



# A comparative study on inclusion complexation of substituted anilidonaphthalene sulfonic acids with 1,6,20,25-tetraaza[6.1.6.1]-paracyclophane and $\beta$ -cyclodextrin

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## Abstract

The inclusion complexations of paracyclophane (CP44) and  $\beta$ -cyclodextrin ( $\beta$ -CD) with several anilidonaphthalene sulfonic acids (ANSs) have been characterized via the enhancement of fluorescence spectra upon inclusion.  $\beta$ -CD and CP44 formed 1:1 inclusion complexes with ANSs, and the high stability of inclusion complexes of the latter was demonstrated. The thermodynamic parameters observed from the temperature dependence of the inclusion constants (van't Hoff analysis) showed that CP44 inclusion complexations with ANSs are enthalpy-driven. Furthermore, the structure of the inclusion complexes was discussed based on <sup>1</sup>H- and 2D ROESY-NMR measurements. It was found that CP44 encapsulates the naphthalene moiety of ANSs. On the other hand, differences in the structures of the  $\beta$ -CD inclusion complexes were observed for the 4-OH-substituted ANS. The molecular recognition for the inclusion of  $\beta$ -CD was found to be sensitive compared with that of CP44. In addition, the local polarity inside the CP44 and  $\beta$ -CD cavities was evaluated using ANSs as the fluorescence probe. Based on these results, we have suggested that the local polarity of ANSs in the hydrophobic cavities of CP44 and  $\beta$ -CD plays an important role in quantum yield enhancement upon inclusion.

**Keywords** Cyclophane · Cyclodextrin · Inclusion complexation · Anilidonaphthalene sulfonic acid · Quantum yield of inclusion complex

## Introduction

Cyclodextrins (CDs) are attractive hosts for inclusion chemistry due to their hydrophobic cavities [1]. They can form inclusion complexes with many organic molecules and are widely used in the pharmaceutical and food industries [2, 3]. Recently, the inclusion behavior of paracyclophanes (CPs)

has attracted much attention because they enable the design of hydrophobic cavities of definite shapes and sizes [4–8]. The development of artificial carriers is of great importance for drug delivery systems and newly functionalized cyclophanes have been designed for this purpose [9]. However, to date, studies on the inclusion complexation of organic molecules with cyclophanes are not well established.

Anilidonaphthalene sulfonic acid (ANS) is sensitive to the polarity of its local environment and constitutes a very useful fluorescence probe [10]. ANS shows high fluorescence in nonpolar solvents, but it is strongly quenched in polar solvents such as water [10]. Therefore, ANS is employed as a polarity probe in a variety of proteins and host–guest inclusion complexes [11, 12]. In addition, the measurement of the quantum yield of inclusion complexes is informative for the characterization of photochemical processes and inclusion behavior.

In this study, using four different anilidonaphthalene sulfonic acids as guest molecules, we have examined the inclusion complexation of 1,6,20,25-tetraaza[6.1.6.1]paracyclophane (CP44) and  $\beta$ -CD, and the enhancement of quantum

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yield ( $\Phi$  values) has been determined upon inclusion. The results observed for CP44 were compared with those of  $\beta$ -CD having a similar cavity size [13]. Furthermore, the structure of inclusion complexes of CP44 and  $\beta$ -CD has been established through  $^1\text{H}$ - and 2D ROESY-NMR experiments. A characteristic inclusion complexation of 4-OH-substituted ANS by  $\beta$ -CD was found by comparing with those by CP44. The difference in the inclusion complex structures (molecular recognition for inclusion) and the dominant factor for the quantum yields enhanced by inclusion were also discussed.

