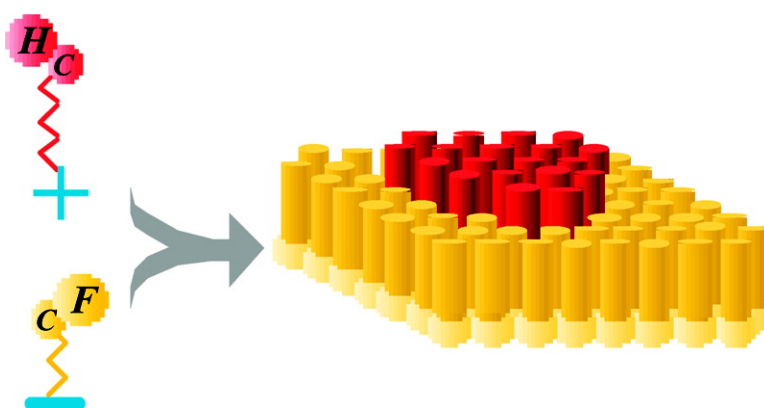# Langmuir

Letter

Nanomosaic: Formation of Nanodomains Confined in a Two-Dimensional Molecular Plane

Yushi Oishi, Takayuki Kato, Takayuki Narita, Katsuhiko Ariga, and Toyoki Kunitake

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

ACS Publications
High quality. High impact.

Nanomosaic: Formation of Nanodomains Confined in a Two-Dimensional Molecular Plane

Yushi Oishi,*,† Takayuki Kato,† Takayuki Narita,† Katsuhiko Ariga,‡ and Toyoki Kunitake§

Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, 1 Honjo, Saga 840-8502, Japan, World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan, and Department of Chemical Processes and Environments, Faculty of Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Wakamatsu-Ward, Kitakyushu 808-0135, Japan

Atomic force microscopy observations of a (hydrocarbon guanidinium/fluorocarbon carboxylic acid) mixed monolayer revealed that a nanoscopic phase-separated structure was formed by a combination of attractive interaction between the oppositely charged head groups and repulsive phase separation of the hydrocarbon and fluorocarbon chains.

Nanostructures having dimensions of 1 to 10^2 nm are often fabricated by a self-assembly process, as typically shown by the nucleic acid helix, virus, and organelle in biological systems as well as by artificially organized quantum dots.[1−5] Fabricating nanostructures by taking advantage of phase separation in molecular layers is a fundamentally advantageous approach because structural control arising from molecular diversity should be versatile. Nanometer-sized domain structures of mixed monolayers[6,7] may be candidates for the fabrication of novel electrical and optical devices by the confinement of organic functional molecules in a finite space. We have developed a new approach for this purpose based on the control of interactions among hydrophobic parts as well as among hydrophilic parts in monolayer components.

Our strategy in this approach is described in Figure 1. From atomic force microscope (AFM), lateral force microscope (LFM), and electron microscope observations, the phase separation of hydrocarbon and fluorocarbon components due to the surface free energy difference is known to produce domains of submicrometers to micrometers.[8−17] However, surface pressure−area
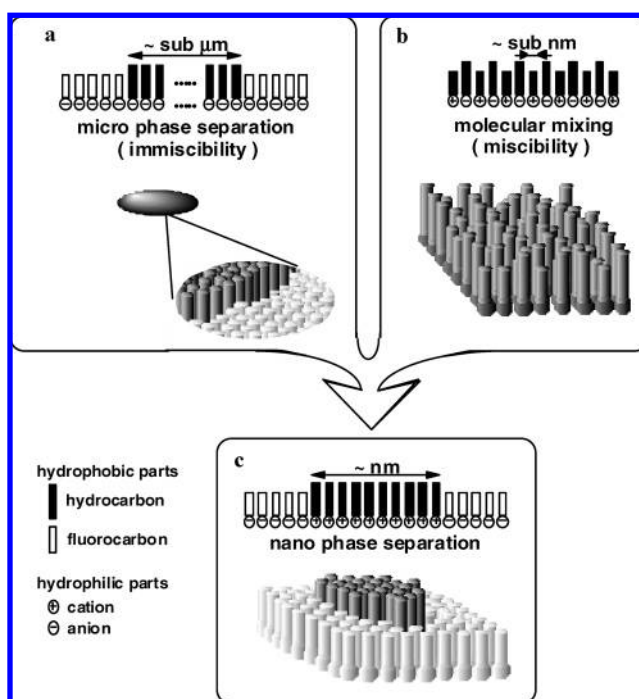

