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Determination of SDS Using Fluorescent γ-Cyclodextrin Based on TICT in Aqueous Solution

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Fluorescent γ-cyclodextrin derivatives, modified using *N*-phenyl-*x*-anthracenecarboxamido (**AC**s; $x = 9$, 1), were synthesized and investigated using fluorescence and UV-vis spectroscopy. Fluorescence enhancements of **AC**s were observed up to 12-fold by the addition of sodium dodecyl sulfate (SDS) below the critical micellar concentration (CMC). In the presence of a nonionic surfactant, such as Triton X-100, fluorescence spectra were scarcely changed. The fluorescence selectivity between SDS and Triton X-100 was clarified from the different spectral behaviors by circular dichroism and ^{1}H NMR spectroscopies.

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Introduction

Fluorescence detection using chemosensors has received attention for use in analytical fields because of its many advantages.[1,2] Especially, the simple composition of analytical equipment enables its use outdoors, yielding analytical results on-site.[3,4] Fluorescent chemosensors comprise a recognition moiety for catching target species and a fluorescent moiety that thereby changes its spectral shape;[5] various types for target species (cations, anions and ionic organic molecules) have been developed extensively in many laboratories.[6-13] To achieve the construction of an analytical system, many environmental samples should be regarded as existing in the aqueous dissolved state. Generally, recognition and fluorescence switching events in many chemosensors are driven by electrostatic interactions between a chemosensor and a target molecule.[5] However, a water solvent decreases the complexation capability of an ionic target through competition with hydration. Consequently, this limits the direct use of low-concentration samples in water. Moreover, a strongly reactive functional group in an organic material is demanded for sensing *via* a chemical reaction.[11-13] To date, the extraction of target species to an organic layer has been used as one application for environmental samples.[14] To address the problem described above, we introduced twisted intramolecular charge transfer (TICT) as a fluorescence-related switching mechanism.[15-18] The utilization of the TICT process enables fluorescence switching of a chemosensor by a degree of the steric barrier. It was reported that TICT was controlled by micellar aggregation[19] and the use of a viscous solvent.[20] Applications using the steric effect were also reported.[21,22] In previous papers, we described the synthesis of fluorescent β-cyclodextrin (β-**AC**) modified by 9-anthracenecarboxamidophenyl (9-AA) derivatives;[15] β-**AC** was demonstrated on a selective determination for Triton X-100 surfactant involving a bulky *tert*-butyl group. Weak fluorescence was emitted from free β-**AC** in water. In contrast, a remarkable enhancement of emission from 9-AA was observed to be ten-fold in the addition of Triton X-100 below a critical micellar concentration (CMC: 0.2 mM[23]). In the absence of Triton X-100, photoexcited 9-AA in β-**AC** induced free rotation around the amide bond with subsequent quenching of the fluorescence by charge transfer between the anthracene and phenyl moiety *via* π-conjugation. However, this rotation event, one TICT process, was suppressed upon complexation between β-**AC** with Triton X-100. This behavior results from the steric effect between 9-AA and the bulky *tert*-butyl group in Triton X-100 incorporated to the CyD cavity. Although solubilization of chemosensors in water is one requirement for direct use, hydrophobic chemosensors have provided a useful prototype for the development of practical chemosensors.

This report describes novel fluorescent γ-CDs (**AC**s) modified by 9-anthracenecarboxamido and 1-anthracenecarboxamido to detect a more "slender" surfactant than Triton X-100. As described above, the fluorescence spectral behavior of the AC system with surfactants is predisposed to the effects of steric structures of both elements. Consequently, the present study specifically examined alkyl groups in surfactants, substituent positions to CyD and in 9-AA, and types of CyDs.

Experimental

Synthesis of Ant-CyD and its analogs

Ant-CyD and its analogs were synthesized by the amide coupling of *x*-deoxy-*x*-monoamino-γ-cyclodextrin (*x*: 3 or 6) and *y*-(*z*-anthracenecarboxamido)phenoxyacetic acid (*y*: 2, 3;