## Experimental

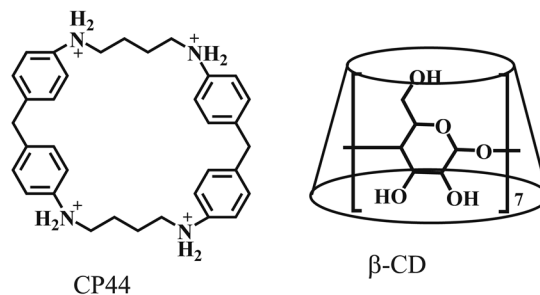
### Materials

The four different types of anilidonaphthalene sulfonic acids and host molecules (CP44 and  $\beta$ -CD) used in this study are shown in Fig. 1. CP44 and  $\beta$ -CD were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan) and Wako Pure Chemicals (Osaka, Japan), respectively, and were used without any further purification. It is useful to compare the inclusion behavior of CP44 having charges in macrocycle with that of hydrophobic  $\beta$ -CD having similar ring size. 6-Anilidonaphthalene-2-sulfonic acid (2,6-ANS), 6-anilino-4-hydroxynaphthalene-2-sulfonic acid (2,4,6-AHNS), and 7-anilino-4-hydroxynaphthalene-2-sulfonic acid (2,4,7-AHNS) were obtained from Funakoshi (Tokyo, Japan), Tokyo Chemical Industry Co. (Tokyo, Japan), and Wako Pure Chemicals, respectively. 7-Anilidonaphthalene-2-sulfonic acid (2,7-ANS) was prepared according to the method reported by Bucherer and Stohmann [14], and recrystallized from basic water. Identification was made by  $^1\text{H}$  NMR measurements. Water and 1,4-dioxane were purified by distillation and were used as solvents.

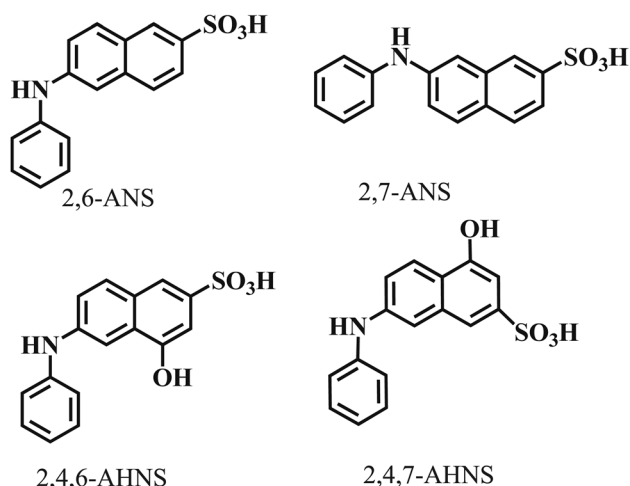
### Fluorescence and NMR measurements of inclusion complexes

Fluorescence spectra of ANS complexes with  $\beta$ -CD in water were measured with a Shimadzu RF-5300PC spectrophotometer:  $[\text{ANS}] = 2 \mu\text{M}$  ( $\text{M} = \text{mol dm}^{-3}$ ) and an excitation wavelength of 320–350 nm. Temperature-controlled water ( $\pm 0.1 \text{ K}$ ) was used to control the reaction temperature. For the inclusion with CP44, an aqueous HCl solution (hydrogen ion exponent (pH) 1) was used as a solvent to solubilize CP44. No change in the absorption spectrum of ANS under these conditions was previously confirmed.  $\Phi$  values were determined using Otsuka Electronics Quantum Efficiency Analysis System (QE 1000) equipped with a half-moon unit (Osaka, Japan) at  $298 \pm 0.5 \text{ K}$ . The quantum yield was calibrated by quinine bisulfate solution in

#### Host molecules



#### Guest molecules



**Fig. 1** Structures of paracyclophane (CP44),  $\beta$ -cyclodextrin ( $\beta$ -CD), and ANS derivatives

sulfuric acid (0.050 M) as a standard:  $\lambda$  (excitation wavelength) = 347.5 nm and  $\Phi = 0.51 \pm 0.02$  [15].