Figure 1. Schematic drawing of the strategy in this study. The mixed monolayer is sketched in a side view by a circle (hydrophilic group: plus, cation; minus, anion) and a rectangle (hydrophobic group: open, fluorocarbon; closed, hydrocarbon), as well as a bird's eye view. (a) Mixed monolayer composed of fluorocarbon and hydrocarbon skeletons with the same ionic hydrophilic parts. In certain cases, the counterionic polymer contains a subphase. (b) Mixed monolayer composed of hydrocarbon amphiphiles with opposite ionic hydrophilic parts involving a complementary hydrogen bonding interaction. (c) Mixed monolayer composed of fluorocarbon and hydrocarbon skeletons with opposite ionic hydrophilic parts.

measurements have indicated the molecular mixing of hydrocarbon multicomponents in monolayers.[18] In fact, AFM observation and X-ray diffraction measurements demonstrated that

* Corresponding author. E-mail: oishiy@cc.saga-u.ac.jp.

† Saga University.

‡ National Institute for Materials Science (NIMS).

§ The University of Kitakyushu.

(1) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418.

(2) Leblanc, R. M. *Curr. Opin. Chem. Biol.* **2006**, *10*, 529.

(3) Becker, W. M.; Kleinsmith, L. J.; Hardin, J. *The World of the Cell*, 6th ed.; Benjamin Cummings: San Francisco, 2005.

(4) Král, K.; Zdenek, P. In *Low-Dimensional Systems: Theory, Preparation, and Some Applications*; Liz-Marzán, L. M., Giersig, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003; p 19.

(5) Nötzel, R.; Niu, Z.; Ramsteiner, M.; Schönherr, H.-P.; Tranpert, A.; Däweritz, L.; Ploog, K.-H. *Nature* **1998**, *392*, 56.

(6) Kadota, S.; Aoki, K.; Nagano, S.; Seki, T. *J. Am. Chem. Soc.* **2005**, *127*, 8266.

(7) Jiang, M.; Zhai, X.; Liu, M. *Langmuir* **2005**, *21*, 11128.

(8) Overney, R. M.; Meyer, E.; Frommer, J.; Brodbeck, D.; Lüthi, R.; Howald, L.; Güntherodt, H.-J.; Fujihira, M.; Takano, H. *Nature* **1992**, *359*, 133.

(9) Kajiyama, T.; Ge, S.-R.; Kojio, K.; Takahara, A. *Supramol. Sci.* **1996**, *3*, 123.

(10) Chi, L. F.; Jacobi, S.; Fuchs, H. *Thin Solid Films* **1996**, *284−285*, 403.

(11) Suga, K.; Yamada, N.; Fujihira, M. *Colloids Surf., A* **2002**, *198−200*, 127.

(12) Matsumoto, M.; Tanaka, K.-I.; Azumi, R.; Kondo, Y.; Yoshino, N. *Langmuir* **2003**, *19*, 2802.

(13) Overney, R. M.; Meyer, E.; Frommer, J.; Güntherodt, H.-J.; Fujihira, M.; Takano, H.; Gotoh, Y. *Langmuir* **1994**, *10*, 1281.

(14) Kunitake, T.; Tawaki, N.; Nakashima, N. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3235.

(15) Kunitake, T. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 709.

(16) Elbert, R.; Folda, T.; Ringsdorf, H. *J. Am. Chem. Soc.* **1984**, *106*, 7687.

(17) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 113.
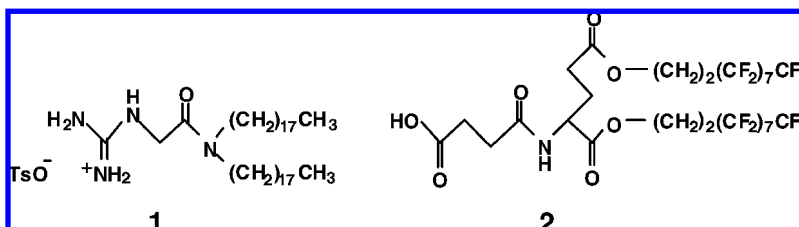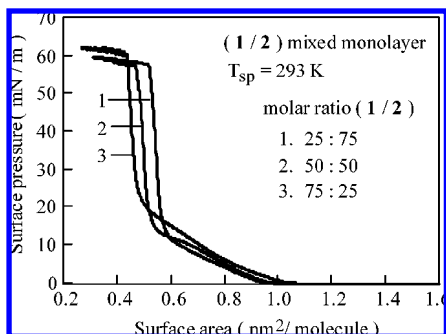
Figure 2. Molecular structure of synthetic lipids **1** and **2**.

