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Molecular Recognition by Cyclophane/Guanidinium Supramolecular Receptor Embedded at the Air–Water Interface

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In order to develop a supramolecular receptor through a self-assembling process, a site-specific host and an inclusion-type host were mixed as a Langmuir monolayer, and guest binding and pressure-induced fluorescence emission were investigated. A guanidinium amphiphile and several cyclophanes carrying hydrophobic moieties were used as the host molecules; molecular recognition of an aqueous fluorescent guest, 6-*p*-toluidino-2-naphthalenesulfonic acid (TNS) by binary mixed receptor monolayers was evaluated by a surface pressure–molecular area (π–A) isotherm and a surface fluorescence measurement. An apparent increase in fluorescence intensity was observed when the mixed monolayers of the guanidinium and cyclophane amphiphiles were compressed on an aqueous TNS solution. In contrast, single-component monolayers of the guanidinium or the cyclophane did not show a significant increase in fluorescence emission. In the mixed monolayers, the guest TNS would be bound to the interface by strong electrostatic interaction with the guanidinium, and inclusion of the formed complex probably suppresses the quenching effect in polar medium and/or self-quenching. Experiments with various mixing ratios of these components suggest selective formation of an equimolar cooperative receptor of the guanidinium and the cyclophane. Investigation of the cyclophane structures by fluorescence emission and a competitive binding experiment with another guest were also carried out.

Keywords: Molecular recognition; Air–water interface; Cyclophane; Guanidinium; Surface fluorescence

INTRODUCTION

Molecular recognition and related functions expressed by proteins have incredible specificity and efficiency that results from a sophisticated arrangement of amino acid residues. The protein interior, *e.g.* with an enzymatic reaction pocket, provides a rather nonpolar microenvironment where well-organized receptor functional groups can form strong interactions such as hydrogen bonding and electrostatic interaction. In order to mimic the biological recognitions, artificial receptors bearing active sites in a pocket- or cleft-like cavity have been extensively developed [1–11]. However, preparation of bio-like elegant receptors by a purely synthetic approach is undoubtedly difficult.

Instead, multi-functional receptor sites would be built in an easier way through a supramolecular concept. Functional parts that have different roles can be spontaneously assembled as molecular assemblies. Langmuir monolayers at the air–water interface provide especially advantageous media for supramolecular-type receptors, because the functional receptor molecules are confined in a limited two-dimensional plane and can be associated with the reduced probability of the assembling variety. In addition, the air–water interface is known to be a relatively nonpolar medium where molecular recognition is effectively promoted [12–18]. Enhanced binding constants have been reported for various recognition systems, which were also theoretically interpreted by a quantum chemical approach [19,20].

Biological receptors often combine two major recognition mechanisms which are discrimination of guest shape and binding to specific sites. In this study, these functions are divided between two molecules and are reconstituted at the air–water

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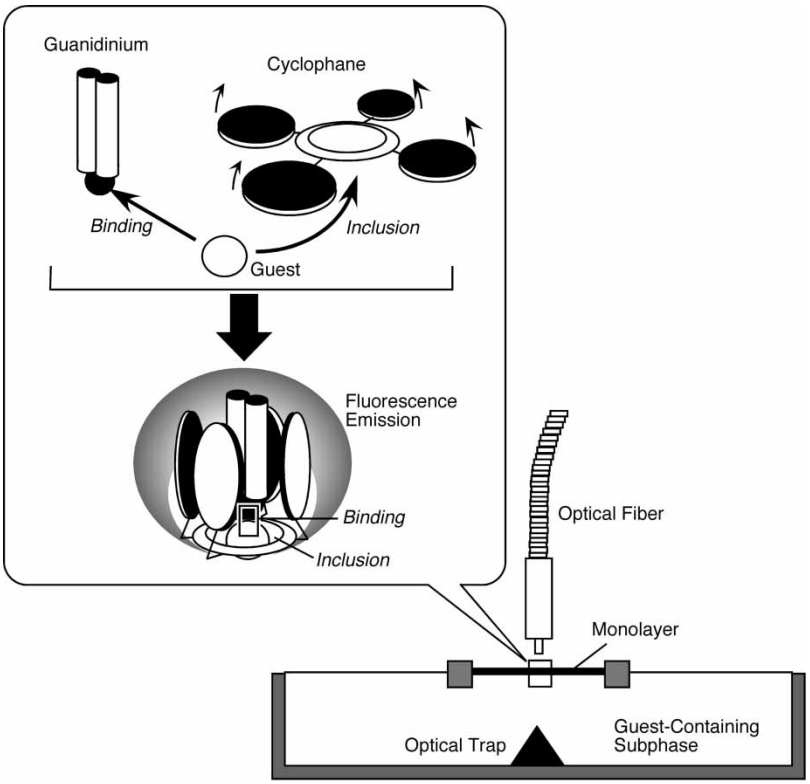