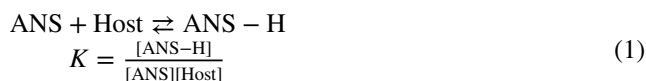
CD and CP44 inclusion complexes  $^1\text{H}$ -NMR spectra were recorded in  $\text{D}_2\text{O}$  and  $\text{DCl-D}_2\text{O}$  acidic solutions respectively with a Varian Mercury 300 spectrometer (300 MHz) at room temperature. Chemical shifts are given as  $\delta$  values relative to HOD ( $\delta$  4.79) as an internal standard. 2D ROESY-NMR measurements were carried out with a Varian VNS 600 NMR spectrometer (600 MHz) at 303 K. The mixing time for ROESY measurements was 200 ms.

## Results and discussion

### The estimation of inclusion constants of $\beta$ -CD and CP44

The typical fluorescence spectra of 2,7-ANS upon consecutive addition of CP44 are shown in Fig. S1 in supplementary

data. A large enhancement in the fluorescence intensity in the vicinity of 460 nm caused by 2,7-ANS inclusion complexes was observed upon addition of CP44 to a solution of 2,7-ANS. To confirm the stoichiometry of the ANS-CP44 complex, fluorescence measurements were conducted by varying the mole fraction of 2,7-ANS and CP44, i.e. continuous variation method (Job's method) [16]. Job's plots for the changes in the fluorescence intensity of ANS showed that the CP44 inclusion complex of 2,7-ANS was formed with 1:1 stoichiometry (see Fig. S1 in supplementary data). Similar results were obtained for the complexation of various ANS derivatives with  $\beta$ -CD and CP44. The equilibrium for the 1:1 inclusion complexations of ANSs can be expressed as:



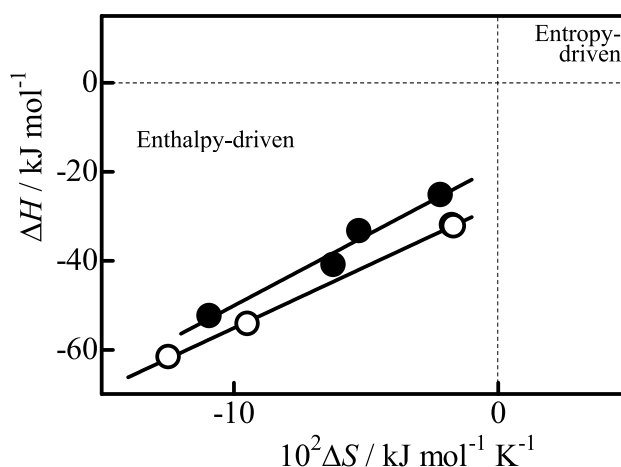
where ANS-H denotes the inclusion complex. Under the condition of  $[\text{Host}] \gg [\text{ANS}]$ , fluorescence spectral data were analyzed according to the Benesi-Hildebrand equation (Eq. 2) [17]:

$$\frac{[\text{Host}]_0}{(F - F_0)} = \frac{1}{F_\infty - F_0} [\text{Host}]_0 + \frac{1}{K[F_\infty - F_0]} \quad (2)$$

where  $[\text{Host}]_0$  denotes initial concentrations of host molecules and  $F$  is the fluorescence intensity. A good linear relationship between  $[\text{Host}]_0/(F - F_0)$  and  $[\text{Host}]_0$  was obtained (see Fig. S1b in supplementary data). The association constants ( $K$ ) for the 1:1 inclusion complex formation of  $\beta$ -CD and CP44 can be determined from the slope and intercept according to Eq. 2. The  $K$  values obtained for the inclusion complexation of  $\beta$ -CD and CP44 at various temperatures are listed in Table 1.  $K$  values for the inclusion with CP44 were found to be larger compared with those with  $\beta$ -CD, suggesting that CP44 forms more stable inclusion complexes.