Figure 3. $\pi-A$ isotherms of the mixed monolayer of **1** and **2** with different molar fractions.

monolayer components of 1-octadecylguanidinium/1′,3′-bis-(octadecyloxy)isopropyl orotate[19] and triacontanoic acid/nonacosylamine[20] were molecularly miscible in a single phase through the electrostatic and hydrogen bonding interactions. We conceived that these opposing effects of immiscibility between hydrocarbon and fluorocarbon skeletons and attractive interaction, both electrostatic and hydrogen bonding, would be combined in controlling 2D molecular mixing, resulting in the construction of nanometer-sized phase-separated surfaces. We fabricated here such a separated surface domain from the hydrocarbon guanidinium of **1** and the fluorocarbon carboxylic acid of **2** (Figure 2).

The synthesis of **1** has been described in elsewhere.[21] **2** was synthesized through the esterification of glutamic acid with 1H,-1H,2H,2H-perfluorodecanol followed by amidation with succinic anhydride. The product was obtained as a white solid (20%, not optimized): mp 94.9 °C (liquid-crystal phase) $\rightarrow$ 136.5−137.0 °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.99−2.78 (m, 12H, 2CH$_2$ in the glutamate side chain, 2CH$_2$CF$_2$, and C(O)CH$_2$CH$_2$C(O)), 4.37−4.54 (m, 4H, 2COOCH$_2$), 4.61−4.68 (m, 1H, α-H in glutamate), 6.44 (d, 1H, J = 7.5 Hz, amide H). Anal. Calcd for C$_{29}$H$_{19}$NO$_7$F$_{34}$: C, 30.57; H, 1.68; N, 1.23. Found: C, 30.64; H, 1.84 N, 1.24.

A benzene/ethanol solution (80/20) of **1** and **2** at a concentration of 8×10^{-4} M was spread on pure water at a subphase temperature of 293 K. The monolayer was transferred onto a freshly cleaved mica by the horizontal drawing-up method,[22] after compressing to a surface pressure of 20 mN m^{-1} where the monolayer is in a condensed state as shown in Figure 3. The transfer ratio was unity, indicating that each monolayer was covered on mica.

Topographic images of the monolayer surfaces were taken with an atomic force microscope (AFM, SPA300, Seiko
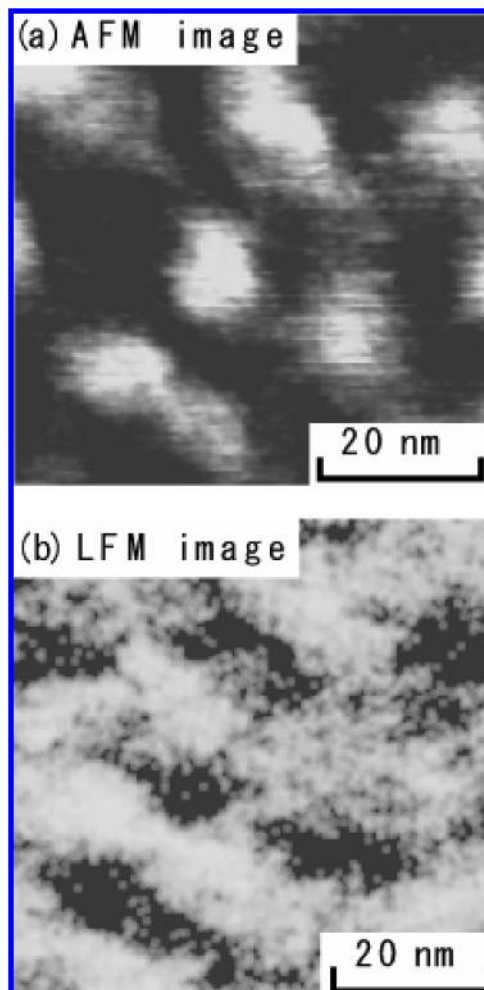
(18) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966.
(19) Oishi, Y.; Torii, Y.; Kato, T.; Kuramori, M.; Suehiro, K.; Ariga, K.; Taguchi, K.; Kamino, A.; Koyano, H.; Kunitake, T. *Langmuir* **1997**, *13*, 519.
(20) Gidalevitz, D.; Weissbush, I.; Bouwman, W. G.; Kjaer, K.; Nielsen, J. A.; Leiserowitz, L. *Langmuir* **1996**, *12*, 1011.
(21) Kamino, A.; Koyano, H.; Ariga, K.; Kunitake, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3619.
(22) For subsequent studies, we adopted the horizontal drawing-up method, which is of wide application. That is, it is capable of transfer even at 0 mN/m: Oishi, Y.; Kuri, T.; Takashima, Y.; Kajiyama, T. *Chem. Lett.* **1994**, 1445.

