Study of the interactions between substituted 2,2′-bithiophenes and cyclodextrins

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Abstract

The interactions of 4,4′-dimethoxy-2,2′-bithiophene (DMO44BT), 4,4′-dibutoxy-2,2′-bithiophene (DBO44BT), and 2,2′-bithiophene (BT) with α- and/or β-cyclodextrins (CD) were investigated by absorption and steady-state fluorescence spectroscopy. The absorption spectra in all cases are only slightly shifted going from water to the CD cavity showing that the ground state conformations of the bithiophenes in the CD cavity remain similar to that found in water. From fluorescence measurements, it was found that DMO44BT and DBO44BT form 1:2 (guest:host) complexes with α-CD, while DMO44BT and BT form 1:1 complexes with β-CD. The nature of the interactions involved in the inclusion complexes are discussed. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Polythiophenes are among the most studied materials because of their good chemical stability and high electrical conductivity in oxidized (doped) state [1]. Some substituted polythiophenes exhibit reversible solvatochromism [2,3], thermochromism, [4] and piezochromism [5], which have been attributed to the twist of adjacent thiophene rings from a coplanar (highly conjugated) conformation to a nonplanar (less conjugated) one. However, relationships between structures and properties of substituted polythiophenes have not been well established yet, mainly

because polythiophenes exhibit a broad and not fully characterized range of conjugated lengths and a distribution of molecular environments and excitonic effects. In contrast, oligothiophenes can be synthesized as well-defined and easily processible compounds [6]. A thorough understanding of their electronic properties should provide a basis for determining the structural and electronic properties, which control the change transport and optical processes in polythiophenes. Furthermore, structurally well-defined oligothiophenes have properties even surpassing those of polymers. For example, they can be used in field effect transistors (FET) [7] and light-emitting diodes (LED) [8]. For these reasons, investigations on oligothiophenes are of importance.

Semi-empirical (AM1, PM3, and ZINDO/S) and ab initio calculations (HF/3-21G [*]) as well as spectroscopic and photophysical methods have been employed to study the ground and excited state confor-

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mations of oligothiophenes including BT and its substituted derivatives [9–18]. Recent conformational and spectroscopic analyses [18] show that bithiophenes substituted with alkoxy groups in the 4,4′ positions have structural features similar to that of BT [11]. Indeed, *anti-gauche* and *syn-gauche* conformations with torsional angles of about 150° and 30°, respectively, are coexisting in the ground state. After the photoexcitation, the molecules relax to quasi-planar S_1 states before the fluorescence occurs.

Cyclodextrins (CD) are toroidally shaped cyclic oligosaccharides, mostly consisting of six, seven and eight glucose units for α-, β-, and γ-CD, respectively. Their hydrophobic cavities enable them to accommodate various kinds of molecules to form inclusion complexes, which leads to widespread applications in pharmaceutical chemistry, food technology, analytical chemistry, chemical synthesis, and catalysis [19–24]. When complexes between guest molecules and CDs are formed, the small cavity of cyclodextrin might make guest molecules to adopt enforced orientation and constrained conformation [25]. Our recent studies on interactions of some $3H$-indoles and CDs show that photophysical properties of guest molecules included in the CD cavity are largely modified [26–31]. For instance, the fluorescence of 2-[(p-amino)phenyl]-3,3-dimethyl-5-cyano-$3H$-indole (**1**) and 2-[(p-dimethylamino)phenyl]-3,3-dimethyl-5-cyano-$3H$-indole (**2**) were found to be quenched by the γ-CD cavity [27].

Little attention has been paid to the spectroscopic and/or photophysical study of inclusion complexes involving oligothiophenes in CD cavities. To the best of our knowledge, only α-terthiophene in β- and γ-cyclodextrins has been studied [32,33]. Here we report a detailed study of the interactions between some substituted 2,2′-bithiophenes (see Scheme 1) and cyclodextrins (α and β).

2. Experimental section

2.1. Materials

Analytical grade reagents BT, methanol, α- and β-CDs were purchased from Aldrich Chemicals and used as received. DMO44BT and DBO44BT were prepared from 4,4′-dibromo-2,2′-bithiophene following procedures described elsewhere [34].