The inclusion behavior can be better understood using the enthalpy and entropy changes ( $\Delta H$  and  $\Delta S$ ) obtained for

the inclusion process. From the linear fit of the van't Hoff plots, the enthalpy and entropy changes were determined for the inclusion complexations of ANSs with CP44 and  $\beta$ -CD. Results for the thermodynamic parameters are listed in Table 1. The enthalpy-entropy compensation effect has been reported for many chemical reactions [18]. In Fig. 2, the  $\Delta H$  values for the inclusion complexation of ANSs with CP44 and  $\beta$ -CD were plotted against the  $\Delta S$  values. The linear relationship obtained suggests that a single mechanism is operating in the inclusion processes [19]. The parallel straight lines between CP44 and  $\beta$ -CD are due to a free energy change caused by the CP44 host rather than to a change in the mechanism. Figure 2 shows that the upper-right and lower-left quadrants correspond to the entropy-driven and enthalpy-driven complexations, respectively. The  $\Delta H$ - $\Delta S$  plots in Fig. 2 suggest that both CP44 and  $\beta$ -CD bind to ANSs with favorable enthalpy. The major contribution to the favorable enthalpy of complexation comes from the van der Waals interactions associated with the inclusion of the non-polar part of ANS into the hydrophobic cavity of



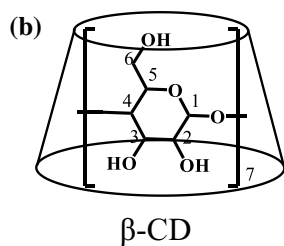
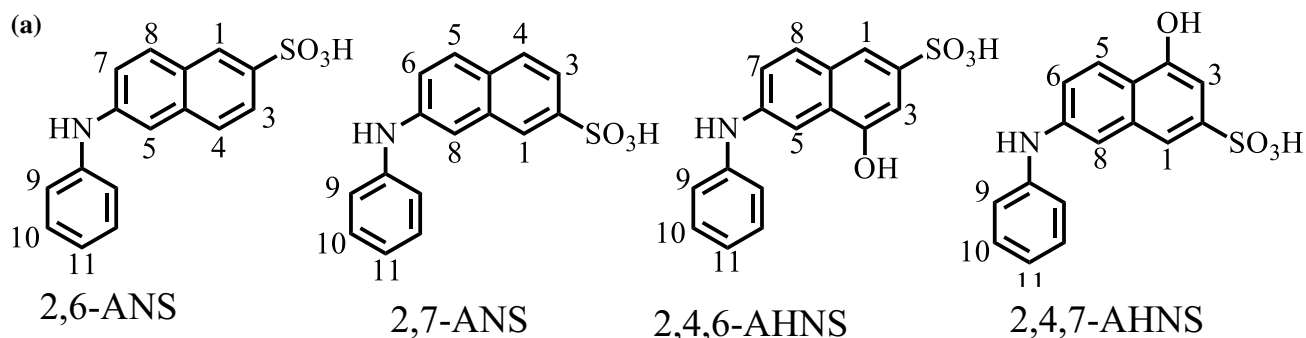
**Fig. 2** Relationship between  $\Delta H$  and  $\Delta S$  for the inclusion complexation with ANS derivatives in an aqueous solution. Open circle: CP44 and filled circle:  $\beta$ -CD