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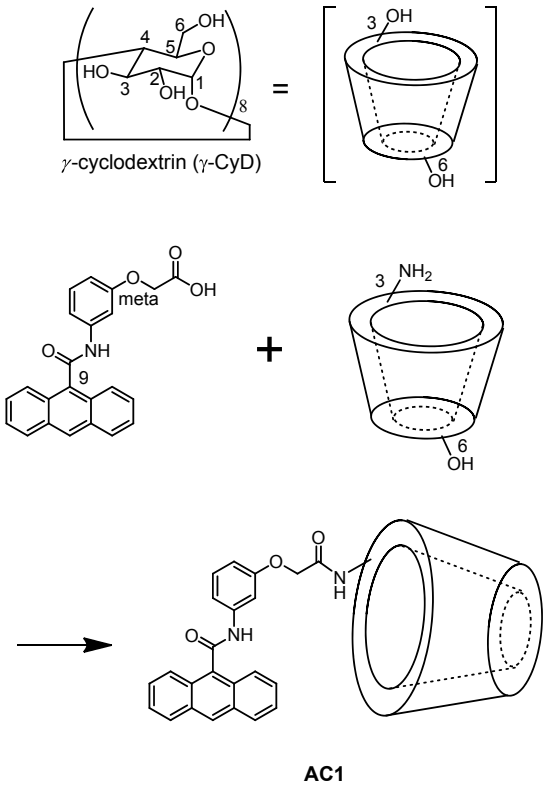


Scheme 1 Synthesis pathway of fluorescent γ-cyclodextrin, with **AC1** as a representative example. Table 1 shows the substituents of anthracene, phenyl, and glucopyranose rings (CyD) of **AC**s.

Table 1 List showing the substituents of anthracene, phenyl, and glucopyranose rings (CyD) of **ACs** in Scheme 1

	Anthracene	Phenyl	CyD
AC1	9	*meta*	3
AC2	9	*meta*	6
AC3	9	*ortho*	3
AC4	9	*ortho*	6
AC5	1	*meta*	3
AC6	1	*meta*	6
AC7	1	*ortho*	3
AC8	1	*ortho*	6

z: 1, 9) according to procedures described in a previous report.[15]

*3-Deoxy-[3-(9-anthracenecarboxamido)phenoxyacetamido]-γ-cyclodextrin (**AC1**).* Yield, 27.1%; light-yellow solid; m.p., 273 – 278°C; decomp. ^{1}H NMR (DMSO-d_6 δ from TMS) 3.22 – 3.76 (including overlapping with a H_2O peak br, *ca*. 36H), 4.40 – 4.59 (br, 8H), 4.72 (m, 2H), 4.91 (m, 7H), 5.48 – 5.90 (–OH, m, 16H), 6.81 (aromatic, d, 1H), 7.32 (aromatic, t, 1H), 7.41 (aromatic, d, 1H), 7.58 (aromatic, m, 5H), 8.00 (aromatic, –CONH–, m, 3H), 8.18 (aromatic, d, 2H), 8.74 (aromatic, s, 1H), 10.83 (–CONH–, s, 1H). Found: C, 49.14; H, 6.07; N, 1.65. Calcd. for $C_{71}H_{96}N_2O_{42}\cdot 4H_2O$: C, 49.53; H, 6.09; N, 1.63.

*6-Deoxy-6-[3-(9-anthracenecarboxamido)phenoxyacetamido]-γ-cyclodextrin (**AC2**).* Yield, 12.5%; light-yellow solid; m.p., 272 – 276°C; decomp. ^{1}H NMR (DMSO-d_6 δ from TMS) 3.20 – 3.90 (including overlapping with a H_2O peak br, *ca*. 50H), 4.42 – 4.58 (–OH, C–H, m, 9H), 4.82 – 4.95 (m, 8H), 5.62 – 5.90 (–OH, m, 16H), 6.77 (aromatic, d, 1H), 7.32 (aromatic, t, 1H), 7.43 (aromatic, d, 1H), 7.59 (aromatic, m, 5H), 7.87 (–CONH–, t, 1H), 8.00 (aromatic, d, 2H), 8.18 (aromatic, d, 2H), 8.74 (aromatic, s, 1H), 10.85 (–CONH–, s, 1H). Found: C, 49.45; H, 5.93; N, 1.68. Calcd. for $C_{71}H_{96}N_2O_{42}\cdot 4H_2O$: C, 50.06; H, 6.04; N, 1.64.