FIGURE 1 Schematic illustration of cooperative recognition by two host components (guanidinium and cyclophane) and the detection system for recognition-induced fluorescence emission at the air–water interface.

interface. Recognition systems and structures of the host molecules used are drawn in Figs. 1 and 2, respectively. Cyclophanes carrying hydrophobic moieties were used as shape-recognition-type hosts. These amphiphilic macrocycles are known to accommodate naphthalene-type guest molecules in bulk and membrane phases [21–23]. The host binding to a specific guest site is a dialkyl-type guanidinium. Amphiphilic guanidiniums at the air–water interface were reported to bind acidic groups with an incredibly high binding constant [24–26]. Mixtures of the two types of host were spread on a subphase containing a guest (6-*p*-toluidino-2-naphthalenesulfonic acid, potassium salt (TNS)) that possesses a naphthalene core and a sulfonate group; fluorescence emission upon the guest binding to the surface receptors was directly detected by surface fluorescence spectroscopy (see Fig. 1).

RESULTS AND DISCUSSION

Surface pressure–molecular area (π–A) isotherms of single component amphiphiles were first investigated with pure water and 0.1 mM aqueous TNS (Fig. 3). Dialkylguanidinium (Gua) showed a condensed monolayer with a limiting area of *ca.* 0.45 nm^2, indicating the well-packed state of the alkyl chains [Fig. 3(A)a]. The presence of TNS in the subphase significantly expanded the monolayer probably due to effective binding of bulky TNS [Fig. 3(A)b]. The π–A isotherms of cyclophane units (SCAsp in Fig. 3(B), SCAsp(OH) in Fig. 3(C) and SCLys(OH) in Fig. 3(D)) were similarly investigated, but the effect of TNS in the subphase was hardly seen. The absence of cationic sites in these host amphiphiles would result in weak interaction with TNS, while an amine-carrying corresponding host was reported to have detectable binding to TNS at the air–water interface [7]. The electrostatic interaction might be a crucial factor in the binding of TNS under this experimental condition.

These cyclophanes all showed a limiting area of *ca.* 2.0 nm^2 in the condensed state, which reflects good packing of four steroid moieties in an edge-on conformation [7,27]. The isotherms of the cyclophanes carrying cholic acid moieties [SCAsp(OH) and SCLys(OH)] showed a transition from an expanded phase to a condensed phase, while a cholanic-type cyclophane (SCAsp) provided π–A isotherms only in the condensed phase. Transition from the side-on to the edge-on orientations would be observed in the former two monolayers, because side-on orientation with contact to three OH groups on the water surface is stable at low pressures and the more condensed edge-on conformation is favorable at high pressures.