**Table 1** The inclusion constants and thermodynamic parameters for inclusion complexations with CP44 and  $\beta$ -CD

Guest	Host	$10^{-3} K/M^{-1}$						$\Delta H/kJ mol^{-1}$	$\Delta S/kJ mol^{-1} K^{-1} (T_{298}\Delta S)$
		288 K	293 K	298 K	303 K	308 K	318 K		
2,6-ANS	CP44	76 ± 7	46 ± 1	34 ± 1	24 ± 1			-54 ± 3	-0.095 ± 0.005 (-28)
2,6-ANS	$\beta$ -CD		2.4 ± 0.1	1.7 ± 0.1	1.8 ± 0.1	1.3 ± 0.1		-25 ± 1	-0.022 ± 0.005 (-6.5)
2,4,6-AHNS	CP44		28 ± 1	20 ± 1	12 ± 1	9.0 ± 0.3		-62 ± 3	-0.13 ± 0.01 (-37)
2,4,6-AHNS	$\beta$ -CD		4.2 ± 0.2	3.1 ± 0.1	2.0 ± 0.1	1.5 ± 0.1		-52 ± 2	-0.11 ± 0.01 (-33)
2,7-ANS	CP44		56 ± 1	54 ± 1	40 ± 1	30 ± 1	23 ± 1	-32 ± 2	-0.018 ± 0.008 (-5.2)
2,7-ANS	$\beta$ -CD			1.2 ± 0.1	0.99 ± 0.01	0.80 ± 0.02	0.58 ± 0.01	-33 ± 1	-0.053 ± 0.003 (-16)
2,4,7-AHNS	CP44		72 ± 2	50 ± 1	52 ± 1	47 ± 1	23 ± 1	-32 ± 3	-0.017 ± 0.001 (-5.0)
2,4,7-AHNS	$\beta$ -CD		9.7 ± 0.2	9.5 ± 0.2	5.9 ± 0.1	4.6 ± 0.1		-41 ± 3	-0.062 ± 0.006 (-19)

**Table 2** Cross peaks observed in ROESY-NMR spectra of inclusion complexes of ANS derivatives with  $\beta$ -CD in D<sub>2</sub>O

Guest	Guest protons <sup>a</sup>	Host protons <sup>b</sup>		
		C(3)H	C(5)H	C(6)H
2,7-ANS	C(1)-H	—	++	+
	C(4)-H	—	+	—
	C(5)-H	—	+	—
	C(8)-H	—	++	—
	C(6,10)-H	+	++	—
2,6-ANS	C(1)-H	+	++	—
	C(8)-H	—	++	+
	C(4,5)-H	—	++	—
	C(9)-H	+	—	+
2,4,6-AHNS	C(1)-H	—	+	+
	C(8)-H	—	+	—
	C(9)-H	++	—	—
2,4,7-AHNS	C(1)-H	—	++	—
	C(5)-H	—	++	—
	C(9)-H	+	—	—



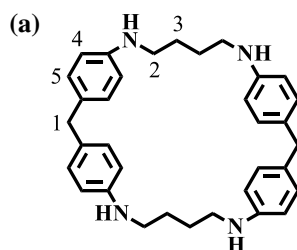
CP44 and  $\beta$ -CD. Furthermore, in the inclusion with CP44, the additional electrostatic interaction of the positive charges in CP44 ring with a negative charge of the sulfonate group in ANS is operative.

Based on thermal parameters for the  $\beta$ -CD complexation, the inclusion processes were discussed in detail by Castronuovo et al. [20, 21]. Upon inclusion of  $\beta$ -CD, water molecules are released from the hydrophobic hydration shells to a bulk. The entropic term for inclusion processes is determined by the loss of degrees of freedom occurring

upon association and the relaxation of water molecules from the cavity. In water, the association process with  $\beta$ -CD is characterized by small and negative entropies, and compensatory enthalpy–entropy relationships exist for inclusion processes dominated by hydration phenomena [20, 21]. Negative enthalpies and entropies for  $\beta$ -CD and CP44 inclusions characterize inclusion systems where van der Waals interactions are dominant due to the tight fit of guest molecule to the host cavity, which is in agreement with the suggestions reported by Castronuovo et al. [20].

**Table 3** Cross peaks observed in ROESY-NMR spectra of inclusion complexes of ANS derivatives with CP44 in DCl–D<sub>2</sub>O solution

Guest	Guest protons	Host protons <sup>a</sup>				
		C(1)H	C(2)H	C(3)H	C(4)H	C(5)H
2,7-ANS	C(4)–H	–	–	–	++	++
	C(8)–H	–	–	+	++	++
	C(9)–H	+	–	+	–	–
2,6-ANS	C(3)–H	++	–	–	++	++
	C(4)–H	+	–	–	–	+
	C(5)–H	+	–	–	–	–
	C(2,7)–H	+	+	–	–	–
	C(8)–H	–	–	–	–	+
2,4,7-AHNS	C(5)–H	–	–	++	–	+
	C(6)–H	–	–	++	–	+
	C(8)–H	–	–	++	+	+
	C(3,9)–H	–	+	+	–	–
2,4,6-AHNS	C(3)–H	–	–	+	–	–
	C(7)–H	–	–	++	–	–
	C(9)–H	–	+	+	+	–

