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Short communication

TritonX-100 selective chemosensor based on β-cyclodextrin modified by anthracene derivative

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ABSTRACT

β-Cyclodextrin (CD) modified by 2-(9-anthracenecarboxamido)phenyl group (Ant-CD) was synthesized and their complexation behavior was investigated by UV and fluorescence spectroscopy. Fluorescence intensity of Ant-CD was dramatically enhanced *ca.* 10-fold by the addition of TritonX-100 (TX-100) in water below the critical micelle concentration. Ant-CD also showed *ca.* 4-fold fluorescence increasing in the addition of analogous materials, *n*-octylbenzenesulfonate in water. These results indicate that Ant-CD can act as a highly sensitive and selective chemosensor for TX-100. Ant-CD and TX-100 formed a pseudorotaxane supramolecular complex. This result was supported by ^{1}H–^{1}H NOESY NMR measurement.

1. Introduction

The detection of nonionic surfactant (NS) has been investigated as the most important topics in environmental chemistry. These NS families are regarded as environmental pollutants due to ecological toxicity of those materials [1,2] and their biodegradation intermediate [3]. Existing useful analytical methods for NS were combined with extraction [4], HPLC [5] and mass spectrometry [6]. However, these analytical techniques include many steps for pretreatment and require expensive instruments. Therefore, simple and rapid detection method for NS in wastewater is desired to establishing. Fluorescence detection of environmental material is largely investigated in chemical and biological studies [7,8]. Especially, cyclodextrin (CD) modified by a fluorescent substituent can give a useful analysis method for a rapid and reasonable detection [9–14]. Ueno et al. reported that fluorescence intensity of fluorescent moiety in CD based chemosensor was decreased with increase in addition of target materials, with displacement of fluorescent moiety from the inside to the outside of the CD cavity [15]. The fluorescence change was explained by twisted intramolecular charge transfer (TICT) quenching process which is prevented in the CD cavity.

Recently, we reported that 2-(9-anthracenecarboxamido) phenyl (ACP) compounds showed fluorescence quenching by TICT [16]. We have also developed new chemosensors based on linear polyether and crown ethers bearing those TICT detection moieties and other fluorescence quenching mechanisms such as photoinduced electron transfer (PET) [17–19]. In the absence of guest ions, these sensors showed weak emission as a result of TICT, although the complexation with guest ions enhanced their emission strongly. These results showed that twisted motion at an excited state can be controlled by the steric hindrance upon a molecular recognition event. To extend our research to new application, we synthesized novel fluorescent cylcodextrin modified by anthracene. It is expected that cyclodextrin and NS will form a pseudorotaxane type supramolecular structure in which a part of NS protrudes from the CD cavity. If the protruding part becomes a barrier of the twisting motion at the anthracene ring in the excited state, ACP moiety in the supramolecule will show fluorescence "Off–On" response (Fig. 1). The "Off–On" response have an advantage compared with "On–Off" type, since "Off–On" response have capability to improve signal to noise ratio due to no limitation of fluorescence intensity against the silent background, whereas maximum response of "On–Off" type is equal to the initial fluorescence intensity.

In this papar, we report a new "Off–On" type chemosensor bearing the TICT moiety, which is a new type of fluorescence-enhancing CD sensor based on TICT process at ACP moiety (Scheme 1). That makes a pseudorotaxane with long structured molecules such as

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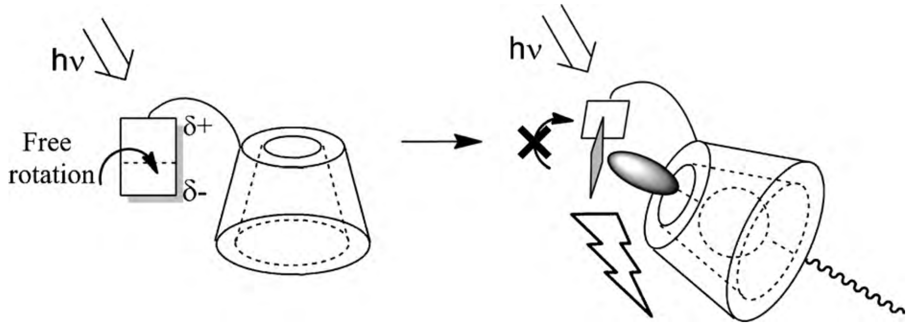


Fig. 1. Fluorescence switching by TICT-inhibiting process outside CD cavity in the presence of target material.

