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FLUORESCENCE QUENCHING IN HOST-GUEST COMPLEXES OF MODIFIED γ-CYCLODEXTRIN

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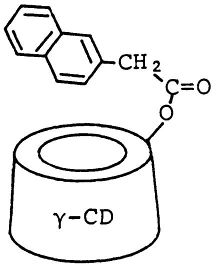
Fluorescence quenching by guest ketones occurs in the complexes of γ-cyclodextrin appended by a naphthyl moiety, demonstrating the multifunctional behavior of the appended moiety that the moiety acts as both spacer and antenna of photoenergy.

Recently γ-cyclodextrin (cyclooctaamylose, γ-CD)$^{1)}$ has excited much attention because of the inclusion of two guest molecules in its large cavity.$^{2)}$ Furthermore, an appended moiety of γ-CD has been shown to act as a spacer which enables γ-CD to form 1:1 complexes with a variety of guests by narrowing the large cavity.$^{3)}$ Here we wish to report the fluorescence quenching which occurs in the complexes of modified γ-CD **1**. In this system, the naphthyl moiety of **1** acts as an antenna of photoenergy as well as a spacer which narrows the large cavity of **1** so as to be suited for inclusion of guest ketones. The system contrasts to the reported rigid system of benzophenone-capped γ-cyclodextrin in which triplet energy transfers from the cap to an included guest.$^{4)}$ Furthermore, it reveals a new aspect in connection with the fluorescence quenching in three-component complexes of native γ-CD reported by Kano et al.$^{5)}$

The compound **1** was prepared by the procedure as reported previously.$^{3b)}$ Fluorescence measurements were performed at 25 °C with Shimadzu RF-500 fluorescence spectrophotometer, the excitation wavelength being 290 nm. No effort has been made to remove air from aqueous solutions of **1**. The quenching of the naphthyl fluorescence by ketones was analyzed by the Stern-Volmer plots after correction for absorptions of the ketones. Lifetime measurements were performed by single-photon counting procedure with a Horiba NAES-1100 instrument, giving the Stern-Volmer plots which enabled evaluation of dynamic nature of the quenching.



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Addition of various ketones to the aqueous solutions of **1** decreases the fluorescence intensity at 335 nm, and linear Stern-Volmer plots were obtained. If the fluorescence quenching$^{6)}$ occurs only in the complexes (static process), the molecular association constants (K) can be equated to the Stern-Volmer constant (K_{SV}) of the equation:$^{7)}$

$$I_0/I = 1 + K_{SV}[Q]$$

Table 1. Association and Stern-Volmer constants

Ketone	$K^{a)}$ / mol^{-1} l	K_{SV} / mol^{-1} l		
		$A^{b)}$	$B^{c)}$	$C^{d)}$
1-Fenchone	758 ± 54	912 ± 54	114 ± 6	124 ± 6
Diisopropyl ketone	89 ± 14	120 ± 3	33 ± 1	32 ± 1
Di-n-propyl ketone		67 ± 3	30 ± 3	24 ± 1
Diethyl ketone		29.7 ± 0.7	22 ± 5	9.0 ± 0.6
Acetone		8.9 ± 0.6	14.7 ± 1.8	2.0 ± 0.4

a) Association constants determined by circular dichroism measurements.

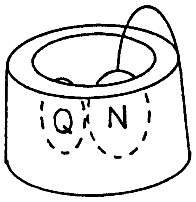
b) Values obtained from the plots of I_0/I vs. [Q].

c) Values obtained from the plots of τ_0/τ vs. [Q].

d) Values obtained from the plots of I_0/I vs. [Q] in the presence of 1-borneol (2×10^{-3} mol l^{-1}).

to the order of their bulkiness.

The ratio of lifetimes in the absence and presence of quencher (τ_0/τ) should not be dependent on quencher concentration if the quenching process is completely static. On the other hand, both Stern-Volmer plots obtained by intensity and lifetime measurements should give the same slopes in the case of complete dynamic quenching. We observed that the τ_0/τ values are dependent on [Q] as shown in Fig. 2 although the extents are lesser than those obtained by intensity measurements. The present data show that both static and dynamic processes are mixed in this system, the extent of static nature decreasing with decreasing size of the ketones. In the case of 1-fenchone, the static quenching is most remarkable as shown by 8-fold greater K_{SV} value obtained by intensity measurements than that by lifetime measurements. On the other hand, the smallest ketone, acetone, shows no evidence of complexation with **1**.



