

# MICROENVIRONMENTAL EFFECTS OF CYCLODEXTRINS I: ENHANCEMENT OF INTRAMOLECULAR EXCIMER FORMATION OF POLYMETHYLENE-BIS- $\beta$ -NAPHTHOATE VIA INCLUSION WITH CYCLODEXTRINS

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## Summary

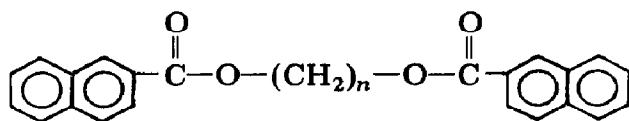
The effects of  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrins (CDs) on the fluorescence spectra of a series of polymethylene-bis- $\beta$ -naphthoates ( $B_n$ ) have been studied. It is observed that  $\beta$ -CD and  $\gamma$ -CD enhance  $B_n$  intramolecular excimer fluorescence, indicating the formation of two-to-one guest host inclusion complexes. The possible conformation of these inclusion complexes is discussed.

## 1. Introduction

Cyclodextrins (CDs) are water-soluble cyclic oligosaccharides consisting of six or more glucose units, and are shaped like doughnuts with hydrophobic cavities [1]. The most commonly used cyclodextrins are  $\alpha$ -,  $\beta$ - and  $\gamma$ -CDs consisting of six units, seven units and eight units with cavity diameters of 4.5 Å, 7.0 Å and 8.5 Å respectively. The remarkable property of the CDs is their ability to form inclusion complexes with a variety of molecules provided that they fit entirely or at least partially into the CD cavity. Because of this substrate selectivity, CDs are often used as models for studying enzyme reactivity (for a review, see ref. 2). Typically, one-to-one guest host complexes are formed with  $\alpha$ - and  $\beta$ -CDs. However, recent studies have shown that one  $\gamma$ -CD molecule can accommodate two aromatic molecules [3-6].

Luminescence probes which are included in the cavity of a CD may undergo characteristic changes in their luminescence intensity, spectral distribution and decay time, and therefore they are suited for the investigation of the complex structure dependence and dynamics of the inclusion process. Many excited aromatic chromophores form excimers which show a structureless red-shifted emission in addition to the normal monomer fluorescence. Bichromophoric compounds can form intramolecular excimers [7-11]. In our previous paper [12] we reported that polymethylene-bis- $\beta$ -naphthoates ( $B_n$ ) in organic solvents exhibit very weak excimer emission

compared with bis- $\beta$ -naphthylalkanes [13]. We show here that  $B_n$  may form two-to-one guest host complexes with  $\beta$ -CD and  $\gamma$ -CD and that, as a result, the excimer fluorescence is markedly enhanced.



$B_2, n = 2$ ;  $B_3, n = 3$ ;  $B_4, n = 4$ ;  $B_5, n = 5$ ;  $B_{10}, n = 10$ .

## 2. Materials

The  $B_n$  were prepared according to the procedure described in a previous paper [12]. The CDs (Aldrich) were used as supplied. Sodium nitrite was recrystallized twice from doubly distilled water.

## 3. Methods

Saturated aqueous solutions of the  $B_n$  were made up and stirred with the CD for at least 2 d. The solutions were passed through millipore filters and then flushed with nitrogen for about 20 min. Uncorrected fluorescence spectra were recorded using a Hitachi MPF-4 spectrofluorometer using 280 nm as the excitation wavelength. The concentration of the probe was determined from the absorption of the filtered solution.

## 4. Results

### 4.1. Fluorescence spectra of complexes of $B_n$ with CDs

The fluorescence spectra of  $B_2 - B_{10}$  ( $5 \times 10^{-6}$  M) in aqueous solution containing CDs ( $5 \times 10^{-3}$  M) are shown in Figs. 1 - 5. Only very weak fluorescence can be detected in the absence of CDs. The intensity of the monomer fluorescence ( $\lambda_{\max} = 360$  nm) of  $B_4$ ,  $B_5$  and  $B_{10}$  increases on adding  $5 \times 10^{-3}$  M  $\alpha$ -CD, while the fluorescence intensity of  $B_2$  and  $B_3$  shows no obvious change.