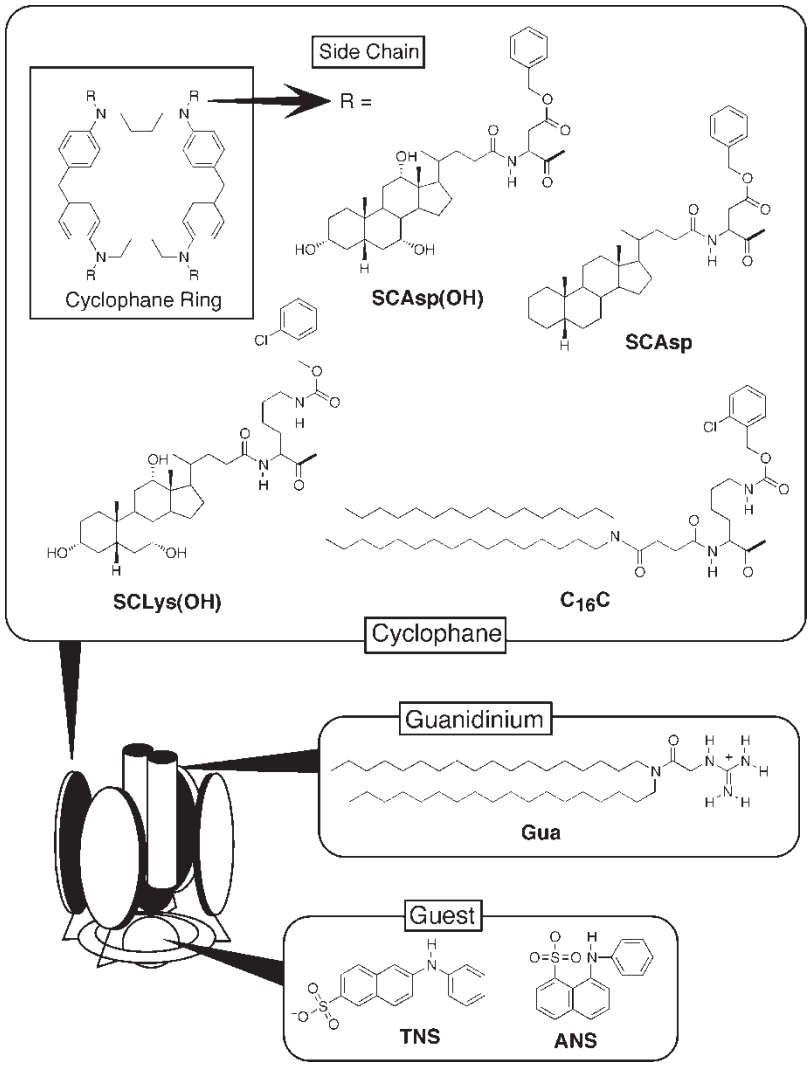

FIGURE 2 Formulae of hosts and guests used in this research.

The binding behavior of aqueous TNS to various monolayers was monitored by simultaneous measurement of the surface pressure and fluorescent emission at 440 nm upon monolayer compression (Fig. 4). A guest molecule, TNS, is known to lose its fluorescence in water, and therefore, strong emission was observed only upon its inclusion into a hydrophobic environment. Single-component monolayers, Gua [Fig. 4(A)] and SCAsp(OH) [Fig. 4(B)], did not show an increase in the fluorescent signal upon monolayer compression. A weak signal in the SCAsp(OH) monolayer reflects inefficient binding of TNS. Unchanged fluorescence intensity observed in the Gua monolayer probably comes from self-quenching in condensed packing and/or quenching upon exposure to water, because the TNS molecules would contact each other and be exposed to water.

Mixing of these amphiphilic components changed this situation, *i.e.*, the fluorescence intensity apparently increased upon compression [Fig. 4(C) and (D)]. We can image a binding motif of this three-component complex from this efficient fluorescence emission. Binding to the guanidinium concentrates TNS at the air–water interface and accommodation of the bound TNS in the hydrophibic core of the cyclophanes supresses TNS quenching (see illustration in Fig. 1). Similar behavior was observed when SCLys(OH) was used as the monolayer component. An apparent increase in the fluorescence intensity was detected in a SCLys(OH)/Gua monolayer [Fig. 4(F)], while this effect was absent in a single-component monolayer of SCLys(OH) [Fig. 4(E)]. We conclude that the copresence of the guanidinium and the cyclophane functionalities only induces effective fluorescence emission of bound TNS.

The observed phenomena were widely investigated for various monolayer systems. Increases in the fluorescence intensity between the uncompressed state and the most condensed state (just before collapsing) are summarized in Fig. 5. Single-component monolayers of any cyclophane did not

