_1 was determined to be 76 ± 5 mol^{-1} dm^3. This value is much smaller than that of naphthalene (685 mol^{-1} dm^3),[6] indicating that AN does not fit as snugly into the CDx cavity as naphthalene.

1:1:1 Inclusion Compounds of CDx–Nonbrominated Alcohols–AN. When 1-propanol (1.34 × 10^{-3} mol dm^{-3}) is added to an AN solution with CDx (8.4 × 10^{-3} mol dm^{-3}), the AN absorption peak intensities are decreased by 5–15%, accompanied by very slight but perceivable red-shifts (~0.5 nm) of the absorption peaks.[8] No absorption spectral change is observed upon addition of 1-propanol to an AN solution without CDx. Consequently, the spectral change is attributable to an inclusion compound composed of CDx, AN, and 1-propanol. At 5 °C, a continuous-variation method[7] could be applied to identify the nature of the inclusion compound.[9] From the result that a 1:1 stoichiometry regarding CDx and 1-propanol was obtained for the inclusion compound and an analogy with the CDx–alcohol–pyrene systems,[7] we assigned the inclusion compound to a 1:1:1 inclusion compound of CDx with AN and 1-propanol. This assignment is consistent with Kano et al.'s suggestion that a 1:1:1 inclusion compound is formed in the system of CDx–trimethylamine–AN[10] and Scypinsky and Cline Love's suggestion that a trimolecular complex is formed among CDx, 1,2-dibromoethane, and aromatic hydrocarbons.[5] Such ternary complexes have also been reported for the systems of CDx–aliphatic amine–pyrene,[11] CDx–aniline–pyrene,[12] etc.[13] The formation of the 1:1:1 inclusion compound (APC) of AN–1-propanol–CDx is shown by the following equilibria:

Table I. Equilibrium Constants for the Complexation in the CDx–Alcohol–AN Systems

alcohol	K_2/mol^{-1} dm^3	K_3/mol^{-1} dm^3	K_4/mol^{-1} dm^3
methanol	0.32[a]	3.8 ± 0.2	900 ± 90
ethanol	0.93[a]	100 ± 10	8600 ± 800
1-propanol	3.72[a]	1600 ± 100	32000 ± 3000
1-butanol	16.6[a]	3100 ± 200	14000 ± 1000
1-pentanol	63.1[a]	5800 ± 300	7000 ± 700
1-hexanol	219[a]	17000 ± 1000	5900 ± 500
2-bromoethanol	3.2 ± 0.3	1200 ± 100[b]	29000 ± 6000[b]
		530 ± 80[c]	13000 ± 4000[c]
2,3-dibromo-1-propanol	49 ± 4	17000 ± 1000[b]	27000 ± 5000[b]
		40000 ± 6000[c]	31000 ± 9000[c]

[a] Data of Matsui and Mochida (ref 14). [b] Evaluated from the fluorescence quenching of AN. [c] Evaluated from the intensity change in the room-temperature phosphorescence from the 1:1:1 inclusion compound.

$$\mathrm{Pr} + \mathrm{CDx} \overset{K_2}{\rightleftharpoons} \mathrm{PC} \tag{2}$$

$$\mathrm{AC} + \mathrm{Pr} \overset{K_3}{\rightleftharpoons} \mathrm{APC} \tag{3}$$

$$\mathrm{PC} + \mathrm{AN} \overset{K_4}{\rightleftharpoons} \mathrm{APC} \tag{4}$$

where PC is a 1:1 inclusion compound of 1-propanol (Pr) with CDx, and K_2, K_3, and K_4 are equilibrium constants for the formation of PC, APC from AC and Pr, and APC from PC and AN, respectively. In Figure 2, the fluorescence spectrum of a CDx solution of AN in the presence of 1-propanol is also exhibited. The fluorescence spectral change can also be ascribed to the formation of APC.

Although a shallow incorporation into the CDx cavity occurs for both pyrene and AN, the dimension of the void interior of the cavity may be different between a 1:1 inclusion compound of pyrene and that of AN. Consequently, there is a possibility that the best fitting alkyl-chain length of an alcohol for the empty space of the cavity in the CDx–AN 1:1 inclusion compound differs from that in the CDx–pyrene 1:1 inclusion compound. In order to

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[8] Error limits for peak shift in the absorption spectra are estimated to be about ±0.2 nm.