Adding  $\beta$ -CD ( $5 \times 10^{-3}$  M) to an aqueous solution of a  $B_n$  results in a strong structureless emission with  $\lambda_{\max} = 420$  nm. The excitation spectra at  $\lambda_e = 420$  nm are identical with those at  $\lambda_e = 360$  nm. Under the same conditions, ethyl  $\beta$ -naphthoate (concentration, below  $5 \times 10^{-6}$  M) shows no emission at  $\lambda_{\max} = 420$  nm. Thus, we attribute the new emission band to intramolecular excimer fluorescence. For the  $\beta$ -CD- $B_2$  complex the ratio  $I_E/I_M$  of excimer to monomer fluorescence intensity equals 2.7. The emission of  $\beta$ -CD- $B_3$  and  $\beta$ -CD- $B_4$  complexes is due almost entirely to the excimer

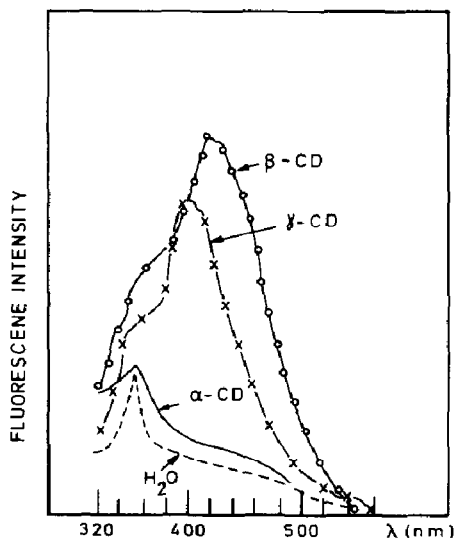


Fig. 1. Fluorescence spectra of  $B_2$  in aqueous solution in the presence of  $5 \times 10^{-3}$  M CD.

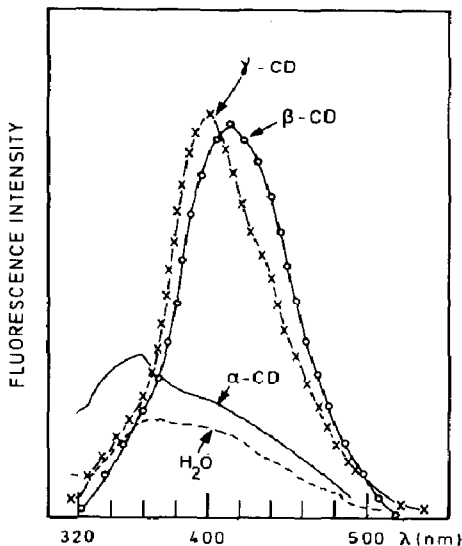


Fig. 2. Fluorescence spectra of  $B_3$  in aqueous solution in the presence of  $5 \times 10^{-3}$  M CD.

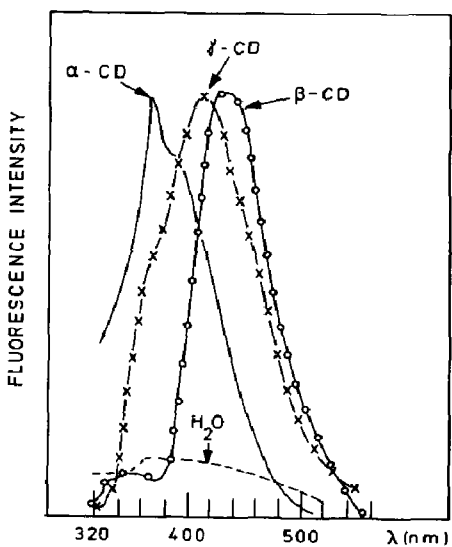


Fig. 3. Fluorescence spectra of  $B_4$  in aqueous solution in the presence of  $5 \times 10^{-3}$  M CD.