2.2. Instruments

Absorption spectra were recorded on a Cary 1 Bio UV–VIS spectrophotometer using 1 cm quartz cells. Fluorescence spectra corrected for the emission detection were measured on a Spex Fluorolog-2 spectrofluorimeter with a F2T11 special configuration. The excitation and emission bandpasses used were 2.6 and 1.9 nm, respectively. Each solution was excited near the absorption wavelength maximum using 1 cm quartz cells.

2.3. Methods

Stock solutions of BT, DMO44BT and DBO44BT were prepared in methanol, and 0.1-ml aliquots of these solutions were added to aqueous solutions of CDs. The final concentrations of BT, DMO44BT and DBO44BT were 3×10^{-6} M for both absorption and fluorescence measurements. Bithiophenes studied were found not to be sensitive to the pH of environments, and thus the pH values of the solutions were not adjusted. Fresh sample solutions were used in the absorption and fluorescence measurements. All corrected fluorescence excitation spectra were found to be equivalent to their respective absorption spectra. All measurements were carried out at room temperature.
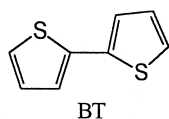
Scheme 1.

3. Results

3.1. Spectral characteristics

3.1.1. Absorption

The absorption spectra of DMO44BT, DBO44BT and BT are not significantly changed going from water to α- and β

3.1.2. Fluorescence

The fluorescence spectra of DMO44BT in α-CD solutions are shown in Fig. 1A. It is noted that the fluorescence intensity decreased as the concentration of α-CD is increased. Moreover a clear isosbestic point is observed indicating the existence of an equilibrium between two species only, i.e., the free molecule and a kind of inclusion complex (see Section 3.2). It is worth mentioning here that the fluorescence quantum yield of the inclusion complex should be smaller than that of the free molecule giving rise to an overall decrease of the fluorescence intensity of the α-CD solutions.

A decrease in the fluorescence intensity is also observed for DMO44BT in β-CD solutions without the appearance of an isosbestic point (see Fig. 1B). However, it will be shown in Section 3.2 that this molecule also forms an inclusion complex with β-CD.

In contrast with the situation of DMO44BT interacting with α-CD, the fluorescence intensity of DBO44BT increases with increasing the α-CD concentration as shown in Fig. 2A. This indicates that the fluorescence quantum yield of the inclusion complex is larger than that of the free molecule. On the other hand, the fluorescence intensity of DBO44BT
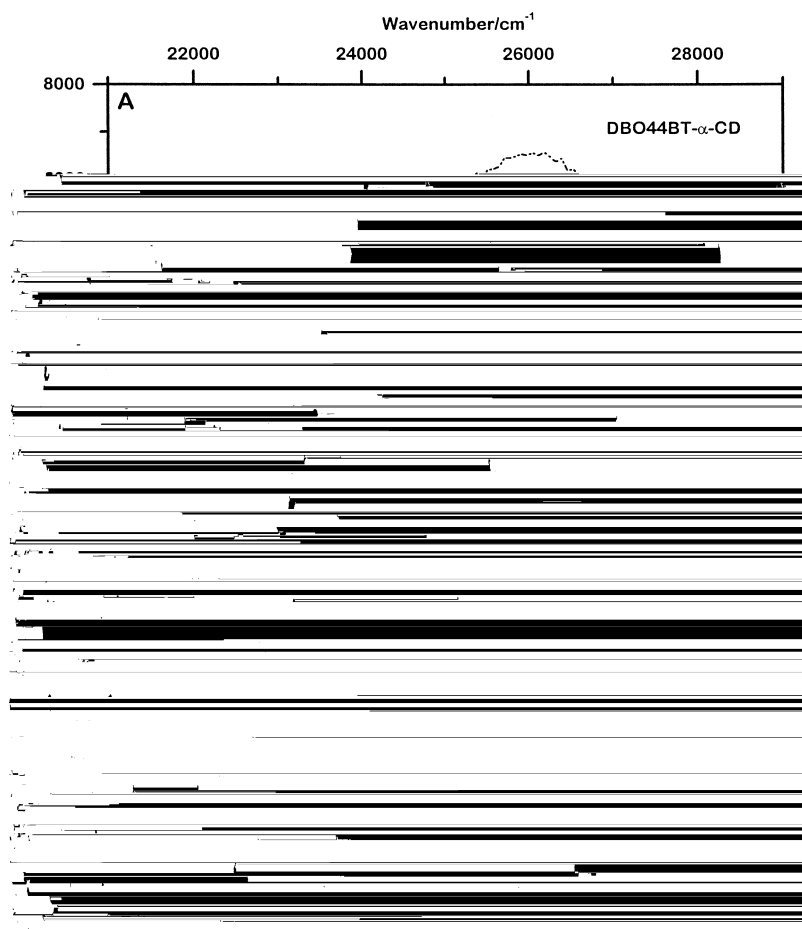