TX-100 used as guest molecules. We also consider that fluorescence moiety of this CD sensor will remain outside CD cavity in the presence and absence of target materials, the characteristic enables a selective fluorescence response for a specifically guest. These considerations will be clearly different from Ueno's work concept.

2. Experimental

2.1. Synthesis of Ant-CD

2.1.1. Preparation of 2-(9-anthracenecarboxamido)phenoxyacetic acid (**AntC**)

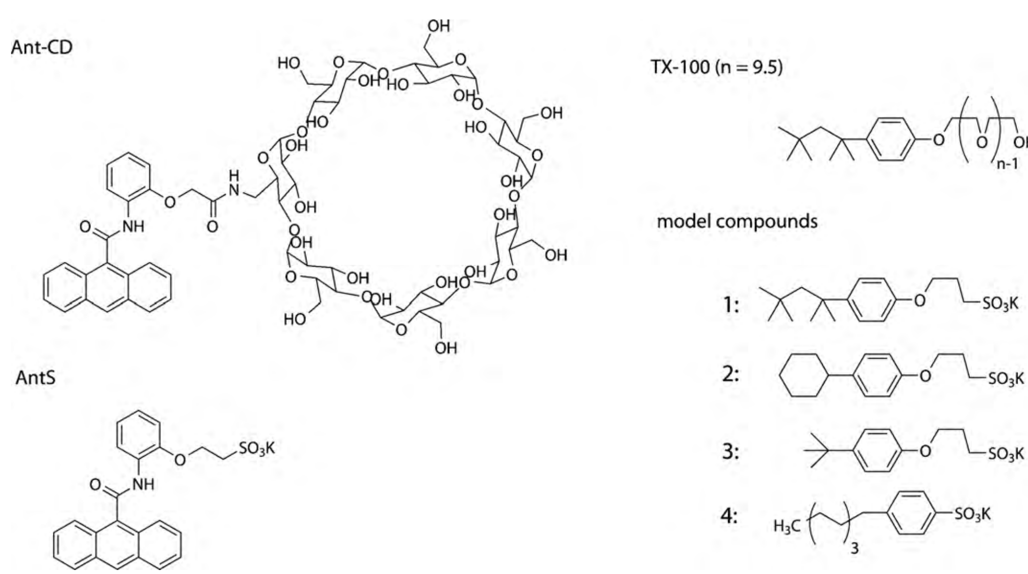
3.13 g (0.01 mol) of *N*-(2-hydroxyphenyl)-9-anthracenecarboxamide [19], 1.67 g (0.01 mol) of ethyl 2-bromoacetate and 1.23 g (0.011 mol) of potassium *tert*-butoxide were dissolved in 60 mL of DMF and stirred overnight at 95 °C. After precipitate was filtered off, the reaction mixture was evaporated under reduced pressure to the half volume. The solution was mixed with 30 mL of EtOH; then added 60 mL of NaOH containing 0.06 g (0.015 mol) aqueous solution and stirred for 3 h. After neutralization, the precipitate was collected by filtration, and recrystallized from EtOH (Scheme 2). Yield: 2.15 g (58%). Yellow solid. ^{1}H NMR (DMSO-d_6; δ from TMS) 4.74 (–CH_2–, s, 2H), 7.11 (aromatic, m, 2H), 7.24 (aromatic, t, 1H), 7.59 (aromatic, m, 4H), 8.01 (aromatic, dd, 1H), 8.15 (aromatic, d, 2H), 8.20 (aromatic, d, 2H), 8.70 (aromatic, s, 1H), 10.10 (–COOH, s, 1H).

