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EXCIMER FORMATION IN THE CAVITY OF γ-CYCLODEXTRIN APPENDED BY A NAPHTHALENE MOIETY

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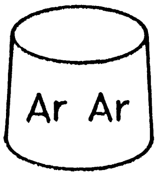
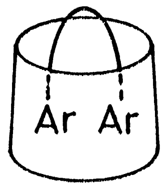
γ-Cyclodextrin appended by a naphthalene moiety forms an excimer with naphthalene in its cavity. The addition of l-borneol causes a decrease in the excimer emission as a result of replacement of the included naphthalene by l-borneol.

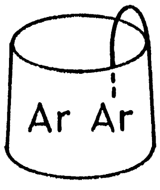
Cyclodextrins are a series of toroidal oligosaccharides and bind good-sized organic molecules in the central cavity.1) Although the cavity size of γ-cyclodextrin (γ-CD) is too large to form 1:1 complexes with usual organic molecules, γ-CD has excited much attention2-4) since we reported its ability to bind two guest molecules.2a) The promoted excimer formation between two aromatic molecules in the presence of γ-CD is direct evidence for two-guest inclusion of γ-CD, and so far the systems, in which two aryl units are free with each other (A)2) or linked at both ends of a chain (B),3) have been studied. The present communication deals with another excimer-formation system of γ-CD (C), in which a naphthalene moiety is covalently attached to γ-CD and forms excimer with guest naphthalene in the γ-CD cavity. With this system, the new ability of γ-CD to include a small molecule has been demonstrated.



A



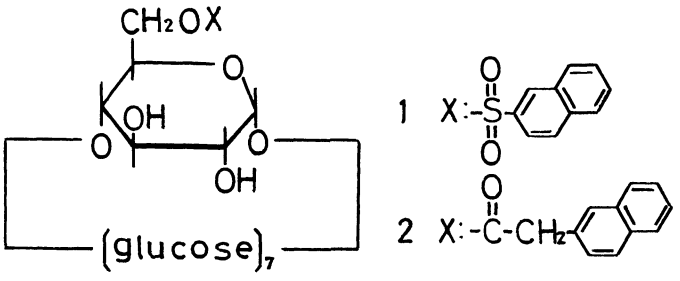
B



C

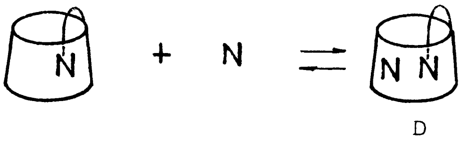
Ar: Aryl moiety

Compound 1 was prepared by reaction of γ-CD with one equiv. of β-naphthalenesulfonyl chloride in pyridine at room temperature for 5 h. After the usual workup, reprecipitation from water with acetone afforded crude product (34% yield). This was further purified by Sephadex chromatography to furnish pure 1.5) Compound 2 was prepared by replacement reaction of 1 with one equiv. of sodium β-naphthylacetate in DMSO at 80 °C for 5 h. Then the mixture was poured into a large amount of acetone. The formed precipitate was subjected to Sephadex chromatography, affording pure 2 (27% yield).6) These compounds were proved to be modified at a primary hydroxyl group by the ^{13}C NMR method established by Ueno and Breslow.7)



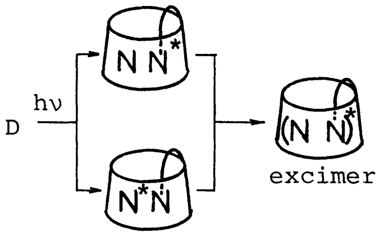
Fluorescence measurements were carried out at 25 °C using 290 nm as an excitation wavelength without eliminating oxygen from the aqueous sample solutions. Naphthalene and l-borneol were added as 0.1 M and 0.5 M (M= mol dm^{-3}) methanol solutions, respectively, and in any case the volume of methanol was below 0.5% of the sample solutions.

The fluorescence spectra of water solutions of 2 (1.5 x 10^{-4} M) at various naphthalene concentrations are shown in Fig. 1. Under this condition, the effect of naphthalene is slight around 335 nm of the normal fluorescence whereas it is remarkable at longer wavelengths with enhanced excimer emission. The small variations around 335 nm suggest that the presumed decrease in the normal fluorescence of 2, which should be caused by excimer formation, is compensated by the fluorescence from the added naphthalene. Since no excimer emission was observed when 2 was replaced by native γ-CD or sodium β-naphthylacetate, the result reveals that the 1:1 complex of 2 and the naphthalene guest (D in equation (1)) is solely responsible for the excimer emission.