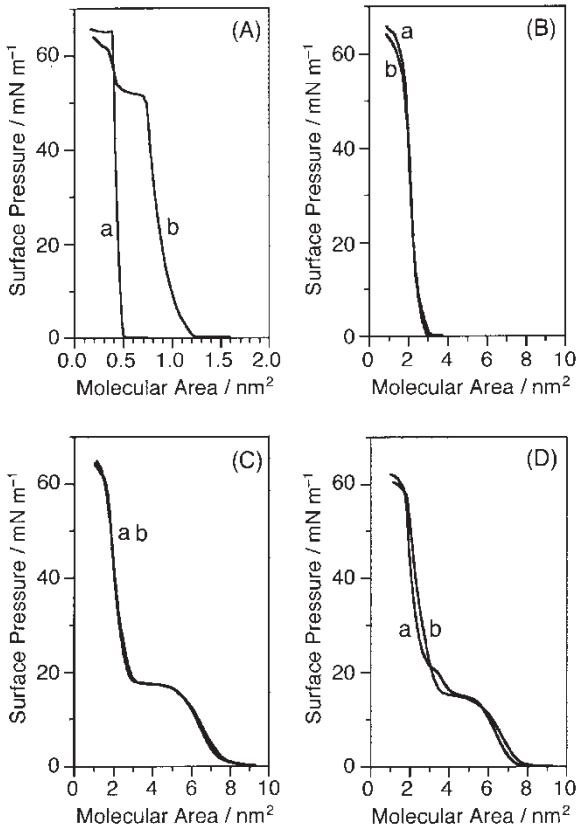

FIGURE 3 Surface pressure–molecular area (π–A) isotherms of single amphiphilic components (a, in pure water; b, in 0.1 mM aqueous TNS) at 20.0 ± 0.1°C: A, Gua; B, SCAsp; C, SCAsp(OH); D, SCLys(OH).

induce a significant increase in fluorescence emission probably due to inefficient binding of TNS. A mixed monolayer of SCLys(OH) and dihexadecylphosphate (DHP) did not cause effective fluorescence emission either, because the anionic DHP cannot strongly interact with TNS. In contrast, a certain amount of fluorescence increase was detected in the mixed monolayers of the cyclophanes and the guanidinium, but the increase in the fluorescence emission significantly depended on the nature of the hydrophobic moieties in the cyclophanes. The mixed monolayers with cyclophanes carrying cholic acid moieties (SCAsp(OH) and SCLys(OH)) both showed a significant increase in the fluorescence emission, while the fluorescence increase was apparently suppressed in the case of a cholanic-type cyclophane (SCAsp/Gua). A dynamic change in the side steroid walls from a side-on to an edge-on conformation would be effective in TNS inclusion. An increase in fluorescence intensity was also observed in the mixed monolayer of Gua and alkyl-type cyclophane ($C_{16}C$/Gua) but was not as large as those observed in the SCAsp(OH)/Gua and SCLys (OH)/Gua monolayers. Accommodation or shielding of TNS may not be as effective when soft alkyl chains were employed.

In order to obtain stoichiometric information on these systems, the fluorescence increase was measured at various guanidinium:cyclophane ratios. Three mixtures Gua/SCAsp(OH) in Fig. 6(A), Gua/SCLys(OH) in Fig. 6(B) and Gua/$C_{16}C$ in Fig. 6(C) showed a change in the fluorescence behavior at around the equimolar mixing state, *i.e.*, an excess of Gua did not significantly emphasize the fluorescence increase. This behavior indicates preferential formation of a cyclophane/guanidinium/TNS (1/1/1) complex. With the previous knowledge about the inclusion of TNS into cyclophanes [7,21,22] and the strong interaction between guanidinium and the anionic group [24–26], the binding motif depicted in Fig. 1 is strongly suggested. However, such stoichiometric behavior was absent in the mixed monolayer of the Gua/SCAsp probably due to inefficient inclusion ability.

Several control experiments were also carried out. In order to demonstrate the importance of the formation of a molecularly-defined complex in the observed fluorescence emission, two amphiphilic components [SCLys(OH) and Gua] were separately spread on aqueous TNS, Fig. 7(A). A π–A isotherm with a less smooth shape suggests incomplete mixing of the two components. The measured fluorescence emission was significantly smaller than that observed in the molecularly mixed monolayers, as shown in Fig. 4(C), which were prepared by spreading the previously-mixed solution. This control experiment straightforwardly demonstrates that the strong fluorescence emission originates from the cooperative binding/inclusion of TNS by SCLys(OH) and Gua.

Competitive binding of TNS and 8-anilino-1-naphthalenesulfonic acid (ANS) with a mixed monolayer of SCLys(OH) and Gua was also investigated [Fig. 7(B)]. Interestingly, mixing of equimolar ANS with TNS completely suppressed any fluorescence emission, although ANS is known to show weaker binding to the cyclophane host than TNS in bulk phase [21]. The molecular area at the condensed phase was apparently enlarged as observed upon comparison between the isotherms in Figs. 4(C) and 7(B) in a range of 10–40 mN m^{-1}. The observed drastic inhibition of fluorescence output is not completely understood but may be explained by preferential binding of ANS to Gua. The hydrophobic phenyl group would point to the air phase in the binding motif between Gua and ANS, while binding of TNS to Gua may cause immersion of the hydrophobic parts of TNS deeply into the water phase. Formation of the former motif is more favorable at the air–water interface, but the formed Gua/ANS is not geometrically suitable for inclusion by the cyclophane embedded at the air–water interface. Non-inclusion mixing between