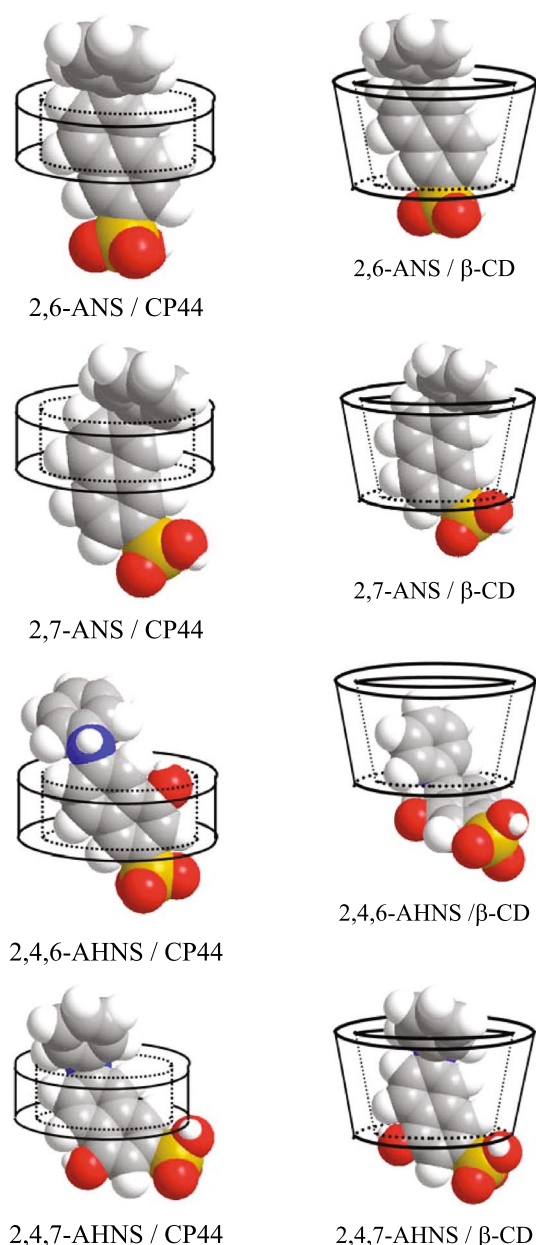


### Structures of inclusion complexes with CP44 and $\beta$ -CD

NMR measurements are informative to elucidate the structures of inclusion complexes with CP44 and  $\beta$ -CD. The induced chemical shifts of the guest protons indicate inclusion of the proton moiety into the CP44 and CD cavities. The  $^1\text{H}$ -NMR spectra of 2,7-ANS in the presence of  $\beta$ -CD and CP44 were shown in Fig. S2 in supplementary data. Larger induced shifts of ANS protons due to aromatic ring current effect were observed upon inclusion by CP44 compared with those by  $\beta$ -CD. For example, the C(8)–H proton of 2,7-ANS shifts upfield from 7.62 to 6.45 ppm upon inclusion by CP44. The large induced chemical shifts are in agreement with those reported for the inclusion of 2,7-dihydroxynaphthalene with paracyclophane [4].