Fig. 2. Fluorescence spectra DBO44BT and BT in α- and β-CD solutions, respectively, of varying concentrations. (A) [α-CD] = 0 (solid), 2.00 (dash), 4.00 (dot), 8.00 (dash dot), and 12.00 mM (dash dot dot). (B) [β-CD] = 0 (solid), 0.05 (dash), 0.30 (dot), and 1.00 mM (dash dot).

Table 1
Spectral characteristics of fluorescence of the bithiophenes in various environments

Molecule	Medium	λ_F [a] /nm	ν_F [a] /cm^{-1}	FWHM$_F$/cm^{-1}
DMO44BT	water	402.0	24800	3900
	methanol	391.0	25600	3900
	0.30 mM α-CD	401.2	24900	3900
	0.75 mM α-CD	398.8	25100	3900
	2 mM α-CD	393.8	25400	4000
	4 mM α-CD	387.0	25800	4000
	0.05 mM β-CD	401.0	24900	4000
	0.15 mM β-CD	399.2	25000	3900
	0.50 mM β-CD	398.3	25100	3900
	2 mM β-CD	398.3	25100	3900
DBO44BT	water	404.5	24700	3600
	2 mM α-CD	399.3	25000	3900
	4 mM α-CD	392.2	25500	3900
	8 mM α-CD	389.8	25700	3900
	12 mM α-CD	391.2	25600	3900
BT	water	366.2	27300	4000
	0.05 mM β-CD	366.2	27300	4100
	0.30 mM β-CD	366.4	27300	4100
	1 mM β-CD	366.6	27300	4100

[a] Taken at the center of mass.

does not significantly changed in β-CD solutions showing that the guest–host interactions are very weak for this system.

The fluorescence spectrum of BT has been measured at various concentrations of α-CD. A very small increase in the fluorescence intensity has been observed so that accurate value of the association constant could not be obtained in this environment. On the other hand, it was found that the fluorescence intensity of BT is significantly reduced on increasing the β-CD concentration.

The spectral characteristics are summarized in Table 1. For the sake of comparison, the spectral characteristics of DMO44BT and DBO44BT in methanol are also included in the table.

3.2. Complexation of the bithiophenes with α- and β-CDs

First, we consider the following general stepwise equilibria:

$$S + CD \overset{K_1}{\rightleftharpoons} SCD, \tag{1}$$

$$SCD + CD \overset{K_2}{\rightleftharpoons} S(CD)_2, \tag{2}$$

where S represents the fluorescence substrate, K_1 and K_2 denote the stepwise association constants for the 1:1 and the 1:2 complexes, respectively. At low fluorescence probe concentrations, the total fluorescence intensity (I) can be expressed by [26–31]

$$I = \frac{\left(I_0 + I_1 K_1 [CD]_0 + I_2 K_1 K_2 [CD]_0^2\right)}{\left(1 + K_1 [CD]_0 + K_1 K_2 [CD]_0^2\right)} \tag{3}$$

where I_0, I_1 and I_2 stand for the fluorescence intensity of the substrate in water, in the 1:1 complex, and in the 1:2 complex, respectively, while $[CD]_0$ is the initial concentration of CD. In particular, the following two limiting cases should be considered:

Case 1: only the 1:1 complex is formed. Thus, one obtains: [26–31]

$$I = \frac{\left(I_0 + I_1 K_1 [CD]_0\right)}{\left(1 + K_1 [CD]_0\right)}. \tag{4}$$

In this case, the analysis by a nonlinear regression program (NLR) [26–31] according to Eq. (4) should

give reasonable results and the plot of $1/(I - I_0)$ versus $[CD]_0^{-1}$ should exhibit a straight line.

Case 2: only the 1:2 complex is formed. The following relationship can be obtained:

$$I = \frac{\left(I_0 + I_2 K [CD]_0^2\right)}{\left(1 + K [CD]_0^2\right)} \qquad (5)$$

where $K = K_1 K_2$. In this case, the NLR analysis according to Eq. (5) should give reasonable results and the plot of $1/(I - I_0)$ versus $[CD]_0^{-2}$ should exhibit a straight line.

