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Pseudorotaxane monolayers of pillar[5]arene and linear fatty acids at the air-water interface[†]

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Pseudorotaxanes, which are formed by macrocyclic host molecules and linear guest molecules, show potential in molecular devices 27 and surface applications. In this study, ethoxy-functionalized ²⁸ pillar[5]arene (P5A) and amphiphilic linear fatty acid guests 29 were self-assembled into oriented monolayers at the air-water 30 The fatty acid structure dictates the monolayer ³¹ interface. formation: [2]pseudorotaxane-based, [3]pseudorotaxane-based ³² and phase-separated monolayers. These findings provide insights ³³ into P5A-based pseudorotaxane monolayers, facilitating their ³⁴ 35 integration into advanced functional materials.

Pseudorotaxanes are formed by a macrocyclic host molecule 37 and a linear guest molecule that exhibits specific non-covalent ³⁸ interactions with the host.¹ The tiling of oriented pseudorotax-³⁹ anes particularly in two-dimensional planes is promising for ap- 40 plications such as molecular shuttles, 2,3 surface wettability con- 41 trol,⁴ sensors,⁵ catalysts,⁶ and transistors.⁷ Compared with the 42 commonly used self-assembled monolayer (SAM) method for sur- 43 face modification, the Langmuir–Blodgett (LB) technique⁸ im- $_{44}$ poses significantly fewer material limitations because of the lack 45 of chemical bonds between the pseudorotaxane terminal func- 46 tional groups and the substrate surface. Additionally, this method 47 allows for control of the density and orientation of pseudorotax- 48 anes through in-plane mechanical compression. 49

Pillararenes, first developed in 2008,⁹ are a class of macro-

cyclic host molecules, with cyclopentamer (P5A) and cyclohexamer (P6A) derivatives being the most commonly used. Compared to other macrocyclic host molecules, such as crown ethers and calixarenes, pillararenes offer advantages in terms of easy synthesis, flexible functionality, and high symmetry.¹⁰ In particular, P5A forms pseudorotaxanes with saturated alkanes via C- $H \cdots \pi$ interactions.^{11,12} Recent studies have demonstrated that P5A-based pseudorotaxanes can exhibit bistable states, 13,14 offering applications such as molecular machines, similar to those investigated in "blue box" systems.³ Accordingly, two-dimensional tiling of P5A-based pseudorotaxanes can maximize the expression of switchable surface functionalities. Therefore, understanding P5A-based pseudorotaxane monolayers at the air-water interface is expected to open new avenues for various applications.

In this study, we found that pseudorotaxanes, which is composed of ethoxy-functionalized pillar[5]arene (EtP5A) and linear fatty acid guests, were oriented and assembled in a monolayer at the air-water interface. The chemical structure of the fatty acid guest dictates the resulting monolayer structure; short-chain linear fatty acids lead to [2]pseudorotaxane monolayers, long-chain linear fatty acids form [3]pseudorotaxane monolayers, and a fatty acid guest unsuitable for EtP5A undergoes phase separation (Fig. 1a).

To elucidate the monolayer state of Langmuir films at the airwater interface, we measured the surface pressure-area $(\pi - A)$ isotherms (Fig. 1b). Pure EtP5A exhibited a lift-off of the surface pressure near 1.3 nm² and monolayer collapse at 10.3 mN/m. Interestingly, given the good agreement with the theoretical calculations (1.42 nm²), the pure EtP5A with simple ethoxy substitution was found to orient its cavities perpendicular to the water surface, as observed in previous studies using pillararene with longer and more complex substitution^{15,16}. The relatively low collapse pressure (π_C) suggested weak intermolecular interactions within the plane. To obtain a stable and oriented pseudorotaxane monolayer, we mixed a chloroform solution with amphiphilic G5-18,

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Fig. 1 Pseudorotaxane of EtP5A at the air-water interface. (a) Molecular structures and schematics of monolayer states for employed EtP5A host and guests. (b) π -A isotherms for pure EtP5A (black line), mixture with G5-18 (red line) and with G6 (blue line). (c) DFT-calculated IR spectrum of EtP5A with experimental one of the powder (section 1.4, ESI†). MAIRS spectra of LB films for pure EtP5A, mixture with G5-18 and pure G5-18 in the 1550-1300 cm⁻¹ (d) and 3000-2800 cm⁻¹ (e) regions. The OP (pink line) and IP (light blue line) indicate the out-of-plane and in-plane directions of the LB films, respectively.