*3-Deoxy-3-[2-(9-anthracenecarboxamido)phenoxyacetamido]-γ-cyclodextrin (**AC3**).* Yield 15.3%; light-yellow solid; m.p., 273 – 277°C; decomp. ^{1}H NMR (DMSO-d_6 δ from TMS) 3.20 – 3.90 (including overlapping with a H_2O peak br, *ca*. 43H), 4.38 – 4.99 (–OH and C–H, m, 21H), 5.47 (d, 2H), 5.57 – 5.85 (–OH, m, 16H), 7.15 (m, 2H), 7.23 (aromatic, m, 1H), 7.59 (aromatic, m, 4H), 8.03 (–CONH–, aromatic, m, 2H), 8.16 (aromatic, t, 4H), 8.70 (aromatic, s, 1H), 10.11 (–CONH–, s, 1H). Found: C, 49.19; H, 5.94; N, 1.67. Calcd. for $C_{71}H_{96}N_2O_{42}\cdot 4H_2O$: C, 50.06; H, 6.04; N, 1.64.

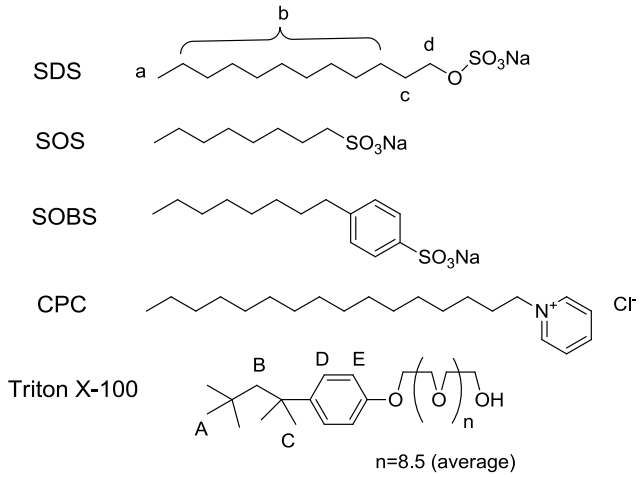
*6-Deoxy-6-[2-(9-anthracenecarboxamido)phenoxyacetamido]-γ-cyclodextrin (**AC4**).* Yield, 21.4%; light-yellow solid; m.p., 273 – 277°C; decomp. ^{1}H NMR (DMSO-d_6 δ from TMS) 2.90 – 3.72 (including overlapping with a H_2O peak br, *ca*. 38H), 4.35 – 4.47 (m, 8H), 4.63 (m, 2H), 4.73 (m, 2H), 4.87 (m, 6H), 5.50 – 5.92 (–OH, m, 16H), 7.09 (aromatic, t, 2H), 7.25 (aromatic, t, 1H), 7.58 aromatic, (m, 4H), 7.87 (aromatic, d, 1H), 8.03 (aromatic, –CONH–, t, 1H), 8.15 (aromatic, d, 4H), 8.71 (aromatic, s, 1H), 10.41 (–CONH–, s, 1H). Found: C, 49.86; H, 6.02; N, 1.65. Calcd. for $C_{71}H_{96}N_2O_{42}\cdot 3H_2O$: C, 50.06; H, 6.04; N, 1.64.

*3-Deoxy-[3-(1-anthracenecarboxamido)phenoxyacetamido]-γ-cyclodextrin (**AC5**).* Yield, 20.0%; light-yellow solid; m.p., 273 – 278°C; decomp. ^{1}H NMR (DMSO-d_6 δ from TMS) 3.20 – 3.98 (including overlapping with a H_2O peak br, *ca*. 51H), 4.38 – 5.02 (–OH, C–H, m, 17H), 5.42 – 5.94 (–OH, m, 16H), 6.79 (aromatic, d, 1H), 7.30 (aromatic, t, 1H), 7.43 (aromatic, br, 1H), 7.58 (aromatic, m, 4H), 7.77 (aromatic, d, 1H), 8.01 (aromatic, d, 1H), 8.13 (aromatic, t, 2H), 8.26 (aromatic, d, 1H), 8.70 (aromatic, s, 1H), 8.86 (aromatic, s, 1H), 10.61 (–CONH–, s, 1H). Found: C, 49.57; H, 6.10; N, 1.64. *Anal*. Calcd. for $C_{71}H_{96}N_2O_{42}\cdot 4H_2O$: C, 49.53; H, 6.09; N, 1.63.