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N: naphthyl moiety
Q: quencher (ketone)

Since all these ketones are too small to form stable 1:1 complexes with native γ-CD, the geometry of the formed complexes is likely to be **2**. The ketone in the complex **2** can be replaced by 1-borneol. Table 1 shows the slopes of the Stern-Volmer plots obtained by intensity measurements in the presence of 1-borneol (C). The K_{SV} values obtained for 1-fenchone and diisopropyl ketone are close to those obtained by lifetime measurements, these observations indicating that the static quenching cannot occur owing to complexation with 1-borneol in place of ketones. This result is consistent with the fact that 1-borneol is much better guest than 1-fenchone.[3a)] It should be noted that the K_{SV} values of small

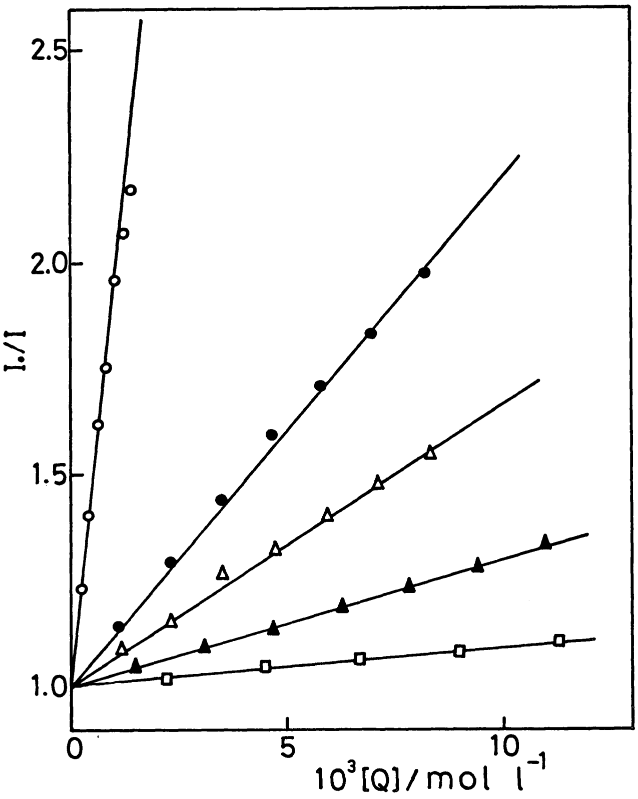

Fig. 1. Stern-Volmer plots for the quenching of fluorescence of **1** (1.5×10^{-4} mol l^{-1}) by various ketones (○, l-fenchone; ●, diisopropyl ketone; △, di-n-propyl ketone; ▲, diethyl ketone; □, acetone).

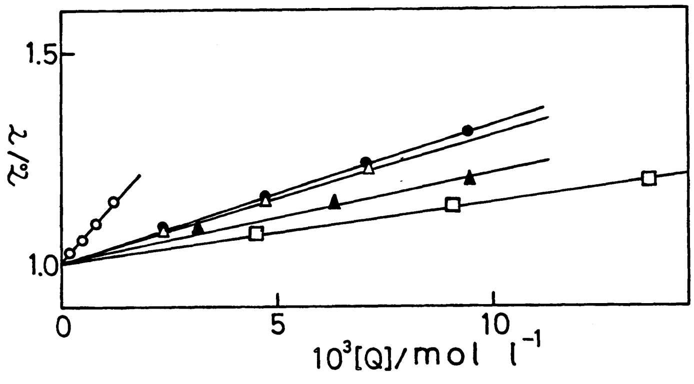

Fig. 2. Plots of τ_0/τ of **1** as a function of ketone concentration (τ_0= 34.1 ns). ○, l-fenchone; ●, diisopropyl ketone; △, di-n-propyl ketone; ▲, diethyl ketone; □, acetone).

where I_0 and I are fluorescence intensities in the absence and presence of ketone, respectively and [Q] is the concentration of ketone.

Table 1 shows K_{SV} values of the Stern-Volmer plots. In the Table, association constants of l-fenchone and diisopropyl ketone obtained by the circular dichroism measurements[3a] are also shown. Although the values are a little smaller than the K_{SV} values, the result may be regarded as an indication of the validity of predominant static quenching at least for these ketones. The ketones used here have various molecular sizes, and the order of the K_{SV} values, l-fenchone> diisopropyl ketone>di-n-propyl ketone>diethyl ketone>acetone, roughly parallels ketones obtained in the presence of 1-borneol are smaller than those of dynamic qenching as shown in the data for diethyl ketone and acetone. This phenomenon can be interpreted by inhibitory effect of 1-borneol on encounter between the naphthyl moiety of **1** and the ketones, that is, the ketones are hard to contact with the naphthyl moiety included into the cavity of **1** together with 1-borneol.

The present system may be regarded as a step to unique functional hosts in which the appended moiety acts as both spacer and catalyst. Constructing such systems is now under way.

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