2.1.2. Preparation of Ant-CD

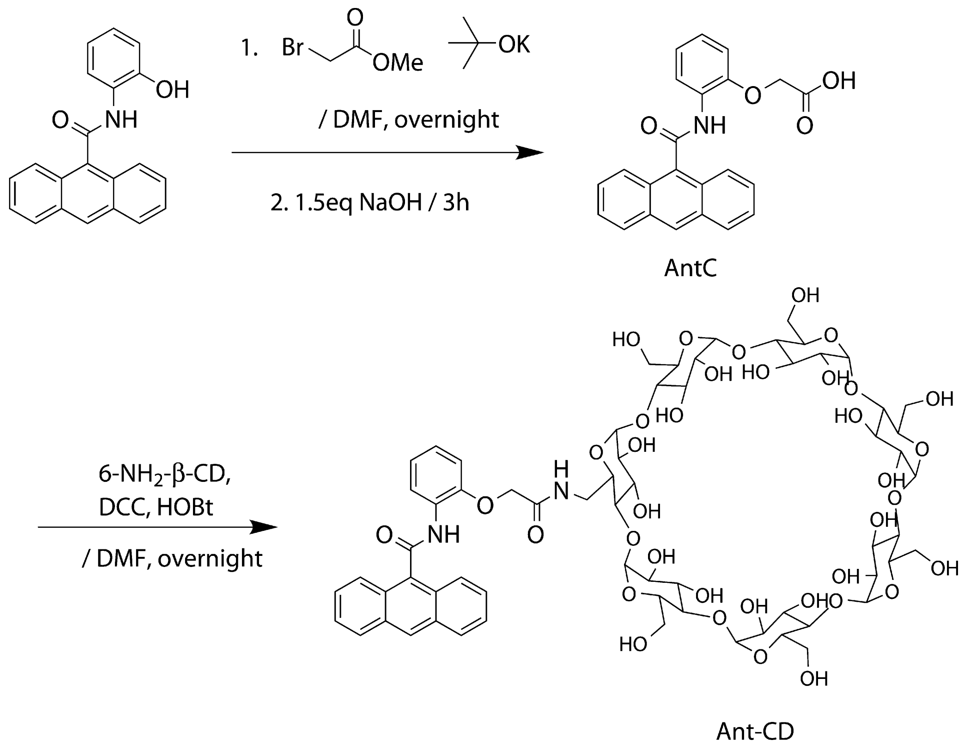
0.093 g (0.25 mmol) of **AntC**, 0.28 g (0.25 mmol) of mono-6-deoxy-6-amino-β-cyclodextrin [12] (6-NH_2-β-CD), 0.038 g (0.28 mmol) of 1-hydroxybenzotriazole (HOBt) and 0.058 g (0.28 mmol) of *N*,*N*′-dicyclohexylcarbodiimide (DCC) were dissolved in 10 mL DMF and stirred for 1 day at r.t. After the precipitate was removed by filtration, the filtrate was poured into acetone (50 mL) and the precipitate was collected. This crude compound (0.3 g) was purified by HPLC with an ODS column (eluent: MeOH:H_2O = 1:1) and dried *in vacuo* for 12 h at 90 °C. Yields: 0.10 g (27%). White solid. ^{1}H NMR (DMSO-d_6; δ from TMS), 2.80–3.75 (excluded overlap with H_2O region, br, ca. 32H), 4.27–4.33 (m, 2H), 4.41 (m, 4H), 4.57 (m, 2H), 4.71 (m, 2H), 4.79 (m, 2H), 4.82 (m, 3H), 7.09 (aromatic, t, 2H), 5.65 (–OH, m, 14H), 7.22 (aromatic, d, 1H), 7.57 (aromatic, d, 4H), 7.89 (aromatic, d, 1H), 7.94 (–CONH–, s, 1H), 8.15 (aromatic, d, 4H), 8.71 (aromatic, s, 1H), 10.39 (–CONH–, s, 1H). Found: C. 49.80%; H, 6.04%; N, 1.75%; calcd. for $C_{85}H_{94}N_2O_{41}\cdot 4H_2O$: C, 50.06%; H, 6.08%; N, 1.80%.