*6-Deoxy-6-[3-(1-anthracenecarboxamido)phenoxyacetamido]-γ-cyclodextrin (**AC6**).* Yield, 20.5%; light-yellow solid; m.p., 272 – 277°C; decomp. ^{1}H NMR (DMSO-d_6 δ from TMS) 3.21 – 3.80 (including overlapping with a H_2O peak br, *ca*. 51H), 4.40 – 4.58 (–OH, C–H, 9H), 4.90 (m, 8H), 5.62 – 5.90 (–OH, 16H), 6.75 (aromatic, d, 1H), 7.30 (aromatic, t, 1H), 7.45 (aromatic, d, 1H), 7.58 (aromatic, m, 4H), 7.77 (aromatic, d, 1H), 7.84 (–CONH–, t, 1H), 8.13 (aromatic, t, 2H), 8.25 (aromatic, d, 1H), 8.69 (aromatic, s, 1H), 8.85 (aromatic, s, 1H), 10.63 (–CONH–, s, 1H). Found: C, 49.45; H, 5.93; N, 1.68. Calcd. for $C_{71}H_{96}N_2O_{42}\cdot 3H_2O$: C, 50.06; H, 6.04; N, 1.64.

*3-Deoxy-3-[2-(1-anthracenecarboxamido)phenoxyacetamido]-γ-cyclodextrin (**AC7**).* Yield, 13.7%; light-yellow solid; m.p., 272 – 276°C; decomp. ^{1}H NMR (DMSO-d_6 δ from TMS) 3.10 – 4.10 (including overlapping with a H_2O peak br, *ca*. 51H), 4.40 – 4.98 (–OH, C–H, m, 17H), 5.38 – 5.92 (–OH, m, 17H), 7.16 (aromatic, m, 3H), 7.55 (aromatic, m, 2H), 7.60 (aromatic, t, 1H), 7.93 (aromatic, d, 1H), 8.03 (aromatic, d, 1H), 8.13 (aromatic, –CONH–, br, 3H), 8.26 (aromatic, d, 1H), 8.69 (aromatic, s, 1H), 9.01 (aromatic, s, 1H), 9.85 (aromatic, s, 1H). Found: C, 48.87; H, 6.05; N, 1.65. *Anal*. Calcd. for $C_{71}H_{96}N_2O_{42}\cdot 4H_2O$: C, 49.53; H, 6.09; N, 1.63.

*6-Deoxy-6-[2-(1-anthracenecarboxamido)phenoxyacetamido]-γ-cyclodextrin (**AC8**).* Yield, 25.7%; light-yellow solid; m.p., 273 – 278°C; decomp. ^{1}H NMR (DMSO-d_6 δ from TMS) 2.98 – 4.00 (including overlapping with a H_2O peak br, *ca*. 52H), 4.46 – 4.89 (–OH, C–H, m, 17H), 5.64 – 5.92 (–OH, m, 16H),



Scheme 2 Structures of guest compounds. Alphabets on hydrogens in guest compounds corresponding to assignments for ^{1}H NMR measurements.

7.08 (aromatic, d, 2H), 7.19 (aromatic, t, 1H), 7.56 (aromatic, t, 2H), 7.61 (aromatic, t, 1H), 7.86 (aromatic, d, 1H), 8.04 (aromatic, d, 1H), 8.12 (aromatic, –CONH–, m, 3H), 8.25 (aromatic, d, 1H), 8.68 (aromatic, s, 1H), 8.99 (aromatic, s, 1H), 10.09 (-CONH–, s, 1H). Found: C, 49.84; H, 6.05; N, 1.68. Calcd. for $C_{71}H_{96}N_2O_{42}\cdot 4H_2O$: C, 49.53; H, 6.09; N, 1.63.

Measurement of fluorescence, UV-vis and circular dichroism (CD) spectra

Fluorescence spectra were monitored (RF-5300; Shimadzu Corp.) in distilled water at 25°C. The excitation wavelength was 363 nm. The sample solution containing guest molecules (Scheme 2) was dropped sequentially in 5 μM **ACs** aqueous solution in all cases. UV-vis spectra were also observed (UV-2400PC; Shimadzu Corp.) under the same conditions using fluorescence measurements. Circular dichroism spectra examinations were conducted (J-720; Jasco Corp.) with both 10 and 100 μM concentrations of Ant-CyD under N_2 gas at r.t.

^{1}H NMR measurement

The ^{1}H NMR spectra for guest molecules with **AC**s were measured at 30°C (JNM-Ex400; JEOL). **AC**s concentrations were 0.5 mM in D_2O. The chemical shift reference used sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an external standard.