Figure 4. Surface images of the 25:75 molar **1**/**2** mixed monolayer. (a) AFM and (b) LFM images were obtained simultaneously over a scan area of 60×60 nm^2.

Instruments, Japan). The AFM was operated in constant force mode in air at 293 K using a 20 μm $\times$ 20 μm scan head and a silicon nitride tip on a cantilever with a spring constant of 0.022 N m^{-1}. Lateral force measurements were made simultaneously with the topographic measurement. To obtain the maximum LFM signal, the sample surface was scanned along the direction perpendicular to the long axis of the cantilever.

Figure 4a shows a 60×60 nm^2 top-view AFM image of the (**1**/**2**) mixed monolayer with a molar fraction of 25:75, where the brighter and darker portions correspond to the higher and lower regions of the monolayer surface, respectively. Round islandlike morphology was observed, with an 18 $\pm$ 2 nm diameter (at the bottom of the domain) and a height of 0.4 $\pm$ 0.1 nm above the surrounding film. The area fraction of the circular domain and the surrounding matrix agreed closely with the 1:3 molar fraction of **1**/**2** in the sample solution. The same image was observed over

almost all of the mica plate. Previous observations by other groups on mixed monolayers composed of hydrocarbon and fluorocarbon skeletons gave phase-separated structures composed of domains with diameters from 150 nm to 3 μm.[8–17] The current system produced much smaller domains, and an AFM image of the (**1/2**) mixed monolayer in a larger scan area of 5 × 5 μm^2 was morphologically homogeneous.

Figure 4b shows an LFM image recorded simultaneously with the AFM image of Figure 4a. The contrast in the LFM image corresponds to the different magnitude of lateral force. The bright part in Figure 4b corresponds to the region with the higher lateral force, and the dark part corresponds to that with lower one.[23] It is clear that the monolayer is composed of two regions different in lateral force. Interestingly, parts a and b of Figure 4 show opposite contrast to individual domains. Overney et al.,[8,13] Briscoe and Evans,[24] and Kajiyama et al.[9] reported that the lateral force on the alkyl surface was lower than that on the fluoroalkyl one. Therefore, we conclude that the regions of lower and higher lateral forces are composed of **1** and **2**, respectively, in agreement with the assignment based on the molar fraction and the AFM area fraction.

The domain size (diameter, about 18 nm) observed in Figure 4a was very close to the radius of curvature (manufacturer-specified 20 nm) of the AFM tip. In such case, the finite size of the tip causes a lateral deformation of the object imaged. We therefore corrected the domain size by the equation $R_d = R_o - (2R_t h - h^2)^{1/2}$, where R_d is the real domain radius, R_o is the observed domain radius (at the bottom of the domain), R_t is the radius of curvature of the AFM tip, and h is the domain height on the assumption that the domain shape is a disc. The real domain diameter in Figure 4a is estimated to be 11 nm on the basis of the above correction. The number of molecules involved in a domain of diameter 11 nm is estimated to be only 200 from the molecular occupied area of 0.4 nm^2 molecule^{-1} in the surface pressure−area isotherm.

Figure 5a,b shows AFM images of the mixed monolayer with molar fractions of 50:50 and 75:25, respectively. The surface morphology of Figure 5a appears to be derived from assembled circular domains. In Figure 5b, the higher flat surface with holes of 12 nm diameter (at hole top) and 0.4 nm depth was observed. The area fraction of the two regions again closely agrees with the molar fraction, and the area fraction of the higher region increased with an increase in the content of **1**. The heights from the mica substrate are estimated to be 1.1 and 0.7 ± 0.1 nm for the higher and lower regions, respectively, by artificially piercing a hole through the monolayer with an applied force stronger than 10^{-9} N. These heights are consistent with the thickness of the respective monolayer of **1** and **2**.