2.2. Spectrometeric measurement

TritonX-100 was obtained from Wako Pure Chemical Industrials, Ltd. and used without further purification. Fluorescence spectra were measured using a RF-5300PC (Shimadzu Corp.) spectrometer in distillated water at 25 °C. The excitation wavelength was set to 363 nm, unless described otherwise. The initial concentration of Ant-CD derivatives was 5 μM. TX-100 were added to a solution of Ant-CD as 1 mM of aqueous solution.



Scheme 1.



Scheme 2.

The [1]H NMR spectra for investigation of the complexation behavior between Ant-CD and TX-100 were measured at 30 °C (JNM-EX400; JEOL). The Ant-CD concentrations were 1 mM in D_2O.

3. Results and discussion

Fig. 2 portrays fluorescence spectra of Ant-CD in the absence and presence of TX-100 in water whose concentration was less than the critical micelle concentration (CMC: 0.2 mM) [20]. Fluorescence intensity from the anthracene moiety was weak in the absence of TX-100. In contrast, dramatically enhanced emission was observed by the addition of TX-100. A model compound for Ant-CD, potassium anthracenecarboxamidophenoxypropanesulfonate (AntS), showed slightly enhanced emission. This enhancement was attributed to the complex formation of Ant-CD with TX-100. The Ant-CD system can take two fluorescence emission states: the fluorescence "Off" state at the free form and the fluorescence "On" state at the complex form with guest compound. This fluorescence "Off–On" switching ability was expressed quantitatively as a fluorescence intensity ratio, I_{max}/I_0, where I_{max} and I_0 represent fluorescence intensities in the presence (I_{max}) and absence (I_0) of guest materials, respectively. The I_{max}/I_0 values were determined for various guests shown in Scheme 1, and they are listed in Table 1. In a previous investigation, this "Off–On" behavior was ascribed to TICT inhibition of the host molecule by the steric repulsion of guest species [17]. Guest materials **1–4** (**4**: sodium 4-*n*-octylbenzenesulfonate) were prepared to compare the effects of TICT inhibition based on the steric barrier of the hydrocarbon moiety.

The I_{max}/I_0 value of Ant-CD with **1** and TritonX-405 (TX-405; $n = 40$) was similar to that of TX-100, whereas those of complexes with **2**, **3**, and **4** were ca. 30% compared to TX-100. Moreover, the fluorescence intensity of Ant-CD was changed only slightly by the addition of polyethylene glycol 1000 (PEG; $I_{max}/I_0 = 1.1$). Those results suggest that the steric barrier of bulky hydrocarbons on the phenyl group dominantly affected the fluorescence enhancement behavior by TICT inhibition, although a hydrophilic moiety such as the polyoxyethylene group did not.

In view of viscosity and polarity, organic solvent effects on TICT behavior of Ant-CD were investigated by water–glycerin and water–dioxane mixed solvent systems. Fluorescence intensity of

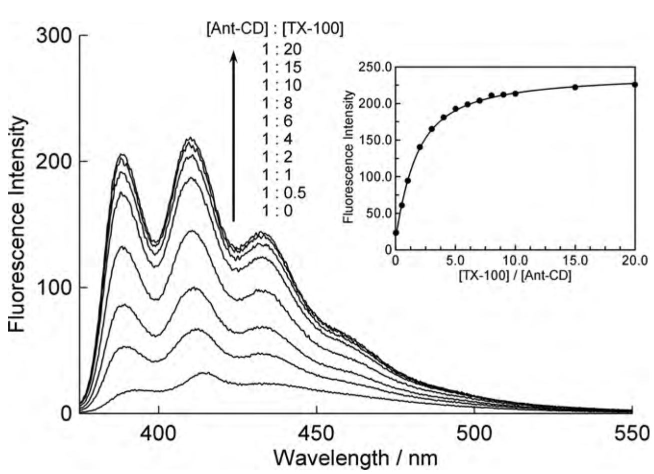


Fig. 2. Fluorescence spectra of Ant-CD and its TX-100 complex in water at 25 °C. Excitation wavelength: 363 nm. [Ant-CD] = 5 μM. Molar ratios for TX-100 are listed in columns. Inset: dependence of fluorescence intensity at 410 nm on the concentration of TX-100, and its theoretical curve for formation of stoichiometric 1:1 complex.