Results and Discussion

Fluoresence spectra

Figure 1 shows fluorescence spectra of **AC1** and its complexes with SDS below the critical micellar concentration (CMC: 8.7 mM)[24] in water. Weak fluorescence of **AC1** was obtained in the absence of SDS. In contrast, a dramatic fluorescence enhancement was observed upon the addition of SDS, which rose 12-fold. CyD lacked a model for **AC1**, potassium 3-(3-(9-anthracenecarboxamido)phenoxy)propanesulfonate, which showed only a 1.1-fold fluorescent enhancement with 8 mM of SDS. Consequently, this result clearly indicates that a fluorescence enhancement of **AC1** results from complexation between its CyD cavity and SDS. On the other hand, nonionic surfactant Triton X-100 (CMC: 0.2 mM) was slightly changed

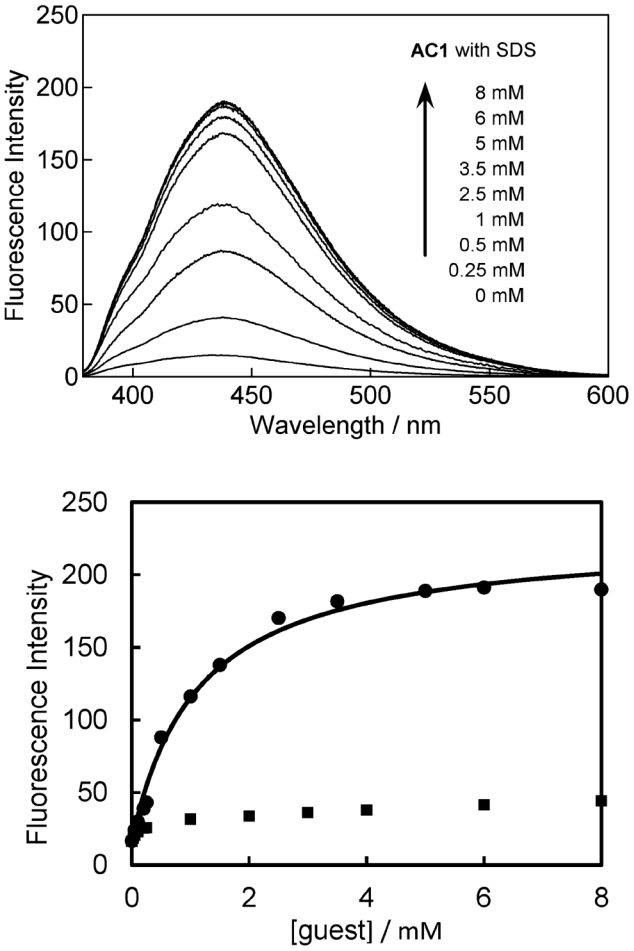


Fig. 1 Fluorescence spectra of **AC1** and its complex with SDS (upper), and dependence of the fluorescence intensity at 438 nm on the concentration of SDS (circle dots) and Triton X-100 (cubic dots) in water at 25°C (lower). SDS and Triton X-100 were added to 5 μM of **AC1** solution. Excitation: 369 nm. Theoretical curve for formation of stoichiometric 1:1 complex under CMC.

at the same concentration with SDS. To investigate this guest selectivity, structurally different analogs of SDS were used. Sodium octanesulfonate (SOS), sodium octylbenzenesulfonate (SOBS), and cetylpyridinium chloride (CPC) have a straight alkyl group as a hydrophobic moiety. Triton X-100 involved a branched alkyl group, which selectively induced an enhancement of β-**AC** fluorescence among those guests. The fluorescence response ratio (I_{max}/I_0) was defined by the fluorescence intensity of a free **AC** (I_0), and upon complete complexation (I_{max}) of that with a guest molecule below CMC. For **AC1**, and **AC5**, higher I_{max}/I_0 values were obtained for SDS and SOBS than others (Fig. 2). In the β-**AC** system, fluorescence emission of the 9-AA in the addition of Triton X-100 is enhanced selectively by about four-fold. However, I_{max}/I_0 values of **AC1** with SDS were about five-fold higher than for bulky molecules, such as Triton X-100. This opposite result to that obtained in our previous study suggests that the complex conformation of **AC** with a guest molecule differs from that of β-**AC**. Moreover, guest selectivity of **AC**s also appeared among linear alkyl compounds, which demonstrates that the **AC** system can exclude structurally similar guests accurately by a steric factor, such as molecular length or bulkiness of alkyl groups.