The size of the domain formed in this study is extremely small compared with that of the previous examples of mixed Langmuir monolayer[25] composed of hydrocarbon and fluorocarbon skeletons.[26] Phase separation by the surface free energy difference for the hydrocarbon **1** chain with a cationic hydrophilic part and the fluorocarbon **2** chain with an anionic one causes thermodynamic instability by excess repulsive energy among the same
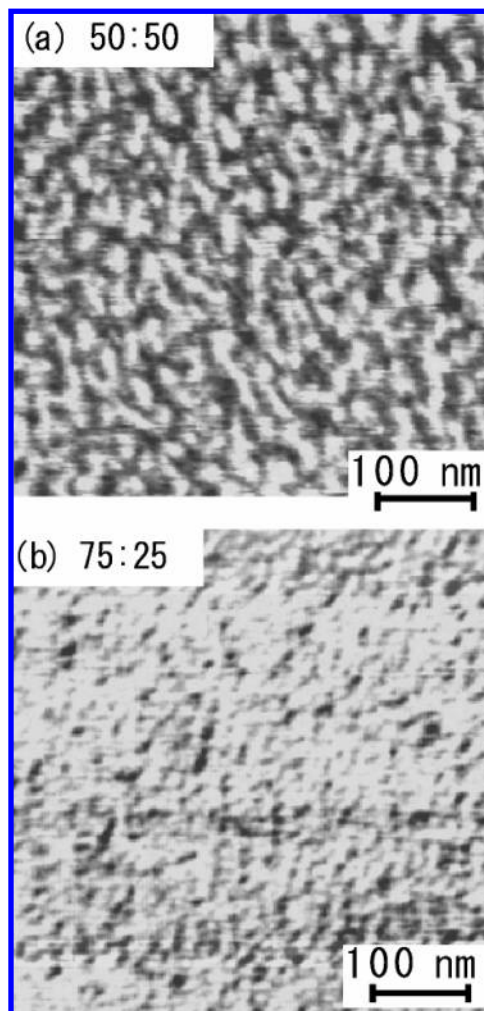

Figure 5. AFM images of the **1/2** mixed monolayer with molar fractions of (a) 50:50 and (b) 75:25 over a scan area of 500 × 500 nm^2.

molecules in the region of the domain or matrix. Hence, the interfacial region between domain and matrix may increase; that is, the domain size decreases to reduce the repulsive energy. The attractive effect of molecular recognition through hydrogen bonding may also contribute to nanophase separation because of **1** and **2** with complementary hydrogen bonding sites, which is unclear at the present stage.

In summary, nanometer-sized surface morphology has been constructed in a mixed monolayer by a combination of the ionic and/or hydrogen bonding interaction between the two polar head groups and the surface free energy difference between the hydrophobic parts of the hydrocarbon and fluorocarbon. Control of domain size from nanometer to micrometer in a phase-separated monolayer may be achieved by varying the pH in the subphase and/or the ionic strength in the hydrophilic part and also by proper molecular design of the hydrophobic (including the alkyl

(23) The difference in lateral force is not due to a change in topography because the lateral force curve shows the reversal of its magnitude depending on the scanning direction. Hence, the magnitude of the lateral force contains frictional force and adhesive force contributions.

(24) Briscoe, B. J.; Evans, D. C. B. *Proc. R. Soc. London, Ser. A* **1982**, *380*, 389.

(25) There have been several studies that exhibited nanophase separation in self-assembled monolayers: Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7164. Tamada, K.; Hara, M.; Sasabe, H.; Knoll, W. *Langmuir* **1997**, *13*, 1558.

(26) The nanometer-sized domain, which is comparable to one obtained in this study, is also formed by the spontaneous aggregation of fluorocarbon chains in a single-component system: Kato, T.; Kameyama, M.; Ehara, M.; Iimura, K. *Langmuir* **1998**, *14*, 1786, Maaloum, M.; Muller, P.; Krafft, M. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 4331, Fontaine, P.; Goldmann, M.; Muller, P.; Fauré, M.; Konovalov, O.; Krafft, M. P. *J. Am. Chem. Soc.* **2005**, *127*, 512. Zhang, G.; Marie, P.; Maaloum, M.; Muller, P.; Benoit, N.; Krafft, M. P. *J. Am. Chem. Soc.* **2005**, *127*, 10412. Then, the formation mechanism is different from that in this study based on phase separation. Our method in multicomponent systems is advantageous with regard to structural control and applications of nanosized domains.

chain length) and hydrophilic parts. The proposed method in this study may appear to be a candidate for the designed self-assembly system.[27−29]

(27) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. *Science* **1999**, *283*, 661.
(28) Ariga, K.; Nakanishi, T.; Hill, J. P. *Soft Matter* **2006**, *2*, 465.

(29) Zhang, F.; Gates, R. J.; Smentkowski, V. S.; Natarajan, S.; Gale, B. K.; Watt, R. K.; Asplund, M. C.; Linford, M. R. *J. Am. Chem. Soc.* **2007**, *129*, 9252.