Table 1
Fluorescence responses (I_{max}/I_0) and complex formation constants (log *K*) of Ant-CD for various guest materials in water at 25 °C.

	TX-100	TX-405	**1**	**2**	**3**	**4**	AntS
I_{max}/I_0	9.8	9.5	9.2	2.7	2.0	2.3	1.1
log *K*[a]	5.20	5.02	5.24	4.46	3.98	3.84	–

[a] K = [complex]/([Ant-CD][guest]). The standard deviation of the log *K* was estimated to be ±0.03.

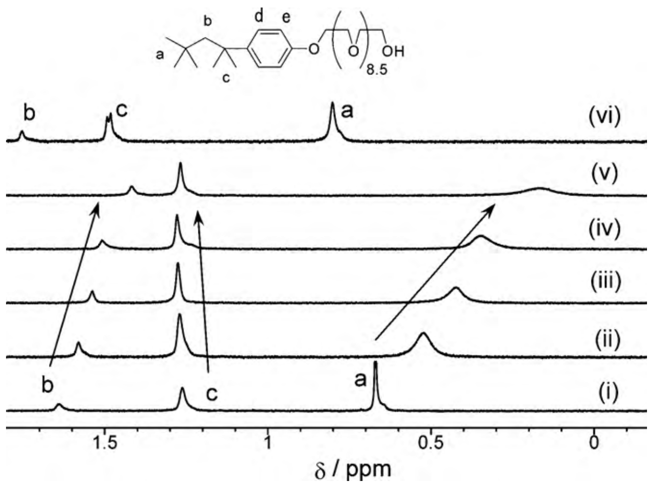


Fig. 3. ^{1}H NMR spectra of TX-100 before and after inclusion of into Ant-CD. (i) 0 mM, (ii) 0.3 mM, (iii) 0.5 mM, (iv) 0.7 mM, (v) 1.2 mM of Ant-CD with 1 mM of TritonX-100, and (vi) 1 mM of native β-CD with 0.5 mM of TX-100 in D_2O at 30 °C.

Table 2
^{1}H NMR chemical shifts (δ ppm) for 1 mM of TritonX-100 before and after complexation consist of Ant-CD and 0.5 mM of TritonX-100 with 1 mM of native β-CD.

	a	*b*	*c*	*d*	*e*
TX-100	0.67	1.64	1.26	7.22	6.82
Ant-CD with TX-100	0.17	1.42	1.27	7.17	6.88
Native β-CD with TX-100	0.80	1.75	1.48	7.37	6.99

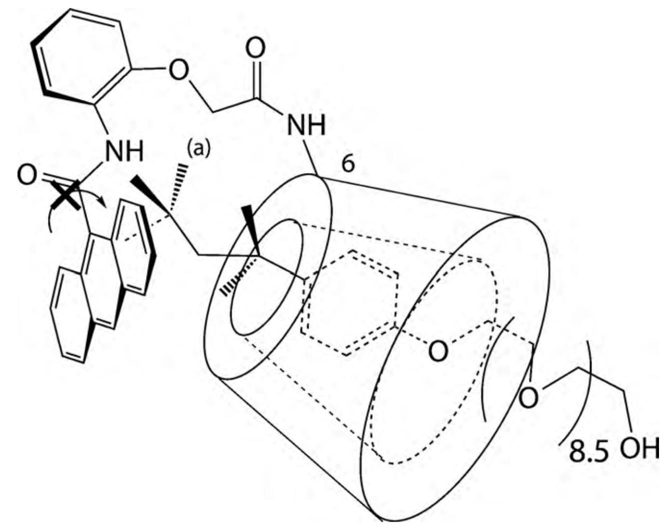


Fig. 4. Schematic representation of TICT inhibiting for ACP based on the pseudorotaxane type complexation between Ant-CD with TX-100.