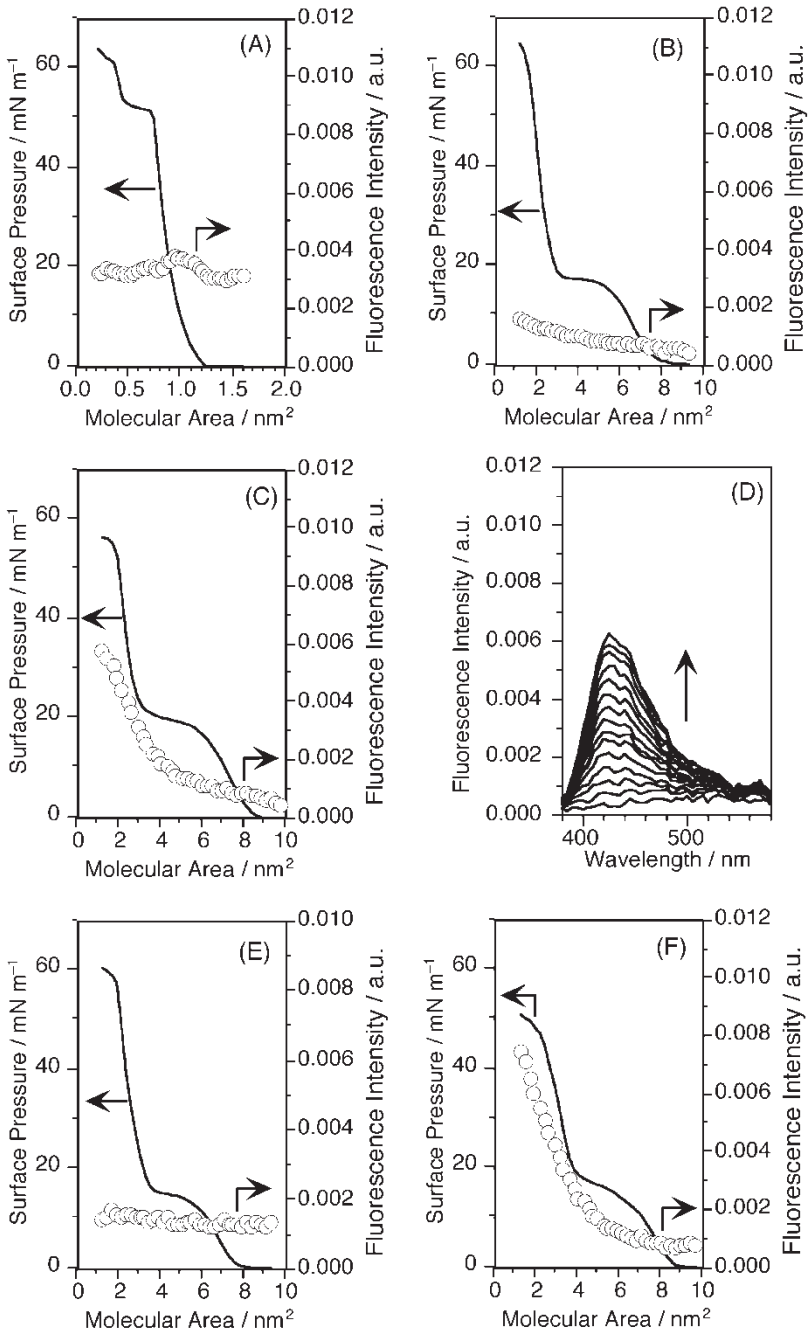

FIGURE 4 Surface pressure (solid line) and fluorescence intensity at 440 nm (open circle) plotted as a function of molecular area ([TNS] = 0.1 mM, 20.0 ± 0.1°C): A, Gua monolayer; B, SCAsp(OH) monolayer; C, SCAsp(OH)/Gua (1/1) monolayer; E, SCLys(OH) monolayer; F, SCLys(OH)/Gua (1/1) monolayer. Actual fluorescence spectra observed on the SCAsp(OH)/Gua (1/1) monolayer are plotted in (D) where the intensity increased upon monolayer compression.

the Gua/ANS complex and SCLys(OH) increases the average molecular area but does not increase fluorescence emission.

