Piezoluminescence Based on Molecular Recognition by Dynamic Cavity Array of Steroid Cyclophanes at the Air−Water Interface

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On one hand considerable work has been done on the luminescence observed under various conditions of stress and pressure.[1] On the other hand, molecular recognition with color changes has been widely researched.[2] Combining these two kinds of research would lead to a novel information conversion where macroscopic mechanical stimulus induces the molecular recognition with a change in luminescence. Phenomena with considerably different scales, that is, macroscale pressure and molecular-scale recognition, can be connected by an approach based on molecular assemblies. A monolayer at the air−water interface is a good candidate, because we can easily compress and expand it. In addition, efficient molecular recognition at the well-oriented monolayer surface has been reported[3] as well as several attempts for a host cavity array at the interface.[4] In this study, we dynamically controlled the cavity structures of steroid cyclophanes placed at the interface and demonstrated repeatable piezoluminescence based on molecular recognition.

The steroid cyclophanes (**1**[5a] and **2**[5b] in Figure 1) are unique hosts with a cyclic core of a 1,6,20,25-tetraaza[6.1.6.1]paracyclophane connected to four steroid moieties through a flexible L-lysine spacer. Cholic acid and cholanic acid were used as the steroid. A rigid plane of cholic acid with hydrophobic and hydrophilic faces is expected to lie flat on the water. In contrast, cholanic acid with only hydrophobic faces would preferably stand on water. The central core accommodates aromatic guests such as the naphthalene derivatives in a 1:1 stoichiometry. The steroid cyclophane **1** binds **3** in aqueous solution with a large binding constant (1.2×10^6 M^{-1}, 30 °C),[5c] while the corresponding cyclophane without the steroidal residues has a smaller binding constant (3.2×10^2 M^{-1}, 25 °C) to the same guest.[6] The formation of a three-dimensional cavity is required for efficient molecular recognition.

The $\pi-A$ isotherms[7] of the steroid cyclophane **1** showed a transition behavior on both pure water and 0.1 mM aqueous **3** (Figure 2A). A transition point was observed at ~4 nm^2, and the curve rose again with the limiting area of ~2 nm^2. The latter value is close to the cross-sectional area of **1** in a closed conformation (2.3 nm^2),[8] and is larger than the area for the close packing of the four cholic acids (1.6 nm^2).[9] Therefore, a three-dimensional cavity is probably formed during the second rise in the isotherm. The model estimation also gives an occupied area of ~7 nm^2 for the open conformation of **1**. This value is close to the molecular area where the surface pressure starts increasing. These $\pi-A$ characteristics strongly suggest that the cavity conversion occurs upon compressing the monolayer of **1** (see illustration in Figure 1). The isotherm of **1** was slightly influenced by the presence of **3** in the subphase. The transition point shifts toward a larger area, but the molecular area during the second rise was not significantly altered. On the other hand, the $\pi-A$ isotherm of **2** (Figure 2B) shows only the condensed phase, indicating that a conformational change hardly occurred upon compression. The molecular area at the condensed phase is ~2.5 nm^2 on water. Therefore, **2** is in an imperfectly packed closed conformation. The presence of **3** in the subphase increased the molecular area.

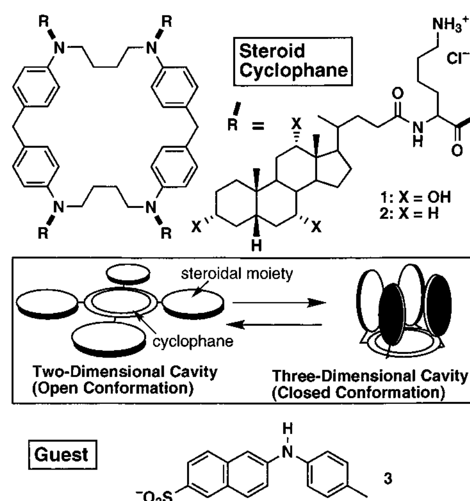

Figure 1. Structure of steroid cyclophanes and guest molecule. Schematic illustration of the cavity conversion of the steroid cyclophane is included.

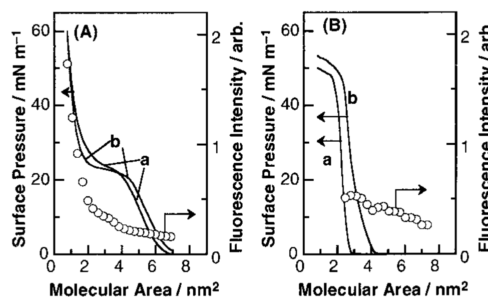

Figure 2. $\pi-A$ Isotherms of **1** (A) and **2** (B) at 20 °C and pH 11: a, on pure water; b, on 0.1 mM aqueous **3**. Open circles represent fluorescence intensity at 440 nm from the monolayers on 0.1 mM aqueous **3**.