3.2.1. Interactions of DMO44BT with α- and β-CDs

Fig. 3A depicts the fluorescence intensity of DMO44BT at varying concentrations of α-CD. The NLR analysis based on Eq. (5) gives reasonable results concerning values of the variables, standard errors, 95% confidence intervals, correlation coefficient, and absolute sum of squares. One can see from Fig. 3A that the fit converged well with a correlation coefficient $r^2 = 0.999$. In contrast, the NLR analyses according to Eqs. (3) and (4) do not work. Fig. 3B further shows that plotting of $1/(I_0 - I)$ against $[\alpha\text{-CD}]_0^{-2}$ yields a straight line ($r = 0.998$). The above results lead us to conclude that only a 1:2 complex is formed between DMO44BT and α-CD.
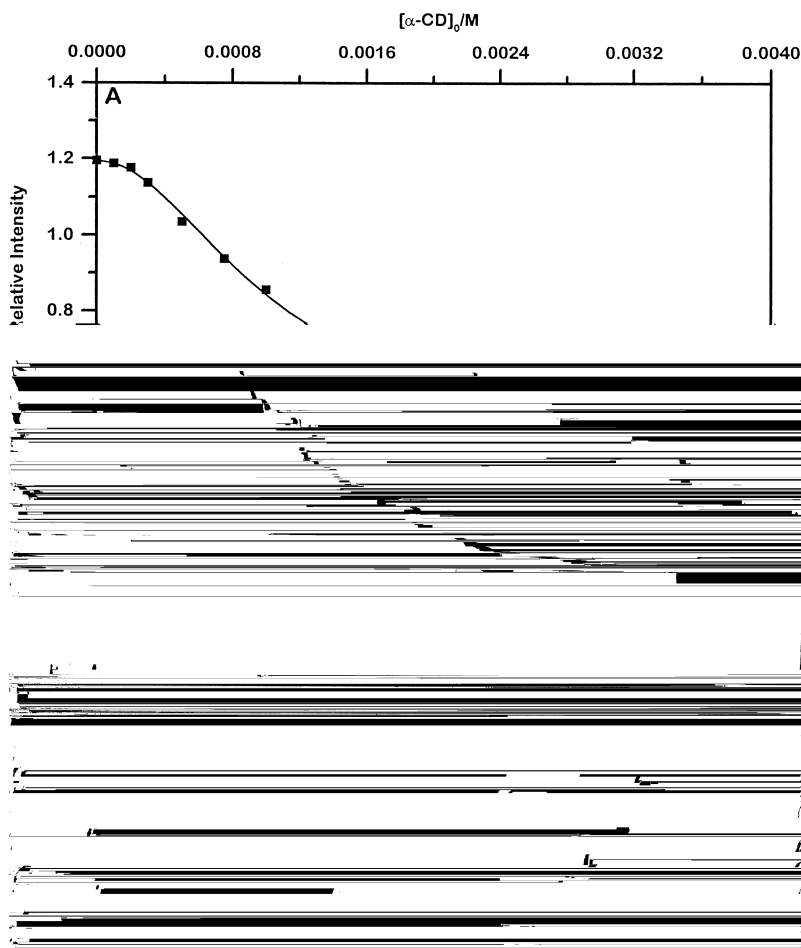

Fig. 3. Plots of the relative fluorescence intensity (A) and $1/(I_0 - I)$ (B) versus $[\alpha\text{-CD}]_0$ and $[\alpha\text{-CD}]_0^{-2}$, respectively, for DMO44BT complexed to α-CD. The full line in (A) is the nonlinear regression fit to the experimental data following Eq. (5).

This is in agreement with the observation of a clear isosbestic point in the fluorescence spectra (Fig. 1A).

The fluorescence intensity of DMO44BT against $[\beta\text{-CD}]_0$ is illustrated in Fig. 4A. A reduction in the fluorescence intensity also appears. In this case, however, the data fit only the 1:1 complexation model described by Eq. (4). Fig. 4A,B show the satisfactory fit according to Eq. (4) ($r = 0.999$) and the straight line of $1/(I_0 - I)$ versus $[\beta\text{-CD}]_0^{-1}$ ($r = 0.999$), respectively. Thus, a 1:1 complex between DMO44BT and β-CD is believed to be formed. In both cases, the double reciprocal plots were well described by single straight lines eliminating the possible coexistence of 1:1 and 1:2 complexes. In-

deed, if it was the case, the plots should be described by two linear segments [26].