(1)

N: Naphthalene unit



(2)

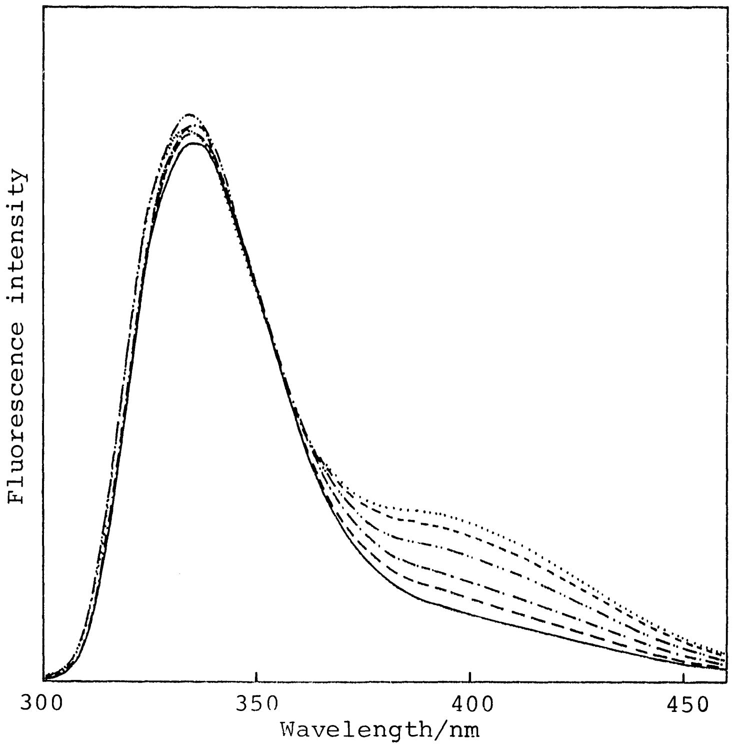
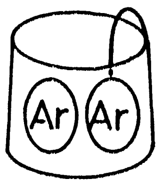


Fig. 1. Fluorescence spectra of 2 (1.5 x 10^{-4} M), alone (———) and in the presence of naphthalene (— — — , 0.33 x 10^{-4} M; —·— , 0.67 x 10^{-4} M; —··— , 1.33 x 10^{-4} M; ---- , 2.33 x 10^{-4} M; ······ , 2.99 x 10^{-4} M).

With regard to the system of pyrene and γ-CD, Yorozu et al. recently reported that the excimer emission is originated only from the pair of pyrene molecules included in the γ-CD cavity.[2e)] This confirms the static excimer formation in the present system since the excimer should be formed within the fluorescence lifetime of naphthalene, which is much shorter than pyrene.[8)]

The observed excimer emission proves that the face-to-face orientation between two naphthalene units is attained in the modified γ-CD. The examination of molecular models (CPK) suggests that the long axis of the appended naphthalene is held to be parallel to the axis of γ-CD and the guest naphthalene is likely to be involved with similar orientation. Therefore, it may be concluded that the excimer formation occurs with long axses of the two naphthalene units parallel to γ-CD axis (E).



E

The intensities of excimer emission were analyzed to obtain binding constant between $\underline{2}$ and naphthalene according to the modified Benesi-Hildebrand equation[9)] when naphthalene is in large excess:

$$\frac{1}{I_{ex}-I^{\circ}_{ex}} = \frac{1}{\alpha[\underline{2}]_{\circ}} + \frac{1}{\alpha K[\underline{2}]_{\circ}}\cdot\frac{1}{[N]_{\circ}} \qquad (3)$$

where I_{ex} and I°_{ex} are the excimer intensities at 440 nm in the presence and absence of naphthalene, $[\underline{2}]_{\circ}$ and $[N]_{\circ}$ are initial concentrations of $\underline{2}$ and naphthalene, K is the binding constant, and α is a proportional constant. Figure 2 shows a linear relationship, confirming 1:1 complexation between $\underline{2}$ and naphthalene with 1680 M^{-1} as the binding constant.

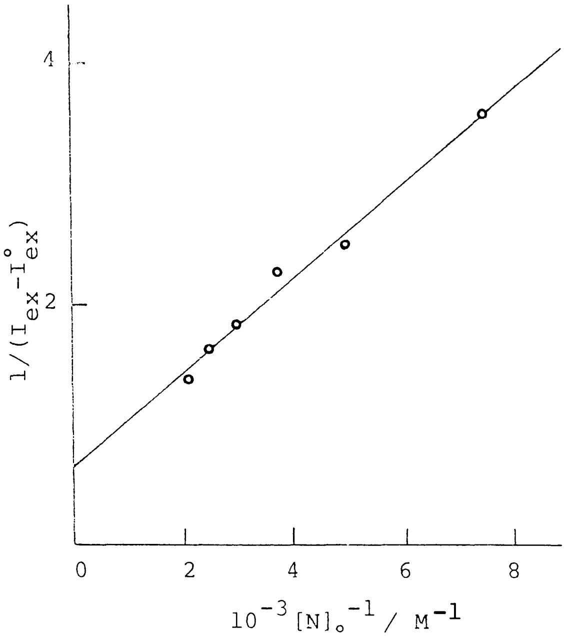


Fig. 2. Modified Benesi-Hildebrand plot for the solution containing $\underline{2}$ (7.5×10^{-6} M) and naphthalene.