Other **AC** analogs (**AC2** – **4**, **AC6** – **8**) were also investigated

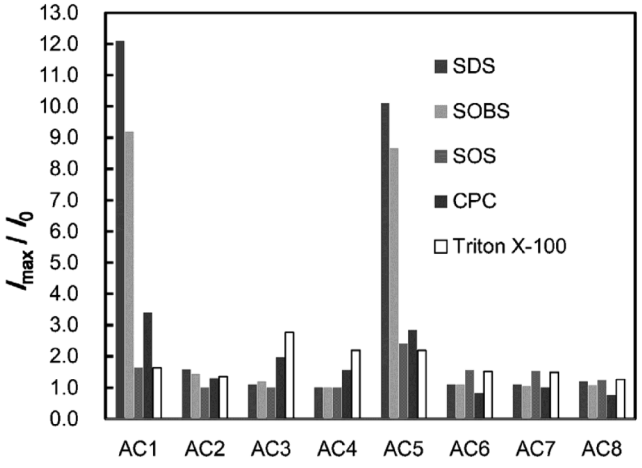


Fig. 2 Fluorescence response ratio (I_{max}/I_0) of **AC**s and its complexes with guest molecules in water at 25°C. [**AC**s] = 5 μM; excitation, 369 nm.

Table 2 1:1 complex formation constants (log *K*) of **AC**s with various guest compounds in water at 25°C

	SDS	SOS[a]	SOBS	CPC	Triton X-100
AC1	3.47	—	2.98	3.79	3.85
AC5	3.16	—	3.07	4.05	3.98

a. This value was not evaluated because of poor change of fluorescence intensity.

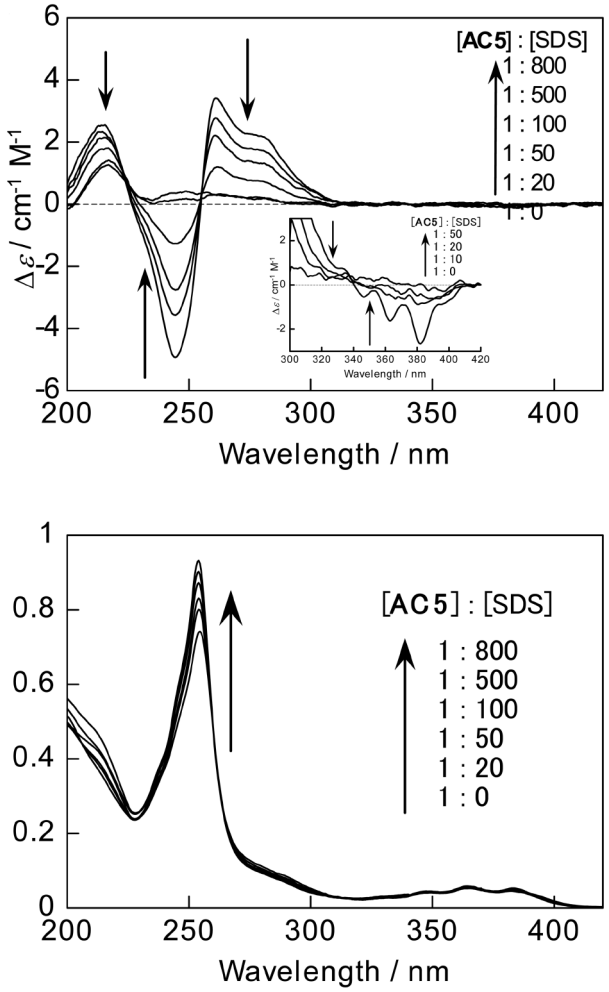


Fig. 3 ICD (upper) and UV-vis (lower) spectra of **AC5** and its complex with SDS in water at r.t. SDS is added to 10 μM of **AC5** solution below CMC. Inset: ICD spectra of 100 μM of **AC5** and its complex with SDS in water at r.t.

to discuss steric effects of host molecules. The type and position of the substituent group on a CyD skeleton are widely known to affect the chemical properties of CyD strongly, such as inclusion capability and selectivity for guest species. From this viewpoint, substituent positions on aromatic rings in the 9-AA, phenyl and hydroxyl group on the CyD skeleton were specifically examined. It is particularly interesting that those **AC**s only weakly responded to any guest compound. This result confirmed that TICT suppression of **AC** results for a steric hindrance between 9-AA, and the guest occurs not only by inclusion events in the CyD cavity.

