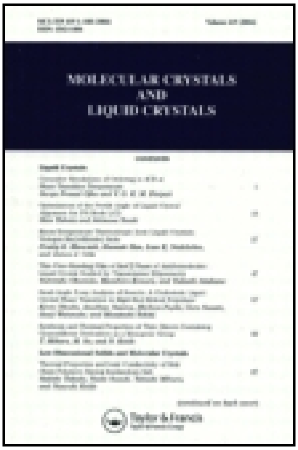

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Monolayer of Cyclophane with Multiple Alkyl Chains for Molecular Tiling

Katsuhiko Ariga [a], Naoko Takagi [a], Ryutaro Tanaka [a] & Jun-Ichi Kikuchi [a]

[a] Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara, 630-0101, Japan

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Monolayer of Cyclophane with Multiple Alkyl Chains for Molecular Tiling

KATSUHIKO ARIGA*, NAOKO TAKAGI,
RYUTARO TANAKA and JUN-ICHI KIKUCHI

Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

Molecular tiling has been developed as a novel technique for controlled molecular arrangements in two-dimensional plane. The π-A isotherm of a cyclophane derivative with eight alkyl chains has a limiting area apparently smaller than the cyclophane core, indicating that the cyclophane core was deformed at high pressures. In contrast, the equimolar-mixed monolayer of the cyclophane derivative and a guanidinium amphiphile on an aqueous naphthalene guest showed an isotherm with a limiting area comparable to the cyclophane core. A drastic increase in surface fluorescence due to the guest insertion was also observed. These results strongly indicate that the cyclophane derivative formed a rigid complex with the guanidinium amphiphile and aqueous naphthalene derivative. The formed complex can be a good candidate for a tiling unit.

<u>Keywords</u> monolayer; molecular recognition; cyclophane

INTRODUCTION

One of the most sophisticated methods of controlling molecular arrangement is the Langmuir-Blodgett (LB) technique. It provides well-defined layered structures, but control of the molecular arrangement within a unit layer was not currently established. One of us developed a methodology to create artificial patterns in two-dimensional plane[1] through specific molecular recognition at the air-water interface[2]. Recently, we have proposed "molecular tiling" as a novel method where molecules with a rigid core and several alkyl chains are used as a tiling unit to fill the two-dimensional plane of water surface with a specific pattern. In this paper, the monolayer properties of a cyclophane-based tiling unit are described.

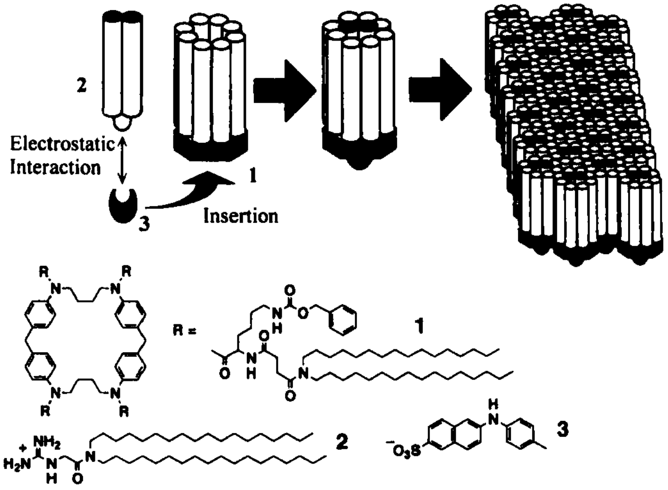

FIGURE 1. Design of "molecular tiling"

RESULTS AND DISCUSSION

Design of the tiling unit used in this study is shown in Fig. 1. The compound **1**[3] has a cyclophane core with eight alkyl chains. Some cyclophane derivatives can selectively accommodate an aqueous naphthalene molecule such as **3** at the air-water interface[4]. A cationic guanidinium amphiphile **2**[5] also interacts with **3** through electrostatic interaction. Therefore, we can expect that the integrated complex drawn in Fig.1 is formed through spreading the mixed monolayer of **1** and **2** on a subphase containing **3**.

The π-A isotherm[4] of a monolayer of **1** on aqueous **3** (0.1 mM) showed a transition from an expanded to a condensed phase (Fig. 2A). However, its limiting area (1.6 nm^2) corresponds to an area for eight well-packed chains, and is apparently smaller than the core area (2.4 nm^2)[6]. The intensity of surface fluorescence[4] did not show a significant increase upon compression. At the high pressures, the cyclophane core probably deformed and **3** cannot be inserted into the core.

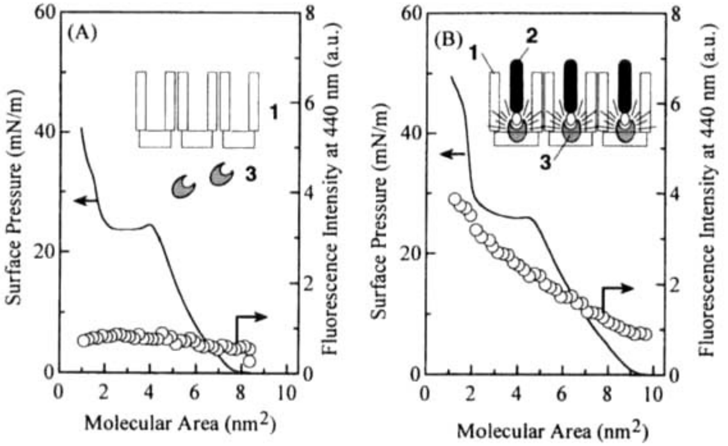

FIGURE 2. π-A Isotherm and surface fluorescence intensity isotherm of monolayer of **1** (A) and mixed monolayer of **1** and **2** (B) on **3** (0.1 mM) at 20 °C

In contrast, the equimolar mixed monolayer of **1** and **2** formed a stable monolayer with a limiting area of 2.4 nm^2 which is comparable to the core area and is larger than the area of 10 (8 + 2) alkyl chains.

The presence of **3** in the core of **1** is strongly indicated by a drastic increase in the surface fluorescence intensity, because the insertion of **3** into the hydrophobic environment of the cyclophane core suppresses the fluorescence quenching[4]. Such a drastic increase in the fluorescence was not observed for a single-component monolayer of **2**. These results indicate that the integrated complex was formed and that the rigidified core structure was packed on water.

CONCLUSION

The obtained results show the formation of a three-component complex through specific molecular recognition. This complex has two kinds of alkyl chains at the center and the surrounding and they are changeable. Therefore, various artificial two-dimensional patterns would be created through appropriate combination of components. An AFM observation on the formed patterns is now under investigation.

References

[1] Y. Oishi, Y. Torii, T. Kato, M. Kuramori, K. Suehiro, K. Ariga, K. Taguchi, A. Kamino, H. Koyano amd T. Kunitake, *Langmuir*, **13**, 519 (1997).

[2] K. Ariga and T. Kunitake, *Acc. Chem. Res.*, **31**, 371 (1998).

[3] Details of synthesis of the compound **1** will be reported in future publication. 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%.

[4] K. Ariga, Y. Terasaka, D. Sakai, H. Tsuji and J. Kikuchi, *J. Am. Chem. Soc.*, in press.

[5] The compound **2** (trifluoroacetate form) was synthesized according to the former report (A. Kamino, H. Koyano, K. Ariga and T. Kunitake, *Bull. Chem. Soc. Jpn.*, **69**, 3619 (1996)). Anal. Calcd for $C_{41}H_{81}F_3N_4O_3$: C, 66.99; H, 11.11; N, 7.62%. Found: C, 67.00; H, 11.09; N, 7.68%.

[6] 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).