CHEMISTRY LETTERS, pp. 253-256, 1987.

Fluorescence Microscopic Study of Change in Pyrene Cluster Size in Mixed Monolayers of Pyrene-Substituted and Normal Fatty Acids with Chain-Length Matching

Masamichi FUJIHIRA,* Katsuhiko NISHIYAMA, Yuichi HAMAGUCHI, and Yoshiro TATSU
Department of Chemical Engineering, Tokyo Institute of Technology,
Ohokayama, Meguro-ku, Tokyo 152

Fluorescence microscopic observation of clusters of pyrene moieties in the mixed monolayer assembly of pyrene(Py)-substituted fatty acid ($Py(CH_2)_nCOOH$; n = 9, 15) and normal fatty acid ($CH_3(CH_2)_nCOOH$; n = 18, 14) deposited from a water surface on a quartz plate was carried out. The cluster size was changed drastically depending upon difference between chain lengths of the constituent fatty acids.

A spatially fixed structure of an assembly of monolayers such as a Langmuir-Blodgett (LB) film is of great importance for application of the assembly to molecular devices.1-4) Based upon the desired spatial arrangement of the electron (or energy) donor and acceptor molecules with an appropriate number of spacer layers, unidirectional photoinduced electron (or energy) transfer normal to the substrate metal or silver halide plate has been attained with the LB assembly.4-16) A specific domain not only with the thickness but also with the area of the molecular dimensions should be created in the LB film in a controlled manner to realize the fabrication of true molecular devices by the LB technique. This letter reports the possibility of size control of the specific domains in the two component LB film of fatty acids with and without a pyrene tail moiety.

10-(1-Pyrene)decanoic acid (PDA) and 16-(1-pyrene)hexadecanoic acid (PHA) from Molecular Probes and arachidic acid (AA; icosanoic acid) and palmitic acid (PA; hexadecanoic acid) of G.R.-grade from Wako Pure Chemicals Co. were used without further purification. The mixed monolayer of PDA - AA was spread with chloroform on the aqueous subphase (made of distilled water) containing 0.3 mM (M - mol dm^{-3}) $CaCl_2$ and 0.05 mM $NaHCO_3$ (Wako G.R.-grade reagents) in a Langmuir trough (Kyowa Kaimenkagaku Co.) and deposited on a nonfluorescent quartz plate (Fujiwara Seisakusho Co.) automatically at 35 mN m^{-1}. The mixed monolayer of PHA - PA was prepared under the same experimental conditions except that the monolayer was deposited at 25 mN m^{-1}. The UV-visible absorption, the fluorescence spectra, and the fluorescence micrographs of the mixed LB films deposited were taken with a Hitachi UV 220A, a Hitachi 850 fluorescence spectrophotometer, and a Nikon XF-EFD2 fluorescence microscope with a 340 nm excitation filter, respectively. All experiments were done at 25 °C.

Pure monolayers of PDA and PHA were unstable and collapsed at low surface pressures less than 40 and 30 mN m^{-1}, respectively. The stabilities of the monolayers of PDA and PHA were, however, increased by mixing with AA and PA, respectively.[16,17] Especially for the PDA - AA mixed monolayer, the surface pressure could be readily raised upto a high value more than 40 mN m^{-1} without an appreciable collapse.[16,18]

The UV absorption and fluorescence spectra of the pyrene moieties[17,18] for the PDA - AA and the PHA - PA mixed monolayer are shown in Figs. 1 and 2, respectively. In the fluorescence spectrum for the PHA - PA system, the excimer band with a peak at ca. 470 nm predominates more strikingly over the monomer band peaking at 378 nm (Fig. 2) compared with the case for the PDA - AA monolayer (Fig. 1). This higher ratio of the fluorescence intensities for the excimer to the monomer bands, I_E/I_M, for the PHA - PA system suggests that segregation of the pyrene-tailed fatty acid phase previously reported for the PDA - AA mixed monolayer took place in a more distinct and complete manner for the PHA - PA system. The ease of segregation for the PHA - PA system is also clear from comparison of the absorption spectra of the pyrene moieties appearing in the wavelength region from 300 to 380 nm. The spectrum of the PDA - AA system in Fig. 1 shows a typical vibrational structure which is commonly observed for free molecules of pyrene derivatives solubilized in organic solvents[19] and aqueous micellar solutions.[20,21] This implies that interaction between pyrene moieties in the ground state in the PDA - AA system is week. On the other hand, the spectrum of the PHA - PA system rather resembles to those of pyrene crystals[22,23] and hence indicates strong interaction.