2D ROESY-NMR experiments are useful to determine the position of the guest molecules inside CP44 and  $\beta$ -CD cavities. The relative intensities of the cross peaks for the inclusion complexes with  $\beta$ -CD and CP44 are listed in Tables 2 and 3, respectively [2D ROESY-NMR spectra were shown in supplementary data (Figs. S3–S6)]. In the inclusion of 2,7-ANS with  $\beta$ -CD, the cross peaks of C(1,4,5,6,8)–H protons in 2,7-ANS were observed with the inner C(3)–H and/

or C(5)–H of  $\beta$ -CD (Table 2), indicating that the naphthalene moiety of ANS was encapsulated inside the  $\beta$ -CD cavity. In CP44 inclusion, the C(3,4,5)–H protons of CP44 strongly interacted with C(4,8)–H protons of 2,7-ANS (Table 3). Cross peaks corresponding to protons in CP44 with the C(10,11)–H protons of anilino-group in 2,7-ANS were not detected. These show that the naphthalene moiety of 2,7-ANS is deeply encapsulated in the CP44 cavity. Based on these NMR results, the plausible structures of the inclusion complexes of ANS derivatives with CP44 and  $\beta$ -CD are depicted in Fig. 3. The results can be summarized as follows. (1) Given the interaction between the protons of the naphthalene moiety in ANSs and the ring protons of CP44 (Table 3), the naphthalene moiety is deeply encapsulated into the CP44 cavity. (2) In the inclusion of 2,6-ANS, 2,7-ANS, and 2,4,7-AHNSs by  $\beta$ -CD, the cross peaks arising from the C(5)–H proton of  $\beta$ -CD and the C(1,4,5,8)–H protons of ANSs were observed, indicating that the naphthalene moiety of ANS is included in the  $\beta$ -CD cavity. (3) In 2,4,6-AHNS/ $\beta$ -CD, the C(3)–H proton of  $\beta$ -CD strongly interacts with the C(6)–H proton in ANS, and the cross peak between the C(6)–H proton of  $\beta$ -CD and the C(1)–H proton in ANS is observed. This suggests that the 2,4,6-AHNS guest is deeply included from the anilino-phenyl group side in the  $\beta$ -CD cavity (reversed

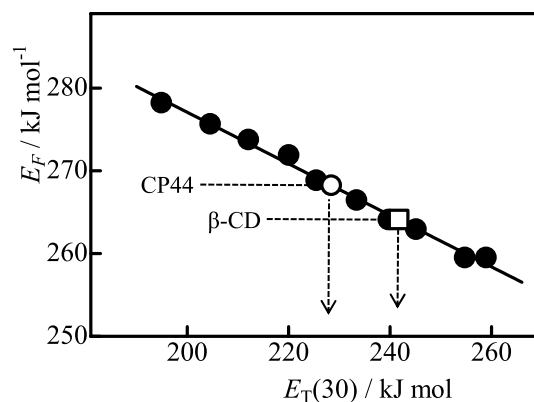


**Fig. 3** Structures of inclusion complexes of ANS derivatives with CP44 and  $\beta$ -CD based on 2D ROESY-NMR measurements

orientation for other ANSs), which is responsible for the interaction by the hydrophilic OH group. These observations suggest that CP44 molecular recognitions are insensitive compared with those of  $\beta$ -CD.

### Enhancement of fluorescence quantum yields

ANS is used as a polarity probe in various heterogeneous systems like proteins. Figure 4 shows the plots of the fluorescence emission energy of 2,7-ANS against the empirical solvent polarity parameter [ $E_T(30)$  value] in a



**Fig. 4** The relationship (closed circles) of the emission energy ( $E_F$ ) of 2,7-ANS in 1,4-dioxane-water mixtures against  $E_T(30)$  values. The local polarities were evaluated from the  $E_F$  values of 2,7-ANS inclusion complexes with CP44 (open circle) and  $\beta$ -CD (open rectangle)

**Table 4** The local polarity and  $\Phi_{\text{complex}}$  values of ANS inclusion complexes with  $\beta$ -CD and CP44 in an aqueous solution at 298 K