CONCLUSION

A novel type of molecular recognition and signal output is presented in this paper through observation of selective fluorescence emission upon binding of a fluorescent guest to guanidinium and cyclophane mixtures at the air–water interface. The two types of hosts play separate roles in binding to a specific group and shape-recognizing inclusion, respectively, and spontaneous complexation would induce their cooperative binding to the guest and consequent efficient fluorescence emission. This strategy would provide ways to construct complicated recognition sites by self-assembly of rather simple components in a dimension-limited space. One example of a competitive experiment suggests that unique selectivity in output would be achieved

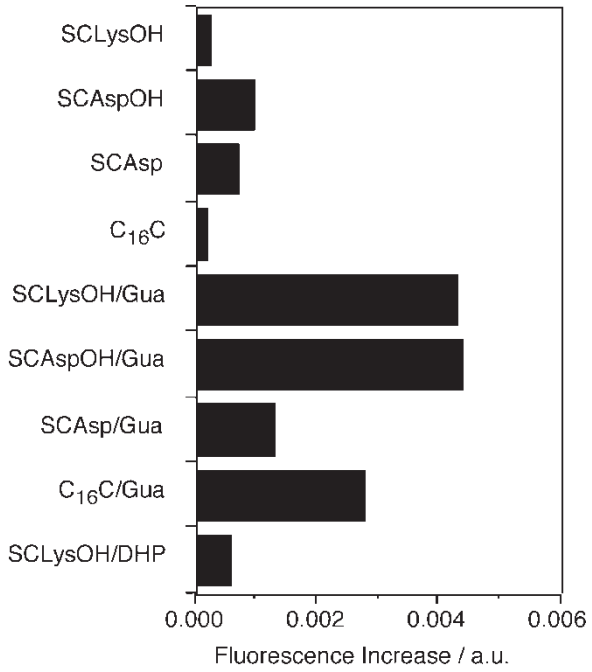

FIGURE 5 Increases in fluorescence intensity between the non-compressed state and the most condensed state in 0.1 mM aqueous TNS at 20.0 ± 0.1°C.

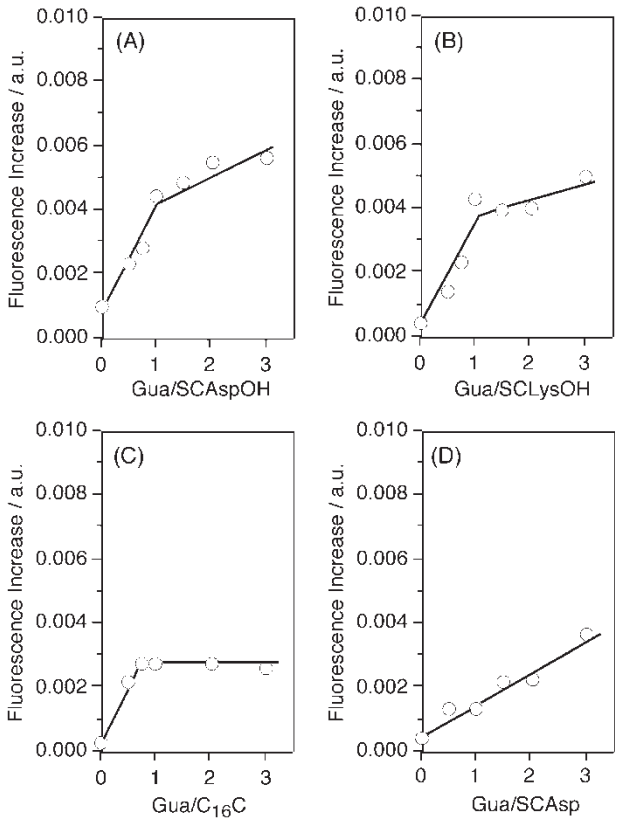

FIGURE 6 Increases in fluorescence intensity between the non-compressed state and the most condensed state plotted as a function of [Gua]/[cyclophane] ([TNS] = 0.1 mM, 20.0 ± 0.1°C): A, Gua/SCAsp(OH); B, Gua/SCLys(OH); C, Gua/$C_{16}C$; D, Gua/SCAsp.

depending on the geometry of the complex formed at hetero-dielectric medium. In the proposed strategy, various combinations in host components could be freely selected and the choice of receptor design would be expanded. This study would bring new concepts and ideas to the design of sensing systems for water-soluble substances including biologically-important materials.