3.2.2. Interaction of DBO44BT with α-CD

On the other hand, similar to the situation of DMO44BT, reasonable results of the NLR analysis can be obtained only when the 1:2 complexation model applies ($r^2 = 0.996$). Furthermore, a linear correlation ($r = 0.9997$) can be observed between $1/(I - I_0)$ and $[CD]_0^{-2}$ as shown in Fig. 5B.

It should be pointed out here that the association constant is only slightly reduced when the NLR analysis excludes the datum in water. This indicates that the possible aggregation of DBO44BT in water
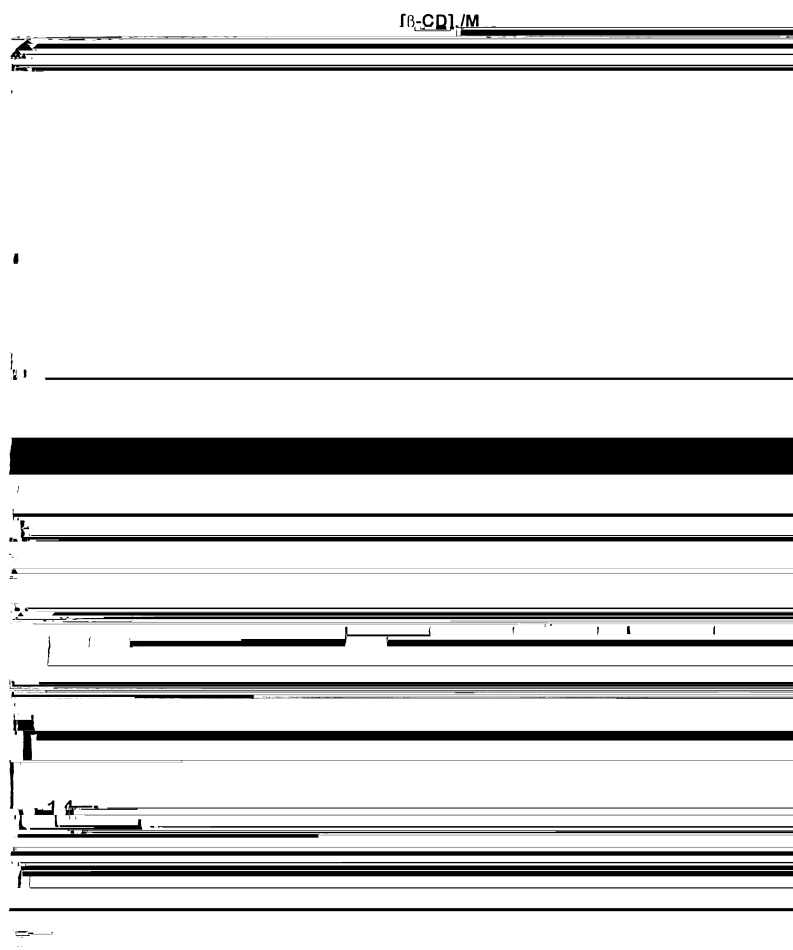