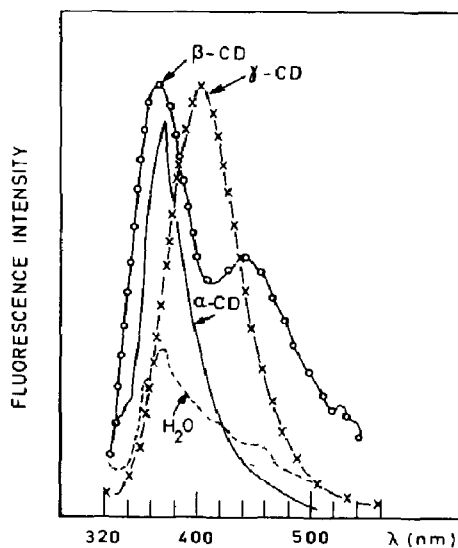


Fig. 4. Fluorescence spectra of  $B_5$  in aqueous solution in the presence of  $5 \times 10^{-3}$  M CD.

( $I_E/I_M > 10$ ). However, for  $\beta$ -CD- $B_5$  and  $\beta$ -CD- $B_{10}$  complexes,  $I_E/I_M$  is about 0.6.

$\gamma$ -CD- $B_n$  complexes show only excimer emission, with the exception of  $\gamma$ -CD- $B_2$  ( $I_E/I_M = 5$ ). It is interesting to note that  $\gamma$ -CD- $B_n$  complexes emit with  $\lambda_{max} = 400$  nm which is quite different from the emission of  $\beta$ -CD- $B_n$  complexes with  $\lambda_{max} = 420$  nm.

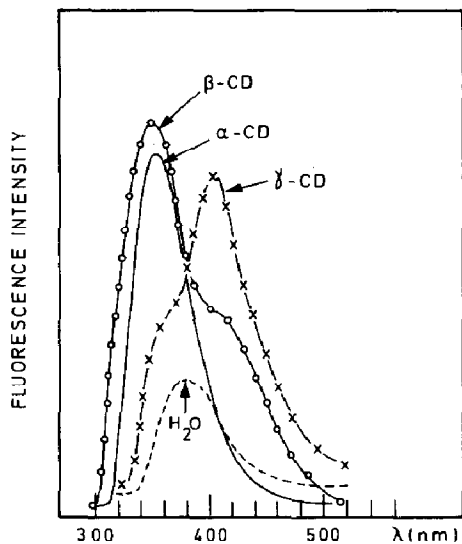


Fig. 5. Fluorescence spectra of  $B_{10}$  in aqueous solution in the presence of  $5 \times 10^{-3}$  M CD.

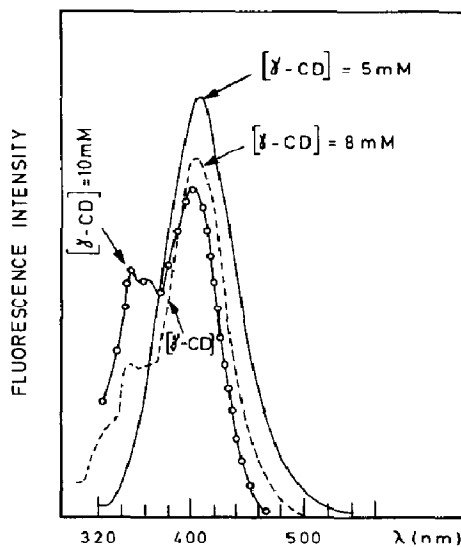


Fig. 6.  $\gamma$ -CD concentration dependence of  $B_5$  fluorescence spectra in  $\gamma$ -CD aqueous solution.

#### 4.2. The effect of CD concentration

The effect of  $\gamma$ -CD concentration on the fluorescence spectra of  $B_5$  in aqueous solution is shown in Fig. 6. Similar results are observed for other members of the  $B_n$  series. Obviously,  $I_E/I_M$  decreases as the  $\gamma$ -CD concentration increases.