[9] When 1-propanol was added to a CDx solution of AN at 5 °C, an absorption spectral change similar to that at 25 °C was observed. Consequently, at 5 °C, the continuous-variation method in which the intensity of the fluorescence excited at 304 nm was plotted against the molar fraction of CDx was employed under the conditions that the sum of the initial concentrations of CDx and 1-propanol was fixed at 5 × 10^{-3} mol dm^{-3}.

[10] Kano, K.; Hashimoto, S.; Imai, A.; Ogawa, T. *J. Inclusion Phenom.* **1984**, *2*, 737.

[11] Kano, K.; Takenoshita, I.; Ogawa, T. *J. Phys. Chem.* **1982**, *86*, 1833.

[12] Hamai, S. *J. Phys. Chem.* **1988**, *92*, 6140.

[13] Ueno, A.; Takahashi, K.; Hino, Y.; Osa, T. *J. Chem. Soc., Chem. Commun.* **1981**, 194. Kobashi, H.; Takahashi, M.; Muramatsu, Y.; Morita, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2815. Hashimoto, S.; Thomas, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 4655.

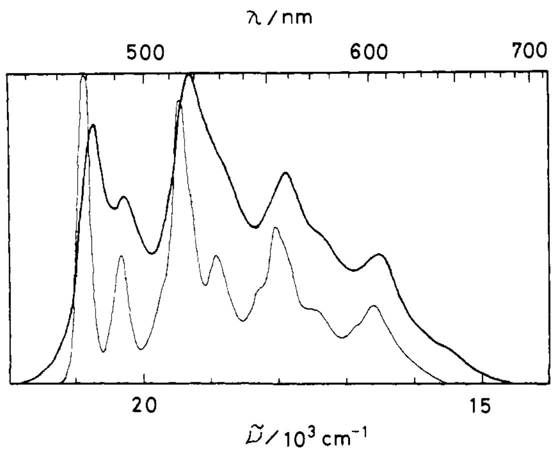

Figure 3. Room-temperature phosphorescence spectrum (–) of an aqueous AN solution containing CDx (8.4×10^{-3} mol dm^{-3}) and BE (1.41×10^{-3} mol dm^{-3}) and the phosphorescence spectrum (–) of AN in methanol–ethanol (1:1) at 77 K. The two spectra are normalized at each maximum wavelength. λ_{ex} = 287 nm.

estimate K_3 values for primary alcohols from methanol to 1-hexanol, we employed the same method as that used for the CDx–alcohol–pyrene systems:[7] comparisons have been made between the observed fluorescence intensities, which are a function of the alcohol concentration, and the intensity curves calculated by assuming parameter values which give K_3. From a $K_1K_3 = K_2K_4$ relationship, corresponding K_4 values were also evaluated. These K_3 and K_4 thus obtained are listed in Table I. The K_3 value, like a value in the K_2 series, which have been obtained by Matsui and Mochida,[14] monotonously increases with an increase in the alkyl-chain length of the alcohol, indicating that a longer alcohol molecule more easily enters the cavity which already accommodates AN. The K_3 value is always 1–2 orders of magnitude larger than the corresponding K_2 value. The K_4 value increases from that for methanol, goes through a maximum at 1-propanol, and then decreases to that for 1-hexanol.[15] The molecular dimension of 1-propanol provides the best fit into the void space of the CDx cavity which is partially occupied by AN. Contrary to our above mentioned expectation, these results are quite similar to those previously obtained for the CDx–alcohol–pyrene systems,[7] indicating that the unoccupied interior dimensions of the cavities which are partly occupied by pyrene and AN are nearly the same.