Fig. 4. Plots of the relative fluorescence intensity (A) and $1/(I_0 - I)$ (B) versus $[\beta\text{-CD}]_0$ and $[\beta\text{-CD}]_0^{-1}$, respectively, for DMO44BT complexed to β-CD. The full line in (A) is the nonlinear regression fit to the experimental data following Eq. (4).
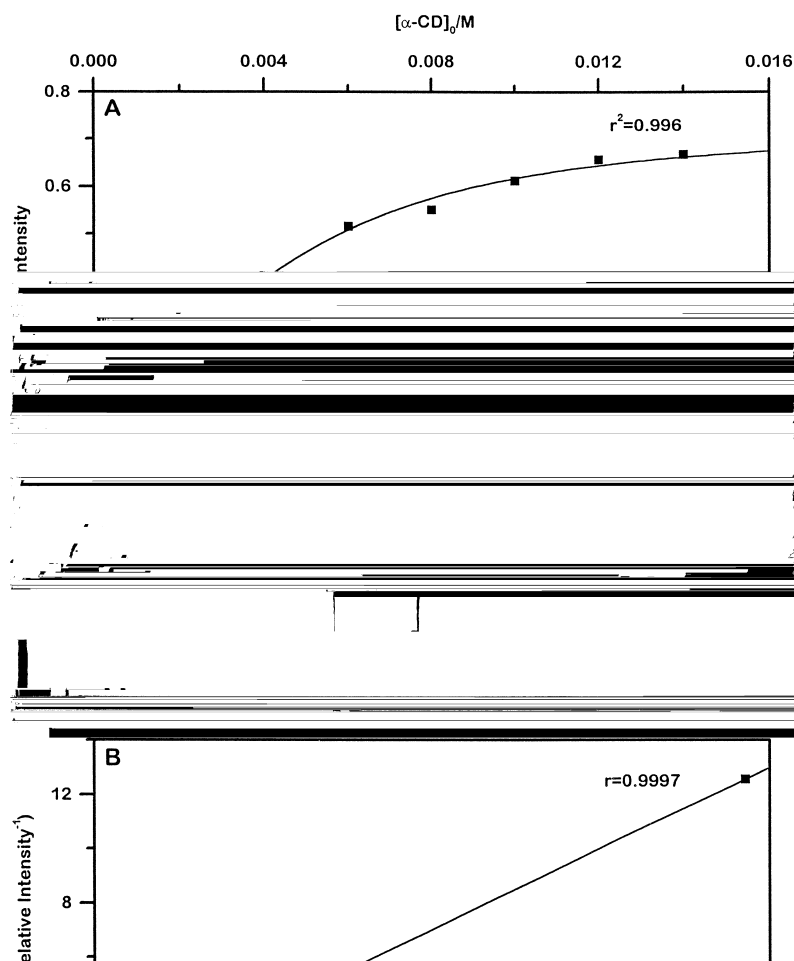
Fig. 5. Plots of the relative fluorescence intensity (A) and $1/(I - I_0)$ (B) versus $[\alpha\text{-CD}]_0$ and $[\alpha\text{-CD}]_0^{-2}$, respectively, for DBO44BT complexed to α-CD. The full line in (A) is the nonlinear regression fit to the experimental data following Eq. (5).

does not affect significantly the accuracy of the association constant.

3.2.3. Interaction of BT with β-CD

The NLR analysis reveals that the interaction pattern of BT with β-CD is similar to that of DMO44BT with β-CD. In other words, only the fit

using the 1:1 complexation model is operative ($r^2 = 0.994$; figure not shown) and plotting of $1/(I -)$

4. Discussion

It is generally accepted that the binding forces involved in the complex formation of molecular probes with CDs are mainly: (1) hydrophobic interactions between the hydrophobic moiety of guest molecules and the CD cavity and (2) hydrogen bonding between polar functional groups of guest molecules and hydroxyl groups of CD [22]. Hydrophobic interactions are more universal than the hydrogen bonding since the polar functional groups for hydrogen bonding are not available for most guest molecules. In a previous paper, we have shown that hydrogen bonding is absent for BT in methanol [9]. Thus, it is reasonable to assume that hydrogen bonding does not occur between hydroxyl groups of CD and sulfur atoms of bithiophene derivatives. However, hydrogen bonding might occur between the hydroxyl group of CD and the oxygen atom in the methoxy group of DMO44BT. Such an interaction between CDs and DBO44BT should be weaker since the electron lone pair on the oxygen atom in the butoxy group is much less available as compared to that in the methoxy group.

It can be seen from Table 2 that the association constant for DMO44BT linked with α-CD is about 23 times larger than that for DBO44BT linked with α-CD. This strongly suggests that the contribution of the hydrogen bonding is involved in the association constant of DMO44BT. If the hydrogen bonding were absent, the association constant would result from hydrophobic interactions which should be smaller compared to that of DBO44BT on the basis of the comparison of their respective molecular volumes.

Comparison of the association constant of DMO44BT and BT linked with β-CD might provide evidence that hydrogen bonding between DMO44BT and water takes place. In our previous studies [26,28], it was found that for two molecules interacting with CD, the ratio of ln K is similar to the ratio of their molecular volumes if only the hydrophobic effect is responsible for the formation of the inclusion complex. The ratio of ln K between DMO44BT and BT

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