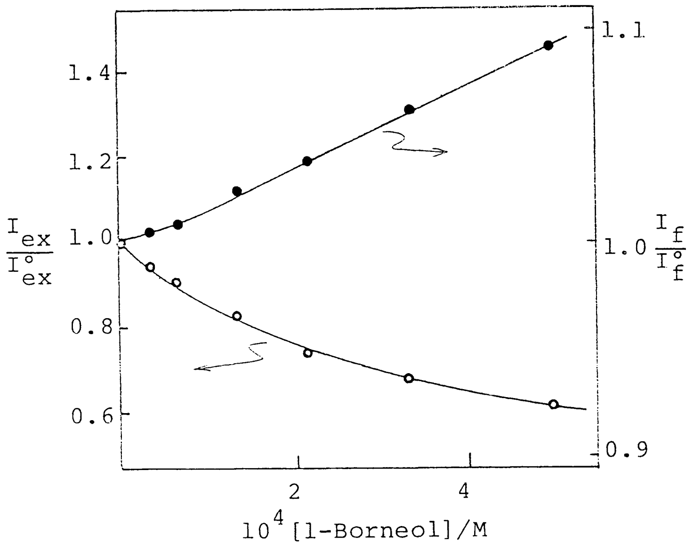


Fig. 3. The effect of l-borneol on the fluorescence spectrum of the solution containing $\underline{2}$ (1.5×10^{-4} M) and naphthalene (2.66×10^{-4} M). The I_f and I°_f values are peak intensities around 335 nm in the presence and absence of l-borneol. The I_{ex} and I°_{ex} values are intensities at 400 nm.

Figure 3 shows that the addition of l-borneol to the system of 2 and naphthalene causes a decrease in excimer emission intensity and an increase in normal fluorescence intensity. This effect of l-borneol demonstrates that the guest naphthalene included in the cavity of 2 is replaced by l-borneol.

The replacement behavior by l-borneol suggests the possible role of the appended naphthalene moiety as a space regulator$^{4a)}$ which narrows the large γ-CD cavity to allow inclusion of various kinds of molecules having too small sizes to form stable complexes with native γ-CD. Detailed examination of this space regulating effect is now under way.

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5) 1: ^{1}H NMR (DMSO-d_6) δ 3.58, 3.42 (broad and shoulder peaks respectively, 48H, cyclodextrin protons other than C_1H and OH), 4.2-4.7 (7H, O_6H), 4.76, 4.89 (1H and 7H respectively, C_1H), 5.8 (16H, O_2,O_3H), 7.4-8.6 (7H, aromatic H); ^{13}C NMR (DMSO-d_6) δ 59.9 (C_6), 69.1 (C_6'), 70.3 (C_5'), 72.3, 72.6 (C_2, C_3, C_5 overlapped peaks), 80.1 (C_4'), 80.8 (C_4), 101.7 (C_1), 122.4-134.8 (aromatic C); R_f 0.52 (n-butanol, ethanol, water 5:4:3 by volume); Found (Calcd for $C_{58}H_{86}O_{42}S\cdot 5H_2O$) C, 44.09 (44.15); H, 5.87 (6.15), S, 1.92 (2.03); UV (H_2O) 327 nm (ε 1280), 314 (1160), 277 (4350), 231 (61700).
6) 2: ^{1}H NMR (DMSO-d_6) δ 3.56 (broad, 48H, cyclodextrin protons other than C_1H and OH), 3.86 (2H, CH_2), 4.54 (7H, O_6H), 4.87 (8H, C_1H), 5.76 (16H, O_2,O_3H), 7.2-8.0 (7H, aromatic H); ^{13}C NMR (DMSO-d_6) δ 60.1 (C_6), 64.2 (C_6'), 69.4 (C_5'), 72.4, 72.9 (C_2, C_3, C_5 overlapped peaks), 81.1 (C_4), 101.8 (C_1), 125.9-133.0 (aromatic C), 171.2 (C=O); IR 1720 cm^{-1}; R_f 0 .52 (n-butanol, ethanol, water 5:4:3 by volume); Found (Calcd for $C_{60}H_{88}O_{41}\cdot 4H_2O$) C, 46.98 (46.87); H, 6.09 (6.31); UV (H_2O) 278 nm (ε 4660), 226 (61200).
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