1:1:1 Inclusion Compounds of CDx–Brominated Alcohols–AN. When 2-bromoethanol (BE) is added to a CDx aqueous solution of AN, the formation of the 1:1:1 inclusion compound is confirmed from an absorption spectral change analogous to those for the nonbrominated primary alcohols already examined. For BE, K_2 was determined to be 3.2 ± 0.3 mol^{-1} dm^3.[16,17] The K_2 value is about 3 times larger than that of ethanol (0.93 mol^{-1} dm^3),[14] indicating the considerably stronger hydrophobicity of BE over ethanol. In contrast to the 1:1:1 inclusion compounds containing nonbrominated alcohol, an efficient quenching of the AN fluorescence takes place with the 1:1:1 inclusion compound containing BE. From the fluorescence quenching,[6] a K_3 value of 1200 ± 100 mol^{-1} dm^3 has been evaluated.[18] A relationship among the equilibrium constants yields K_4 = 29000 ± 6000 mol^{-1} dm^3.[19] These K_3 and K_4 values are close to those for 1-propanol rather than ethanol. In Table I, K_2, K_3, and K_4 for 2,3-dibromo-1-propanol are also summarized. As in the case of BE, hydrophobic substituents (bromine atoms) appear to cause these equilibrium constants to be much larger than those for 1-propanol except for K_4, which is almost the same as that of 1-propanol.

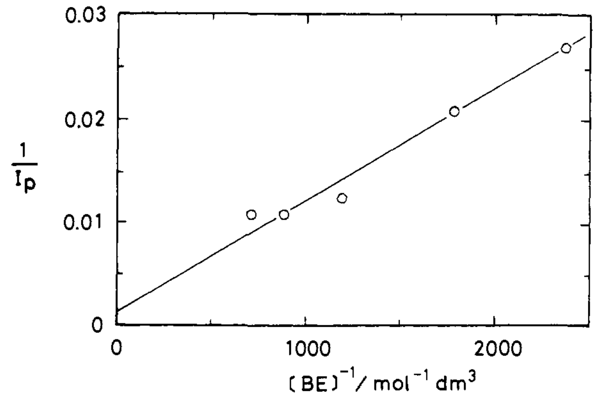

Figure 4. Plot of $1/I_p$ against $1/[\mathrm{BE}]_0$.

Room-Temperature Phosphorescence from the 1:1:1 Inclusion Compounds Including Brominated Alcohols. Upon deaeration of an AN solution containing both CDx (8.4×10^{-3} mol dm^{-3}) and BE (1.41×10^{-3} mol dm^{-3}), a new emission appears at longer wavelength regions than the fluorescence (Figure 3). For the AN solution, the intensity of the new emission is nearly a factor of 6 weaker than that of the AN fluorescence. Figure 3 also depicts the normalized AN phosphorescence in methanol–ethanol (1:1) at 77 K.[20] In view of a close resemblance between the two spectra, the longer wavelength emission can be assigned to the room-temperature phosphorescence of AN. In the absence of BE, a very weak phosphorescence was observed with an intensity less than 2% of that in the presence of BE (1.41×10^{-3} mol dm^{-3}). Therefore, the room temperature phosphorescence occurs predominantly from the 1:1:1 inclusion compound including BE. Since the AN phosphorescence intensity (I_p) is proportional to the 1:1:1 inclusion compound concentration, I_p is represented as a function of the initial concentration of BE ($[\mathrm{BE}]_0$):

$$1/I_p = b(1 + K_1[\mathrm{CDx}]_0)/K_1K_3[\mathrm{CDx}]_0[\mathrm{AN}]_0[\mathrm{BE}]_0 + b/[\mathrm{AN}]_0 \quad (5)$$

where b is a constant. Figure 4 shows a plot of $1/I_p$ against $1/[\mathrm{BE}]_0$, from which a K_3 value has been evaluated to be 530 ± 80 mol^{-1} dm^3.[21] Next, K_4 = 13000 ± 4000 mol^{-1} dm^3 was obtained from a relationship among the equilibrium constants.[19] These K_3 and K_4 values, which have been determined from the room-temperature phosphorescence intensity, are about half of the values obtained from the quenching of the AN fluorescence, respectively. Since the phosphorescence is much weaker than the fluorescence, the K_3 and K_4 values evaluated from the fluorescence quenching seems to be much more reliable compared with those from the phosphorescence intensities. For 2,3-dibromo-1-propanol, K_3 and K_4 have similarly been evaluated and are also given in Table I. In this case, an excellent agreement was seen between the K_4 values which have been estimated from the two different methods, whereas K_3 estimated from the phosphorescence intensity change is approximately twice that obtained from the fluorescence quenching.