Complex formation constant (log K) and limit of detection (LOD)

The complexation ability of **AC**s with surfactants is an important parameter to investigate fluorescent reagents. Complex formation constants (log *K*) of **AC1** and **AC5** were calculated using nonlinear least-squares curve fitting (Marquardt's method)[25] below CMC. The obtained log *K* values are presented in Table 2, and calibration curves are shown in Figs. S1 and S3 (Supporting Information). Good fitting of the theoretical curve for experimental data indicates that the process between an **AC** and a guest molecule is dominated strongly by simple equilibrium as the inclusion process of a guest molecule into the cyclodextrin cavity. No **AC**s, except **AC1** and **AC5**, yielded reliable log *K* values for any guest, because of the low I_{max}/I_0 values or weak complexation ability. The complexation ability for Triton X-100 superficially seems inconsistent fluorescence selectivity for SDS of **AC1** and **AC5**. However, a fluorescence efficient enhancement by SDS clearly takes priority of Triton X-100 at the same concentration (Figs. 1, S1 and S3). Thus, the fluorescence selectivity is mainly dominated by the difference of the I_{max}/I_0 values between SDS and Triton X-100.

The limit of detection (LOD) value for SDS is estimated to be 0.4 μM (0.12 ppm), as follows: a margin of error for the fluorescence intensity is calculated as a standard deviation (SD) of the background noise obtained from 10 times measurements of a blank solution. The three-folds of the regards LOD and converted into SDS concentration from the calibration curve between **AC1** and SDS (Fig. S1). We consider that the LOD values can be further enhanced by optimization of the experimental condition. The development of LOD is proceeding.

Circular dichroism (CD) spectrum measurement

An induced circular dichroism (ICD) spectrum is observed for an aromatic chromophore onto the CyD cavity axis through the narrow or wide rim of a CyD.[26-31] It supports the clarification of those complex structures.[32-35] Figure 3 shows induced circular dichroism (ICD) and UV-vis spectra of **AC5** (10 and 100 μM) in aqueous solution with 0 – 8 mM of SDS. An asymmetrically split Cotton effect of the ICD spectrum was observed for free **AC5** in the region of 240 – 260 nm. This result clearly illustrates the exciton interaction between anthracene and the phenyl moiety existing on the CyD cavity axis. Consequently, their split peaks decreased concomitantly with increasing SDS

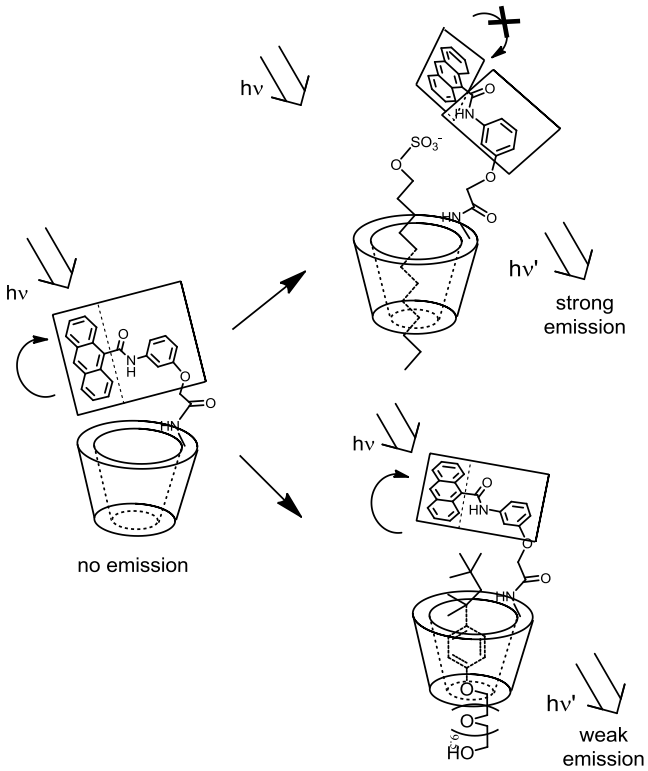


Fig. 4 Schematic representation of TICT suppression by complexation between **AC1** and SDS.

concentration. This behavior suggests that 9-AA of **AC5** faded out from the CyD cavity axis by a steric repulsion with **AC5**·SDS formation. The signal at the 340 – 380 nm region, which shows ICD peaks of the anthracene moiety, disappeared with increasing SDS concentration, which supports the consideration described above. In ICD spectra of **AC1**, the appearance and disappearance of the asymmetrically split Cotton effect also occurred before and after the addition of SDS in a short-wavelength region (200 – 300 nm). However, the ICD peak in the region of long wavelength changed only slightly in any SDS concentration range (0 – 8 mM), which indicates that the 9-anthracene moiety of **AC1** more closely resembles SDS than it resembles **AC5** upon complexation. This structure of the complex is advantageous for effective TICT suppression by 9-anthracene in **AC1** with a short rotation radius compared to that of 1-anthracene in **AC5** (Fig. 4).