which has been widely employed in insoluble monolayer stud- 86 62 ies,^{8,17} at a molar ratio of 1:1. Mixing with G5-18 decreased 63 the limiting cross-sectional area (A_L) per EtP5A molecule from ⁸⁷ 64 1.28 nm² to 0.91 nm², as calculated by extrapolating the π -A ⁸⁸ 65 isotherms. The reduction in molecular area by as much as 0.37⁸⁹ nm²does not occur if EtP5A and G5-18 form no complexes or 90 67 1:1 complexes, suggesting the formation of [3]pseudorotaxane ⁹¹ 68 structure at the air-water interface. Note that the A_L per EtP5A ⁹² 69 molecule of 0.91 nm^2 is close to the sum of one-half of the A_L ⁹³ 70 of 1.28 nm^2 for a single PA molecule and the A_L of 0.2 nm^2 ⁹⁴ 71 for an alkyl chain, which support [3]pseudorotaxane formation. 95 72 Furthermore, the [3]pseudorotaxane structure might contribute 96 73 to the formation of a more in-plane rigid film as confirmed by 97 74 the significant increase in π_C of 43.2 mN/m compared to 10.3 ⁹⁸ 75 mN/m of pure EtP5A. On the other hand, when mixed with G6, 99 76 a guest molecule incompatible with the cavity size of EtP5A, π^{-100} 77 A isotherm shifted toward larger molecular areas corresponding¹⁰¹ 78 to the cross-sectional area of G6, with minimal changes in π_C^{102} 79 compared to pure EtP5A. This behavior indicates phase separa-103 80 tion within the two-dimensional film.¹⁸ Similar phase separation¹⁰⁴ 81 was observed when EtP5A and G5-18 were sequentially spread¹⁰⁵ 82 on the water surface (Fig. S6, ESI[†]). Note that host-guest chem-¹⁰⁶ 83 istry strongly influences these phenomena, as demonstrated by¹⁰⁷ 84 the formation of pseudorotaxanes with G6 and phase separation¹⁰⁸ 85 109

with G5 when using EtP6A as the host (Fig. S7, ESI \dagger).

To investigate the molecular orientation and pseudorotaxane formation, we performed multiple-angle incidence resolution spectroscopy (MAIRS) measurements on LB films transferred from the water surface. This method involves tilting the thin film relative to the optical axis and analyzing the infrared absorption spectra acquired at varying polarization angles.¹⁹ The MAIRS method can separate the out-of-plane (OP) and in-plane (IP) absorption components of the film materials. Unlike traditional approaches that combine transmission and reflection methods, ¹⁷ the MAIRS method offers the advantage of measuring one identical film with fewer substrate constraints. EtP5A exhibited similar absorption characteristics in both the powder and LB films (Fig. 1c,d). According to density functional theory (DFT) calculations, the most intense absorption bands at 1502 cm^{-1} and 1408 cm⁻¹ were mainly consisted of aromatic C-H bending, aromatic C-H stretching, CH₂ wagging, and CH₃ wagging vibrations (section 1.4, ESI[†]). The strong transition moments along the cavity direction of EtP5A can be useful for assessing the molecular orientation. For both LB films of EtP5A and the mixture of EtP5A and G5-18, these vibrational bands were more prominent in the OP spectrum than in the IP spectrum, indicating the vertical orientation of the EtP5A cavity, both at the air-water interface and after transfer to solid substrates. This vertical orientation of EtP5A corOpen Access Article. Published on 05 June 2025. Downloaded on 6/8/2025 11:40:14 AM.

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Fig. 2 Pseudorotaxane monolayers depending on the guest alkyl length. (a) π -A isotherms for mixtures of EtP5A and G5-n. (b) Correlation between extrapolated limiting area per EtP5A molecule and guest carbon number. (c) Characteristics of monolayer collapse for mixtures of EtP5A and G5-n.



Fig. 3 Stoichiometric analysis of pseudorotaxane at the air-water interface. (a) π -A isotherms for mixtures of EtP5A and G5-20. (b) Correlation between extrapolated limiting area per EtP5A molecule and stoichiometric ratio. (c) Characteristics of monolayer collapse for mixtures of EtP5A and G5-20

This article is licensed under a Creative Commons Attribution 3.0 Unported Licence. responds to the fact that the A_L obtained by π -A isotherm is close₁₃₉ to the calculated cross-section value of 1.42 nm² for EtP5A. Ad-140 ditionally, pure G5-18 exhibited characteristic vibrational peaks141 due to CH₂ trans-zigzag packing owing to its crystallinity, specif-142 ically CH₂ antisymmetric stretching vibrations (2920 cm⁻¹) and 143 CH_2 symmetric stretching vibrations (2850 cm⁻¹) (Fig. 1e).^{20,21}₁₄₄ Upon mixing with EtP5A, these peaks shifted to higher wavenum-145 bers, indicating that the alkyl chains adopted a gauche conforma-146 tion and supporting the formation of inclusion complexes with147 EtP5A.

Considering that the formation behavior of EtP5A-based 120 pseudorotaxanes depends on the chain length of the guest150 121 molecules, ¹² the monolayer state was investigated using guests₁₅₁ 122 with carbon numbers ranging from 14 to 26, which can indepen-152 123 124 dently form insoluble monolayers. In this study, the molecules 153 were mixed at a 1:1 molar ratio before spreading to the air-water 154 125 interface. The π -A isotherms for each system, guest-dependent¹⁵⁵ 126 A_L , and guest-dependent collapse areas and π_C are shown in 156 127 128 Fig. 2a, b, and c, respectively. All the molecular areas were 157 calculated per EtP5A molecule. Compared to pure EtP5A, the158 129 π_C for all mixed systems increased, suggesting that pseudoro-159 130 taxane formation and concomitant lateral hydrophobic interac-160 131 tions between alkyl chains improved monolayer rigidity. The con-161 132 stant A_L and π_C indicate that EtP5A forms a nearly identical two-162 133 dimensional film when mixed with guests having carbon numbers 163 134 greater than 18, where [3]pseudorotaxane is stabilized as dis-164 135 cussed later. In contrast, the mixed systems with G5-14 and G5-165 136 16 exhibited larger A_L and lower π_C than those with G5-18 and 166 137 other guests. Note that a similar collapse area of 1.20 nm² for 167 138