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(14) Matsui, Y.; Mochida, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2808.

(15) On the left-hand side of eq 4 associating with K_4, the dimension of the unoccupied space of the CDx cavity which accommodates alcohol varies according to the alkyl-chain length of the alcohol, while, on the left-hand side of eq 3 associating with K_3, the dimension of the unoccupied space of the cavity, which always accommodates AN, is constant. On the other hand, in eq 2 associating with K_2, an alcohol molecule enters the empty cavity whose dimension is constant. In the cases of eq 2 (K_2) and eq 3 (K_3), therefore, the CDx cavity is expected to behave similarly to a variation of the alkyl-chain length of the alcohol when the complexation occurs, although there is a difference such that the cavity is empty or partially occupied. Since K_2 increases with an increase in the alkyl-chain length of the alcohol, it seems to be reasonable that K_3 increases when going from methanol to 1-hexanol. In contrast to K_3, K_3/K_2, which represents the extent to which an alcohol molecule is incorporated into the cavity including AN, exhibits a maximum for 1-propanol.

(16) K_2 was evaluated according to a competition method of Matsui and Mochida (ref 14), in which disodium 1-[(4-nitrophenyl)azo]-2-naphthol-3,6-disulfonate was used as an indicator dye.

(17) The error comes from the uncertainty in the absorbance.

(18) The error comes mainly from the uncertainty in the fluorescence intensity.

(19) The error comes from the uncertainties in K_1, K_2, and K_3.

(20) The low-temperature phosphorescence is much stronger than the room-temperature phosphorescence.

(21) The error comes mainly from the uncertainty in the phosphorescence intensity.

Scheme I[a]

$$\mathrm{AN^* + CDx} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{AC^*}$$

$$\mathrm{AN^* + BC} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{ABC^*}$$

$$\mathrm{AC^* + BE} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \mathrm{ABC^*}$$

$$\mathrm{ABC^*} \xrightarrow{k_\mathrm{p}} \mathrm{ABC} + h\nu_\mathrm{p}$$

$$\mathrm{AN^*} \xrightarrow{k_\mathrm{d}} \mathrm{AN}$$

$$\mathrm{AC^*} \xrightarrow{k_\mathrm{d}'} \mathrm{AC}$$

$$\mathrm{ABC^*} \xrightarrow{k_\mathrm{d}''} \mathrm{ABC}$$

$$\mathrm{AN^* + Q} \xrightarrow{k_\mathrm{q}} \mathrm{AN + Q}$$

$$\mathrm{AC^* + Q} \xrightarrow{k_\mathrm{q}'} \mathrm{AC + Q}$$

$$\mathrm{ABC^* + Q} \xrightarrow{k_\mathrm{q}''} \mathrm{ABC + Q}$$

[a] An asterisk refers to the triplet state of AN.

The phosphorescence decay of AN in the 1:1:1 inclusion compound including BE was observed to be single-exponential. For an AN solution with both CDx (8.4×10^{-3} mol dm^{-3}) and BE (1.41×10^{-3} mol dm^{-3}), a phosphorescence lifetime (τ_p) has been evaluated to be 0.37 s, while at 77 K, $\tau_\mathrm{p} = 2.9$ s has been determined for AN in methanol–ethanol (1:1). The τ_p obtained for the 1:1:1 inclusion compound in a solution containing 2,3-dibromo-1-propanol (9.75×10^{-5} mol dm^{-3}) was 0.17 s.