Guest	Host	$E_T(30)/\text{kJ mol}^{-1}$	$\Phi_{\text{complex}}$
2,6-ANS	—	—	$\sim 0$
2,6-ANS	$\beta$ -CD	236.3	$0.22 \pm 0.02$
2,6-ANS	CP44	240.2	$0.17 \pm 0.01$
2,4,6-AHNS	—	—	$0.031 \pm 0.001$
2,4,6-AHNS	$\beta$ -CD	251.4	$0.16 \pm 0.01$
2,4,6-AHNS	CP44	251.4	$0.17 \pm 0.01$
2,7-ANS	—	—	$0.047 \pm 0.001$
2,7-ANS	$\beta$ -CD	241.8	$0.16 \pm 0.01$
2,7-ANS	CP44	228.5	$0.24 \pm 0.01$
2,4,7-AHNS	—	—	$0.041 \pm 0.001$
2,4,7-AHNS	$\beta$ -CD	233.4	$0.12 \pm 0.01$
2,4,7-AHNS	CP44	243.9	$0.10 \pm 0.01$

1,4-dioxane-water mixture. The emission energy of 2,7-ANS decreases with increasing  $E_T(30)$  values for the solvent mixture. Using the fluorescent probe 2,7-ANS, the micro-environmental polarity inside the  $\beta$ -CD and CP44 cavities was shown in Fig. 4. The local polarities of 2,7-ANS in the  $\beta$ -CD and CP44 cavity were estimated to be 241.8 and 228.5  $\text{kJ mol}^{-1}$ , respectively. The local polarities of ANSs and AHNSs in  $\beta$ -CD and CP44 cavities are listed in Table 4. In the inclusion by  $\beta$ -CD, 2,4,6-AHNS incorporated from the phenyl group side shows high polarity, which is comparable to that by CP44. In the inclusion by CP44, 2,6-ANS and 2,4,7-AHNS are located in polar environment, compared with those by  $\beta$ -CD.

The quantum yields ( $\Phi$  values) of inclusion complexes were determined using an Otsuka fluorescence spectrometer and are given by the following equation.

$$\Phi_{\text{Complex}} = \frac{FP_{\text{Complex}}}{AP_{\text{Complex}}} = \frac{FP - FP_{\text{Guest}}}{AP - AP_{\text{Guest}}} \quad (3)$$

where FP and AP denote fluorescence photon number and excitation photon number of inclusion complex, free guest, and apparent solutions, respectively. FP and AP values of apparent and guest solutions were measured and the concentration of free guest ANS estimated using the above mentioned inclusion constant  $K$  (Table 1). The thus-obtained  $\Phi_{\text{complex}}$  values are listed in Table 4. The inclusion by CP44 and  $\beta$ -CD produces high enhancement in  $\Phi$  values, compared with  $\Phi$  values in aqueous solution. In inclusions of  $\beta$ -CD and CP44, the binding modes of 2,6-ANS, 2,7-ANS, and 2,4,7-AHNS are similar, but the of 2,4,6-AHNS is different. However, the  $\Phi$  values for  $\beta$ -CD inclusion of 2,4,6-AHNS is comparable to that of CP44 inclusion (Table 4). The inspection of Table 4 shows that the magnitude of  $\Phi$  values is related to the local polarity of ANSs and AHNSs in inclusion complexes. Kosower et al. previously reported that in polar solvent, ANS charge-transfer emission occurs and the increase of solvent polarity favors the quenching reaction [22]. This is in agreement with the above observations.

In summary, we have determined the inclusion constants of ANS derivatives with CP44 and  $\beta$ -CD. It was found that CP44 forms more stable 1:1 inclusion complexes with ANSs compared with those formed with  $\beta$ -CD. Based on the ROESY-NMR spectra of the inclusion complexes, the characteristic disposition of the guest molecules inside the CP44 and  $\beta$ -CD cavities could be confirmed. In the case of inclusion by CP44, the difference in inclusion modes for HO-induced AHNSs was not observed, and thus molecular recognition of CP44 occurs at a minor extent than that by  $\beta$ -CD. Finally,  $\Phi$  values for the inclusion complexes of ANSs with CP44 and  $\beta$ -CD were determined. Based on these values, we have suggested that the local polarity of ANS plays an important role for the difference observed in quantum yields.

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