MATERIALS AND METHODS

Syntheses of SCAsp(OH) and SCLys(OH) have already been reported [28]. Related cyclophane, SCAsp, was synthesized according to this literature. An alkyl-type cyclophane, $C_{16}C$, was similarly synthesized using *N*,*N*-dihexadecylsuccinamic acid. The synthetic method for dialkylguanidinium is reported elsewhere [26].

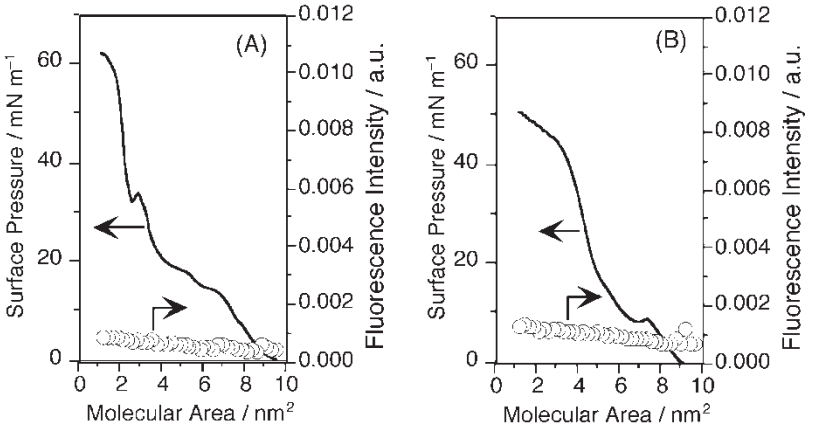

FIGURE 7 (A) Surface pressure (solid line) and fluorescence intensity at 440 nm (open circle) plotted as function of the molecular area of the SCLysOH/Gua (1/1) mixed monolayer ([TNS] = 0.1 mM, 20.0 ± 0.1°C). In this case, the two host components were spread separately on the aqueous surface. (B) Surface pressure (solid line) and fluorescence intensity at 440 nm (open circle) are plotted as a function of the molecular area of the SCLys(OH)/Gua (1/1) mixed monolayer on the subphase containing the TNS/ANS mixture ([TNS] = [ANS] = 0.1 mM, 20.0 ± 0.1°C).

SCAsp

Trifluoroacetic acid (6.01 g, mmol) was added to a solution of 1,6,20,25-tetrakis[2-[(*tert*-butoxycarbonyl)amino]-3-(benzyloxycarbonyl)propanoyl]-1,6,20,25-tetraaza[6.1.6.1]paracyclophane [28] (300 mg, 0.17 mmol) in dry dichloromethane (30 ml) and the mixture was stirred for 4 h at room temperature. After the mixture was evaporated to dryness under reduced pressure, the residue was dissolved in dry DMF (15 ml). Cholanic acid (377 mg, 1.04 mmol) was added to the solution at 0°C, and the mixture was allowed to stand at the same temperature while being stirred for 20 min. Diethyl cyanophosphate (170 mg, 1.04 mmol) and dry triethylamine (670 mg, 6.62 mmol) were added to the mixture; the resulting mixture was stirred for 1 h at 0°C and for an additional 5 h at room temperature. The mixture was evaporated to dryness under reduced pressure and the residue was purified twice by gel-filtration chromatography on a Sephadex LH-20 column with methanol/chloroform (1/1 v/v) as the eluent. The obtained fraction was again purified by silica gel chromatography on a Wakogel C-300 column with methanol/chloroform/dichloromethane (1/4/9 v/v/v) as the eluent. The residue obtained by evaporation of the appropriate fractions was further recrystallized from a mixture of hexane and ethyl acetate to give the title compound as a white solid (244 mg, 20%), mp 122.8–123.4°C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.63 (12H, s, *18-H* steroid), 0.88 (12H, d, $J = 5.6$ Hz, *21-H* steroid), 0.92 (12H, s, *19-H* steroid), 0.93–2.26 (complicated peaks, steroid + NCH_2CH_2), 2.38 (4H, dd, $J = 15.0$, 5.6 Hz, $COCHCH_2$ non-equivalent), 2.60 (4H, dd, $J = 15.0$, 5.6 Hz, $COCHCH_2$ non-equivalent), 3.36 (4H, br, NCH_2 non-equivalent), 3.75 (4H, br, NCH_2 non-equivalent), 3.87 (4H, s, Ar-CH_2-Ar), 4.77 (4H, m, NHCHCO), 5.05 (8H s, $COOCH_2$Ar), 6.33 (4H, d, $J = 7.6$ Hz, NHCO), 7.06 (8H, d, $J = 7.6$ Hz, NArH *ortho*), 7.16 (8H, d, $J = 7.6$ Hz, NArH *meta*), 7.31–7.37 (20H, m, OCH_2ArH). Anal. Calcd for $C_{174}H_{236}N_8O_{16}$: C, 77.52; H, 8.82; N, 4.16. Found: C, 77.37; H, 8.89; N, 4.18.