Under the conditions of $[\mathrm{CDx}]_0 = 8.4 \times 10^{-3}$ mol dm^{-3} and $[\mathrm{BE}]_0 = 1.41 \times 10^{-3}$ mol dm^{-3}, an experiment on the quenching of the AN phosphorescence by NaNO$_2$ (Q) was performed. On the basis of Scheme I, the kinetic equations are the following:

$$-\mathrm{d}[\mathrm{AN}^*]/\mathrm{d}t = -k_4[\mathrm{ABC}^*] - k_2[\mathrm{AC}^*] + k_3[\mathrm{BC}] + k_\mathrm{d} + k_\mathrm{q}[\mathrm{Q}] + k_1[\mathrm{CDx}]_0 \tag{6}$$

$$-\mathrm{d}[\mathrm{AC}^*]/\mathrm{d}t = -k_6[\mathrm{ABC}^*] - k_1[\mathrm{AN}^*][\mathrm{CDx}]_0 + (k_5[\mathrm{BE}] + k_\mathrm{d}' + k_\mathrm{q}'[\mathrm{Q}] + k_2)[\mathrm{AC}^*] \tag{7}$$

$$-\mathrm{d}[\mathrm{ABC}^*]/\mathrm{d}t = -k_3[\mathrm{AN}^*][\mathrm{BC}] - k_5[\mathrm{AC}^*][\mathrm{BE}] + (k_4 + k_6 + k_\mathrm{p} + k_\mathrm{d}'' + k_\mathrm{q}''[\mathrm{Q}])[\mathrm{ABC}^*] \tag{8}$$

where ABC is a 1:1:1 inclusion compound including BE, and BC is a 1:1 inclusion compound of CDx with BE. Assuming steady-state conditions, $-\mathrm{d}[\mathrm{AN}^*]/\mathrm{d}t = 0$ and $-\mathrm{d}[\mathrm{AC}^*]/\mathrm{d}t = 0$, one can obtain equations for [AN*] and [AC*]:

$$[\mathrm{AN}^*] = (k_4[\mathrm{ABC}^*] + k_2[\mathrm{AC}^*])/(k_3[\mathrm{BC}] + k_\mathrm{d} + k_\mathrm{q}[\mathrm{Q}] + k_1[\mathrm{CDx}]_0) \tag{9}$$

$$[\mathrm{AC}^*] = (k_6[\mathrm{ABC}^*] + k_1[\mathrm{AN}^*][\mathrm{CDx}]_0)/(k_5[\mathrm{BE}] + k_\mathrm{d}' + k_\mathrm{q}'[\mathrm{Q}] + k_2) \tag{10}$$

Because observed phosphorescence decay curves were single-exponential even in the presence of a quencher, the right-hand side of eq 8 has to be proportional to [ABC*]. This requires that the right-hand side of eq 9 and 10 should be proportional to [ABC*]. Thus, we neglected $k_2[\mathrm{AC}^*]$ versus $k_4[\mathrm{ABC}^*]$ in eq 9. Since, in general, an excited guest molecule within the CDx cavity is protected from a quencher by CDx, the two terms $k_\mathrm{q}'[\mathrm{Q}]$ and $k_\mathrm{q}''[\mathrm{Q}]$ are also ignored in eq 7 and 8. As a consequence, the following relationship is derived:

$$1/\tau_\mathrm{p} = A - B/([\mathrm{Q}] + C) \tag{11}$$

where

$$A = k_4 + k_6 + k_\mathrm{p} + k_\mathrm{d}'' - k_5k_6[\mathrm{BE}]/(k_5[\mathrm{BE}] + k_\mathrm{d}' + k_2)$$

$$B = (k_3k_4[\mathrm{BC}](k_5[\mathrm{BE}] + k_\mathrm{d}' + k_2) + k_1k_4k_5[\mathrm{BE}][\mathrm{CDx}]_0)/k_\mathrm{q}(k_5[\mathrm{BE}] + k_\mathrm{d}' + k_2)$$

$$C = (k_3[\mathrm{BC}] + k_\mathrm{d} + k_1[\mathrm{CDx}]_0)/k_\mathrm{q}$$

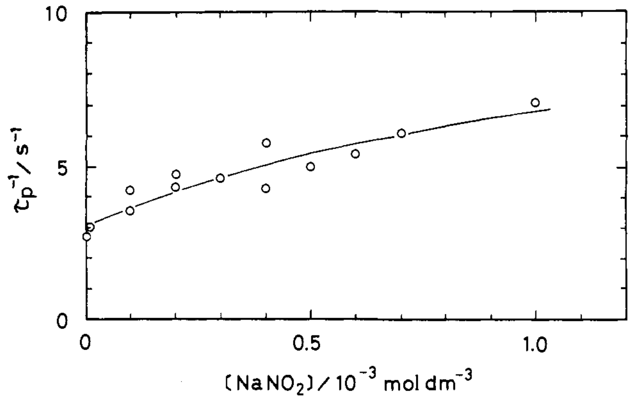

Figure 5. Plot of $1/\tau_\mathrm{p}$ against [NaNO$_2$]. $[\mathrm{CDx}]_0 = 8.4 \times 10^{-3}$ mol dm^{-3}. $[\mathrm{BE}]_0 = 1.41 \times 10^{-3}$ mol dm^{-3}.