#### 4.3. Quenching of $B_n$ fluorescence by sodium nitrite

In aqueous solution the fluorescence of  $B_n$  is easily quenched by sodium nitrite. For example, adding  $\text{NaNO}_2$  in a concentration higher than  $10^{-4}$  M is sufficient to quench the fluorescence of  $B_3$  completely. However, association of the probes with the CD inhibits the quenching very effectively (an alternative explanation could be the inclusion of the nitrite ion in the CD cavity; see ref. 7, p. 350), *i.e.* emission is still observable from  $B_3$  in aqueous solution containing  $5 \times 10^{-3}$  M  $\gamma$ -CD even in the presence of  $5 \times 10^{-3}$  M  $\text{NaNO}_2$ . In order to quench completely the emission of  $B_3$  in aqueous solution containing  $5 \times 10^{-3}$  M  $\beta$ -CD,  $10^{-3}$  M  $\text{NaNO}_2$  is required.

#### 4.4. Quenching by oxygen

The effectiveness of  $\text{O}_2$  quenching of monomer and excimer emission of  $B_5$  in aqueous solution containing  $\gamma$ -CD and  $\beta$ -CD ( $5 \times 10^{-3}$  M) are summarized in Table 1.  $I_{N_2}$ ,  $I_{\text{air}}$  and  $I_{\text{O}_2}$  refer to the fluorescence intensity under nitrogen, air and oxygen purging respectively.

### 5. Discussion

The probes included in a CD cavity are protected from the dynamic bimolecular quenching process, and thus the quantum yield of fluorescence

TABLE 1

Effect of oxygen on the fluorescence intensity of  $B_5$  in aqueous solutions of  $\gamma$ -CD and  $\beta$ -CD

Emission maximum <sup>a</sup>	Relative fluorescence intensity			
	$I_{N_2}$	$I_{air}$	$I_{O_2}$	Quenching <sup>b</sup>
$\gamma$ -CD				
E ( $\lambda = 400$ nm)	1	1	0.98	2
M ( $\lambda = 360$ nm)	1	1	1	0
$\beta$ -CD				
E ( $\lambda = 420$ nm)	1	0.76	0.36	64
M ( $\lambda = 360$ nm)	1	1	1.02	0

<sup>a</sup>E and M denote excimer and monomer respectively.

<sup>b</sup>Expressed as a percentage:

is enhanced compared with that in aqueous solution. This observation is often taken as evidence of the formation of an inclusion complex [14]. The enhancement of  $B_n$  fluorescence, particularly the intramolecular excimer fluorescence via association with  $\beta$ -CD and  $\gamma$ -CD, indicates that  $B_n$  can form a two-to-one guest host complex with  $\beta$ -CD and  $\gamma$ -CD. Examination of molecular models suggests that a  $B_n$  molecule may be buried entirely in a  $\gamma$ -CD cavity, where the polymethylene chain folds together and the two naphthalene rings adopt a planar sandwich configuration. Thus,  $\gamma$ -CD- $B_n$  complexes exhibit only excimer fluorescence with the exception of the  $\gamma$ -CD- $B_2$  complex which shows both monomer and excimer emission: the polymethylene chain of  $B_2$  is too short to enable the two end naphthalene rings to attain a sandwich configuration.

Two plausible but structurally different complexes (endo and exo) which favour excimer formation are shown in Fig. 7. The whole  $B_n$  molecule in either conformation can be deeply buried in the  $\gamma$ -CD cavity; hence the hydrophobic environment around the probes protect it from quenching by sodium nitrite located in the aqueous phase. It has been proposed [15] that the CD cavity strongly inhibits quenching of aromatic luminophors by dissolved oxygen. The data in Table 1 show that  $\gamma$ -CD provides substantial protection of both excimer and monomer emission of the  $B_n$  from quenching by  $O_2$ .

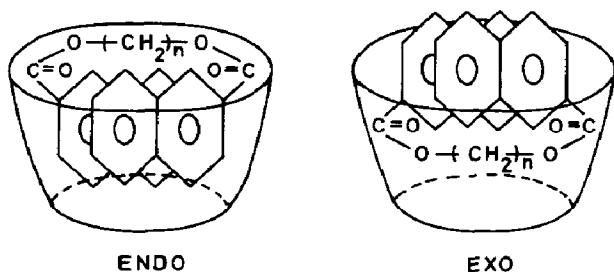


Fig. 7. Conformation of  $B_n$ -CD inclusion complex.



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