For Triton X-100, as a low-responsive guest, ICD spectra of both **AC1** and **AC5** changed similarly, increasing along with the Triton X-100 concentration (see Supporting Information). However, the ICD signal did not disappear completely in the region of 240 – 260 nm. The spectral residue of **AC1** and **AC5** indicates that 9-AA exists in the position of the ICD effective column on the complex with Triton X-100. For weakly responsive hosts for any guests, the asymmetrically split Cotton effect of the ICD spectra was scarcely changed (**AC7**), or was not observed (**AC2** – **4**, **AC6** and **AC8**) in the absence and presence of SDS (see Supporting Information). ICD spectra behaviors among a series of **AC**s corresponded to a low fluorescence response. Consequently, these results showed that the conformation of 9-AA on the CyD scaffold is not sufficient for the steric repulsion for TICT inhibition upon complexation. As explained above, a suitable structure of **AC**s for the detection of SDS needs that anthracene and benzene rings in 9-AA are initially oriented on the CyD axis, and that a move to a conformational change will arise during complex formation with SDS.

Table 3 ^{1}H NMR chemical shift changes[a] ($\Delta\delta$ ppm) of guest molecules before and after complexation by **AC1**, **AC5**, and native γ-CyD

		a	b	c	d	
SDS	**AC1**	0.09	0.2	0.14	0.1	—
	AC5	0.1	0.29	0.26	0.18	—
	Native γ-CyD	0.02	0.01	–0.04	–0.04	—
		A	B	C	D	E
Triton X-100	**AC1**	0.14	0.13	0.21	0.09	0.17
	AC5	0.06	0.11	0.08	0.24	0.14

a. Positive values show higher field shifts.

^{1}H NMR measurement

Proton NMR spectroscopy has been used for the investigation of complex conformations between host and guest molecules. The chemical shift changes ($\Delta\delta$) of SDS and Triton X-100 were measured in both the absence and presence of **AC1** (including 9-AA) and **AC5** (including 1-AA) as hosts. The obtained values are presented in Table 3. High field chemical shift changes were observed on all protons of alkyl group (a – c) in SDS ($\Delta\delta$ = 0.09 – 0.26) and Triton X-100 hydrophobic moieties ($\Delta\delta$ = 0.13 – 0.21). They are attributed to a ring current effect on the aromatic ring in both **AC**s by approaching 9-AA and 1-AA with those protons in guests. In contrast, lower field shifts of alkyl protons in guests were observed for native γ-CyD as a host, which confirms that a high-field shift was induced by the interaction between hydrophobic protons in guests and aromatic rings in **AC**s.

Structural details of the complex were investigated further using the CPK model. The revealed conformations are portrayed in Fig. 4. The 9-AA and 1-AA moieties in the hosts were thrown up by the elongated SDS projected from the CyD cavity. Rotations of those excited moieties were inhibited. A hydrogen bond can assist an approach of SO_3^- in SDS to the 9-AA and 1-AA moiety. However, Triton X-100 incorporated by **AC**s was covered over by the 9-AA moiety on the CyD cavity axis. Free rotation of excited 9-AA remains possible. The interpretation presented above for the complexation behavior is consistent with results obtained from a CD spectral study. Consequently, the fluorescence response selectivity between SDS and Triton X-100 will reflect the steric difference from the host-guest complex structure.

Conclusions

Fluorescence emission of *N*-phenyl-*x*-anthracenecarboxamido-γ-CyD derivatives (**AC**s; x = 9, 1) was enhanced selectively and strongly by sodium dodecyl sulfate (SDS) in several surfactants below the critical micellar concentration. The fluorescence enhancement efficiency was found to be related to substituent positions among **AC**s. An asymmetrically split Cotton effect in ICD spectra was observed in suitable combinations of **AC** substituents. ^{1}H NMR spectra measurements and CPK model investigation revealed that the fluorescence selectivity between SDS and Triton X-100 in **AC1** and **AC5** originates from the difference of the host-guest complex structure. The findings of

this study expand the application of the fluorescent chemosensors based on twisted intramolecular charge transfer.

Supporting Information

Chemical structure details of **AC1** – **AC8**, CD spectra and ^{1}H-NMR spectra of host-guest complex. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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