A plot of $1/\tau_\mathrm{p}$ versus [Q] is shown in Figure 5, along with a best fit curve which has been calculated with the assumed values $A = 12.2$ s^{-1}, $B = 0.0132$ mol dm^{-3} s^{-1}, and $C = 0.00145$ mol dm^{-3}. Because rate constants for the 1-bromonaphthalene triplet quenching by NaNO$_2$ are reported to be 3.8×10^9 mol^{-1} dm^3 s^{-1} at 28 °C[22] and 5.1×10^9 mol^{-1} dm^3 s^{-1} at room temperature,[23] k_q for AN is assumed to be 3×10^9 mol^{-1} dm^3 s^{-1}. Parker and Joyce have determined the triplet lifetime of AN in ethanol to be 2.39×10^{-3} s.[24] As k_d for AN, a value of 42 ($1/2.39 \times 10^{-3}$) s^{-1} is taken. For 1-bromonaphthalene, Turro et al. have estimated a rate constant for the association with CDx to be $(1 \pm 0.5) \times 10^8$ mol^{-1} dm^3 s^{-1}.[22] For AN, k_1 (rate constant for the association with CDx) is assumed to be 1×10^8 mol^{-1} dm^3 s^{-1}. Thus, if we use these assumed k_q, k_d, and k_1 values and the C value which has been evaluated by the simulation method, $k_3 = 1 \times 10^{10}$ mol^{-1} dm^3 s^{-1} is obtained for AN. It should be noted that k_3 is 2 orders of magnitude larger than k_1. This finding that the rate for the association of AN with CDx is enhanced by an incorporation of BE into the CDx cavity is consistent with Turro et al.'s result that acetonitrile, which presumably complexes with a CDx–1-bromonaphthalene 1:1 inclusion compound, accelerates the rate for the association of 1-bromonaphthalene with CDx.[22] Since a relationship of $k_3/k_4 = K_4$ seems to hold even in the triplet state of AN, a k_4 value of 4×10^5 s^{-1} can be estimated. In contrast to the association with CDx, k_4 (rate constant for the dissociation from the 1:1:1 inclusion compound) is 1 order of magnitude smaller than k_2 (1×10^6 s^{-1}), which is estimated from the assumed k_1 value and the K_1 value determined, indicating that the rate for the dissociation of AN from CDx is retarded by the formation of the 1:1:1 inclusion compound. As suggested for the CDx–1-bromonaphthalene–acetonitrile system,[22] the increase in the association rate constant and the decrease in the dissociation rate constant enhance the equilibrium constant for the complexation between AN and CDx into which the other kind of a guest molecule is already incorporated.

Exit-rate constants of naphthalene and 1-methylnaphthalene from the sodium dodecylsulfate micelle are 2.5×10^5 and 1×10^5 s^{-1}, respectively,[3,23] and these values are comparable with k_4 (rate constant for the dissociation from the 1:1:1 inclusion compound) for AN. In addition, an entrance-rate constant (7×10^9 mol^{-1} s^{-1})[3,23] for the micelle is nearly the same as k_3 (rate constant for the association with the 1:1 inclusion compound) for AN. It should be emphasized that these similarities in the rate constants are observed in two different organized media in which the room-temperature phosphorescence occurs.

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[22] Turro, N. J.; Bolt, J. D.; Kuroda, Y.; Tabushi, I. *Photochem. Photobiol.* **1982**, *35*, 69.

[23] Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279.

[24] Parker, C. A.; Joyce, T. A. *Trans. Faraday Soc.* **1966**, *62*, 2785.