$C_{16}C$

1,6,20,25-Tetrakis[2-[(*tert*-butoxycarbonyl)amino]-6-[(2-chlorobenzoyloxycarbonyl)amino]hexanoyl]-1,6,20,25-tetraaza[6.1.6.1]paracyclophane [28] (270 mg, 0.13 mmol) was dissolved in trifluoroacetic acid (6.0 ml) and the mixture was stirred for 1 h at room temperature. After the mixture was evaporated to dryness under reduced pressure, the residue was dissolved in dry DMF (5 ml). Separately, 1-hydroxybenzotriazole monohydrate (120 mg, 0.79 mmol), and *N,N*-dihexadecylsuccinamic acid (440 mg, 0.79 mmol) were dissolved in dry DMF (5 ml). (Benzotriazole-1-yloxy)tris-(dimethylamino)phosphonium hexafluorophosphate (98 mg, 0.22 mmol) and triethylamine (0.15 ml, 1.0 mmol) were added to the solution at 0°C and the mixture was allowed to stand at the same temperature while being stirred for 2 h. To this solution, the formerly prepared dry-DMF solution of the deprotected cyclophane derivative was added dropwise at 0°C. The resulting mixture was stirred for 5 h at 0°C and reacted further overnight at room temperature. The mixture was evaporated to dryness under reduced pressure and was dissolved in chloroform. The organic layer was washed with 10% aqueous citric acid and 4% aqueous Na_2CO_3; the aqueous layer was then removed by a liquid-phase separation filter. The concentrated residue was purified by silica gel chromatography on a Wakogel C-200 column with methanol and dichloromethane as the eluent. The obtained fraction was again purified by gel-filtration chromatography on a Sephadex LH-20 column with methanol/chloroform (1/1 v/v) as the eluent. Evaporation of the appropriate fractions gave the title compound as a white solid (290 mg, 57%), mp 116–118°C. ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.88 (24H, t, $J = 6.4$ Hz, CH_3), 1.23 (216H, br, CH_2 in alkyl chains + Lys γ-CH_2), 1.40–1.59 (40H, m, NCH_2CH_2 in alkyl chain and ring + Lys β-CH_2 and δ-CH_2), 2.48–2.67 (16H, m, $COCH_2CH_2CO$), 2.92–3.31 (32H, m, NCH_2 in alkyl chain and ring + Lys ϵ-CH_2), 3.91 (4H, s, Ar-CH_2-Ar), 4.52 (4H, m, Lys α-CH), 5.19 (8H, s, $COOCH_2$Ar), 5.46 (4H, br, NHCO), 6.52 (4H, br, NHCO), 7.05–7.08 (8H, m, NArH *ortho*), 7.17–7.24 (16H, m, OCH_2ArH), 7.33–7.42 (8H, m, NArH *meta*). Anal. Calcd for $C_{234}H_{384}Cl_4N_{16}O_{16}\cdot 5H_2O$: C, 71.88; H, 10.12; N, 5.73. Found: C, 71.80; H, 9.95; N, 5.49.

TNS, ANS, and DHP were commercially available and used without further purification. Water used for the subphase was distilled in an Autostill WG220 (Yamato) and deionized by a Milli-Q Lab (Millipore). Spectroscopic grade benzene and ethanol (Wako Pure Chem.) were used as the spreading solvents.

π–A Isotherms were measured using an FSD-300 computer-controlled film balance system (USI System). A mixture of benzene/ethanol (80/20 v/v) was used as the spreading solvents. Compression was started about 10 min after spreading at a rate of 0.2 mm s^{-1} (or 20 mm^2 s^{-1} based on area). The subphase temperature was maintained at 20.0 ± 0.1°C. Surface-reflective fluorescence spectra were measured using a photodiode array-equipped spectrometer (Otsuka Electronics, Model MCPD-7000) with an excitation wavelength of 323 nm. The fluorescence was negligible when the monolayers were absent.

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