pure EtP5A and the mixture with G5-14 implies that the mixture system mainly consists of a 1:1 complex, that is, [2]pseudorotaxane. The gradual shift in the A_L with increasing carbon number indicates that the stoichiometry of pseudorotaxane formation depends on the carbon number of the guest molecules.¹² In other words, it is plausible that the composition of the monolayers-[2]pseudorotaxane, [3]pseudorotaxane, and uncomplexed molecules-varies depending on the type of guest molecule, given that the π -A isotherms provide average information about the Langmuir films on the water surface, which extend over an area of several hundred cm².

To assess the effect of the molecular mixing ratio, we analyzed π -A isotherms for a mixture with G5-20, which has a sufficiently long carbon chain to stabilize the monolayer state, as shown in Fig. 2b,c. Here, when n_A represents the number of molecules of A, the host-guest stoichiometric ratio (SR) is defined as n_{G5}/n_{EtP5A} in the mixing solution. The horizontal axis in Fig. 3a and the A_L in Fig. 3b are plotted against the area per EtP5A molecule. Given that the collapse behavior of Langmuir films depends on the compressibility of the entire film, the collapse area is represented as a mean value for all mixed molecules (Fig. 3c). As expected, π -A plots approached the characteristics of pure EtP5A (or pure G5-20) as the stoichiometric ratio approached zero (or infinity) (Fig. S8, ESI \dagger). Interestingly, the A_L per EtP5A molecule and the collapse behavior exhibited a clear bifurcation at a stoichiometric ratio of 3/7. Within each of the two groups, the A_L can be approximated by a linear trend with an intersection of approximately 0.33. The decrease in the molecular area of binary Langmuir films is often indicative of specific attractive interac-

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tions.^{8,22} In this system, such a trend strongly suggests pseudoro-221 168 taxane formation. Assuming that all G5-20 molecules participate222 169 170 in complex formation under excess conditions of EtP5A (e.g., SR₂₂₃ = 1/9, 2/8, 3/7), the number of EtP5A molecules involved in₂₂₄ 171 each pseudorotaxane can be estimated from the A_L . The results 225 are 2.1, 2.3, and 2.0 EtP5A molecules, respectively, strongly in-226 dicating that [3]pseudorotaxane is the dominant species in the₂₂₇ mixed monolayer films. Conversely, under conditions where G5-228 20 is in excess, the decrease in area surpasses the value expected $_{220}$ from molecular interactions associated with pseudorotaxane formation, making it challenging to describe the behavior with a221 simple additivity rule. Further investigations are necessary to elucidate this phenomenon. Nonetheless, the identical collapse behavior implies that the monolayers include [3]pseudorotaxane.

In conclusion, we systematically investigated monolayers of ethoxy-substituted P5A and mixtures with fatty acid guests. Linear fatty acid guests lead to pseudorotaxane monolayers with P5A cavities oriented toward the water surface. The mixing ra-²³⁷ tio and chain length of the guests influenced the stoichiometry²³⁸ of pseudorotaxane formation and monolayer composition. This²³⁹ study provides insight into P5A-based pseudorotaxane monolay-²⁴⁰ ers for various applications. The simple procedure employed²⁴¹ for monolayer formation also offers the possibility of introducing²⁴² functional properties by appropriately selecting host and guest²⁴³ molecules. Furthermore, by removing guest molecules after the²⁴⁴ formation of aligned pseudorotaxane films, these materials can²⁴⁵ be explored for applications in sensors and filters.^{23–25} 246

M. I. and Y. N. conducted comprehensive experiments and anal-²⁴⁷ yses, with the support of Y. Y. The synthesis of pillararenes was²⁴⁸ carried out by K. O. and T. S. under the supervision of T. O. The²⁴⁹ MAIRS measurements were overseen by T. H. and N. S. This study²⁵⁰ was conducted by K. A. and H. S., and T. M. M. I. was supported²⁵¹ by JST, the establishment of university fellowships towards the²⁵² creation of science technology innovation (Grant Number: JP-²⁵³ MJFS2144). This work was also supported by KAKENHI (Grant²⁵⁴ Numbers: JP25H00898, JP23H05459 and JP23K04703). The cal-²⁵⁵ culations in this study were performed on the Numerical Materi-²⁶⁶ als Simulator at NIMS.

- 206 Conflicts of interest
- ²⁰⁷ There are no conflicts to declare.
- 208 Data availability
- The data supporting this article have been included as part of the
 Supplementary Information.⁺
- 211 References

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The data supporting this article have been included as part of the Supplementary Information.⁺