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(7) The $\pi-A$ isotherms were measured at 20.0 ± 0.2 °C and at a compression rate of 0.2 mm s^{-1} with an FSD-300 computer-controlled film balance (USI System, Fukuoka). The subphase pH was adjusted to 11 with aqueous KOH.
(8) The molecular conformation of the cyclophane ring was estimated by a Cerius[2] calculation (version 3.8, Molecular Simulation Inc.) based on the DREIDING force field (version 2.21). The structure error was minimized in bond, angle, torsion, inversion, van der Waals, and Coulomb terms, then the conformational energy was optimized (minimum rms gradient, 0.001). The DREIDING parameters given in the program were used without any modification.
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The fluorescence intensity of **3** is significantly suppressed in a polar medium. Therefore, **3** has a large fluorescence only when it is inserted into the hydrophobic core of the monolayer. The fluorescence intensities at 440 nm[10] are plotted as a function of the molecular area of **1** (Figure 2A). The intensity value abruptly increased at the molecular area of 2 nm^2, indicating that the completion of the three-dimensional cavity was crucial for the efficient binding of **3**. The clear increase in the fluorescence intensity and the small change in the molecular area indicate the insertion of **3** into the cavity of **1**. In contrast, the fluorescence intensity was hardly increased in the case of the monolayer of **2**. Since the increase in the molecular area of **2** was significantly observed in the presence of **3** in water, the bound **3** might locate on the outside of the core of **2**. The lack of a dynamic nature in the cavity of **2** leads to the inefficient inclusion ability of **3**. In the monolayer state, **2** forms a rigid crystalline phase in which the cyclophane cavity might not be in a conformation favorable for the guest inclusion.

Figure 3A shows the repeated compression−expansion $\pi - A$ isotherm of **1** on aqueous **3**. Although the first compression curve has a wider area, the $\pi - A$ isotherm qualitatively traced the same hysteresis loop after the second cycle. The repeated compression and expansion induced a periodic change in the fluorescence (Figure 3C(a)) upon the binding of **3** (Figure 3D) When the cycle was repeated below the transition pressure, no significant change in the fluorescence intensity was observed. Therefore, the formation of the three-dimensional cavity is required for the periodic luminescence. The faster compression−expansion cycles showed a quantitatively reproducible intensity change after the eighth cycle (Figure 3C(b)). These results confirm that the dynamic pressure application is converted to luminescence based on the molecular recognition. A similar experiment was carried out with the monolayer of **2** (see $\pi - A$ isotherm in Figure 3B). Only a small change in the fluorescence intensity was detected (Figure 3C(c)). This control experiment confirms that the dynamic characteristic of the cavity is crucial for the periodic pressure-induced luminescence.

The preliminary experiments under various concentrations of **3** suggest a 1:1 binding between **1** and **3**, and more precise analyses by FT-IR, XPS, and AFM are now in progress. However, the presented results clearly show that the dynamic change in the steroid cyclophane cavity can be converted into a reproducible photosignal. It is a good demonstration of the connection between the macroscopic pressure stimuli with molecular motion and the resultant spectral response. The steroid cyclophane can be used as a molecular actuator which controls the size of the cavity and intervals in the cavity array. For example, the dynamic controllability of the cavity size and interval would be of significant use in a quantum-sized system[11] and in the oriented array of organic dyes.[12]

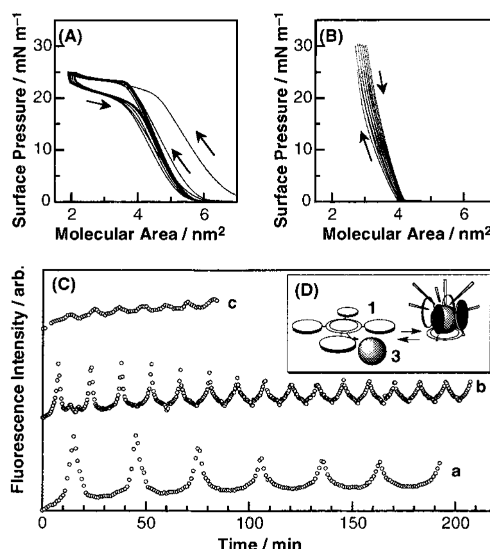

Figure 3. Repeated compression−expansion isotherms of **1** (A) and **2** (B) on 0.1 mM aqueous **3** at 20 °C and pH 11 with an area change rate of 0.2 mm sec^{-1}. Fluorescence intensity changes at 440 nm during the compression−expansion cycles are plotted in (C) where curves a and c represent the fluorescence response for the repeated cycle of (A) and (B), respectively. Curve b shows the fluorescence response with the area change rate of 0.4 mm sec^{-1}. The vertical axes of these curves are shifted from each other to more clearly show the curves. Inserted illustration (D) represents the plausible model for the piezoluminescence upon the dynamic cavity conversion of **1**.

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(10) 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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