Ant-CD was dramatically increased to 40-fold with increase of volume fraction of glycerin (see Supplementary data in Fig. S2). On the other hand, solvent polarity effect on Ant-CD was obtained in presence of dioxane fraction in solution (Fig. S3). Although the decrease of the solvent polarity causes fluorescence enhancement by decreasing the stability of the charge separated state, fluorescence intensity of Ant-CD was slightly changed compared to that of viscosity. These results indicate that the major effect on fluorescence enhancement of Ant-CD is the rotational suppression of the anthacenecarboxamido moiety by the viscosity.

The 1:1 complex formation constant log *K* was determined by nonlinear least-squares curve fitting method (Marquardt's method [21]) for the fluorescence intensity change. The obtained constants for various guest materials are presented in Table 1. The order of log *K* values for guest materials is nearly parallel to those of I_{max}/I_0 values. The good curve fitting (Fig. 2) suggests that the inclusion phenomenon for this system is dominantly a simple equilibrium as a 1:1 complex formation. The difference of the log *K* values of Ant-CD with various guest compounds have significant difference, which is TritonX-100 selectivity based on steric repulsion between the substituent moiety in CD and those guest.

To confirm these considerations, ^{1}H NMR measurement was performed. Model compound **1** was used to ^{1}H–^{1}H NOESY measurement because its complex can be prepared in sufficient concentration (10 mM) for 2D measurement. Compound **1** showed the same fluorescence response for TX-100. Then ^{1}H NMR spectral experiments of TX-100 and **1** were also conducted to consider the effect of micelle association concentrations below (0.1 mM) and over CMC (10 mM) in D_2O. However, no significant spectral difference was found between the two concentrations except for small peak broadenings on TX-100 ($\Delta\delta < 0.02$ ppm). Consequently, the effect on a chemical shift of TX-100 by micelle association is negligible at less than 10 mM. The ^{1}H NMR spectra were conducted in 1 mM of TX-100 with various concentrations of Ant-CD in D_2O (Fig. 3). Their peak assignment for free Ant-CD and TX-100 and their complexes were also conducted using ^{1}H–^{1}H COSY, NOESY, along with data referred from the literature [20]. Large chemical shift changes were observed on an edge moiety (a) of the branched alkyl group in TX-100 (Table 2). In contrast, chemical shift changes of TX-100 at complexation with native β-CD were smaller than those of TX-100 with Ant-CD [20]. This result demonstrates that a ring current by anthracene ring on CH_3 proton (a) at the complexation event. ^{1}H–^{1}H NOESY spectra of Ant-CD were obtained in the presence of **1** (see Supplementary data in Fig. S5). Correlation peaks between the CD moiety and the branched alkyl and phenyl group in **1** were observed. This finding strongly suggests that Ant-CD forms a pseudorotaxane type complex as elongate guests stick into CD cavity. Consequently, the TICT-inhibiting process in Ant-CD at the excited state is expected to have originated from steric interaction between the edge CH_3 proton (a) of branched alkyl groups in TX-100 and the anthracence ring in Ant-CD (Fig. 4).

4. Conclusion

Fluorescence response of Ant-CD was clearly controlled by TX-100 as a guest molecule below the critical micelle concentration (CMC) in water. Fluorescence intensity of Ant-CD·TritonX-100 was dramatically enhanced *ca.* 10-fold by effective inhibition of TICT. This response was selective for TritonX-100 compared with materials of linear molecules. The selective response between branched and linear alkyl group was ascribed to the bulkiness of *tert*-butyl group of TX-100 which caused an effective inhibition of TICT. The TICT controllable Ant-CD will provide a useful fluorescent cyclodextrin sensor for simple and rapid analysis, which supports a molecular-level insight into analytical applications of environmental materials.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.07.049.

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