The nonlinear increase in I_E/I_M with increase in PDA concentration and difference between the excitation spectra for the excimer and the monomer for the PDA - AA mixed monolayer were pointed out previously as evidence for the phase separation.[18] The similar difference between the excitation spectra was observed more

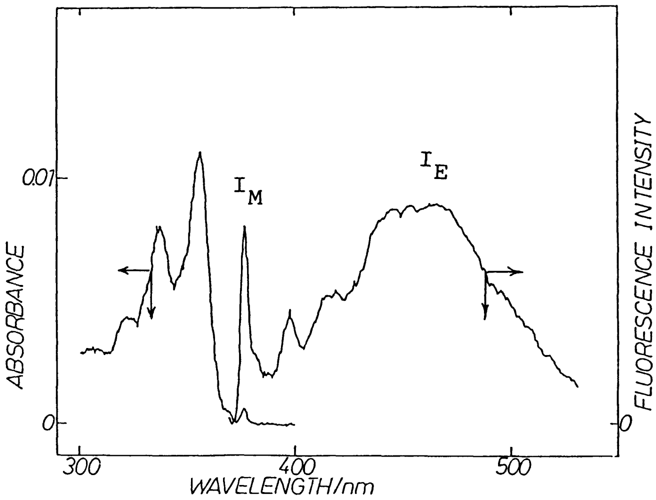

Fig. 1. The absorption and fluorescence spectra of the mixed monolayer of PDA - AA (1:2) deposited on a quartz plate at 35 mN m^{-1}. The excitation wavelength, λ_{ex}, was 337 nm.

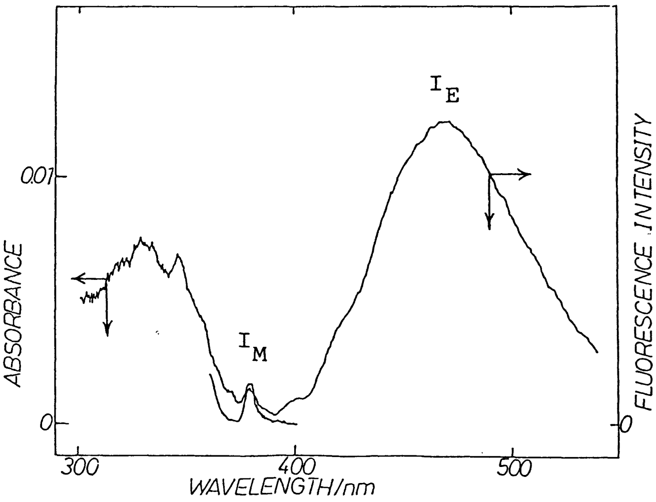

Fig. 2. The absorption and fluorescence spectra of the mixed monolayer of PHA - PA (1:2) deposited on a quartz plate at 25 mN m^{-1}. λ_{ex} = 337 nm.

markedly for the PHA - PA system.

In order to observe the phase separation directly, fluorescence microscopy of these mixed monolayers[24,25] was carried out with an excitation beam of 340 nm. The micrographs taken for the PDA - AA and the PHA - PA mixed monolayers are shown in Figs. 3A and 3B, respectively. The many bright spots, i.e. the parts emitting the visible light, in the dark surroundings can be assigned to the segregated pyrene-tailed fatty acid phase, because the excimer forming pyrene species predominates in this phase while the fatty acid phase dissolves mainly monomeric pyrene-tailed fatty acid emitting only the invisible UV light. It is of great interest to note that pyrene cluster sizes in these two systems are very much different from each other. As we would expect from some indications of strong interaction in the ground state of pyrene moieties for the PHA - PA system described above, the segregated pyrene phase grows well to fairly large islands. The increase in the cluster size in the PHA - PA monolayer can be interpreted by facility for the pyrene moieties protruded beyond the outermost surface of the PA layer to be oriented and aligned to more preferable positions to interact strongly with each other as depicted in Fig. 4.

In other words, the cluster size can be controlled intentionally by selecting an appropriate combination of pyrene tailed and normal fatty acids with alkyl chains of different carbon numbers. A more detailed study is now in progress with various combinations of pyrene-substituted and normal fatty acids

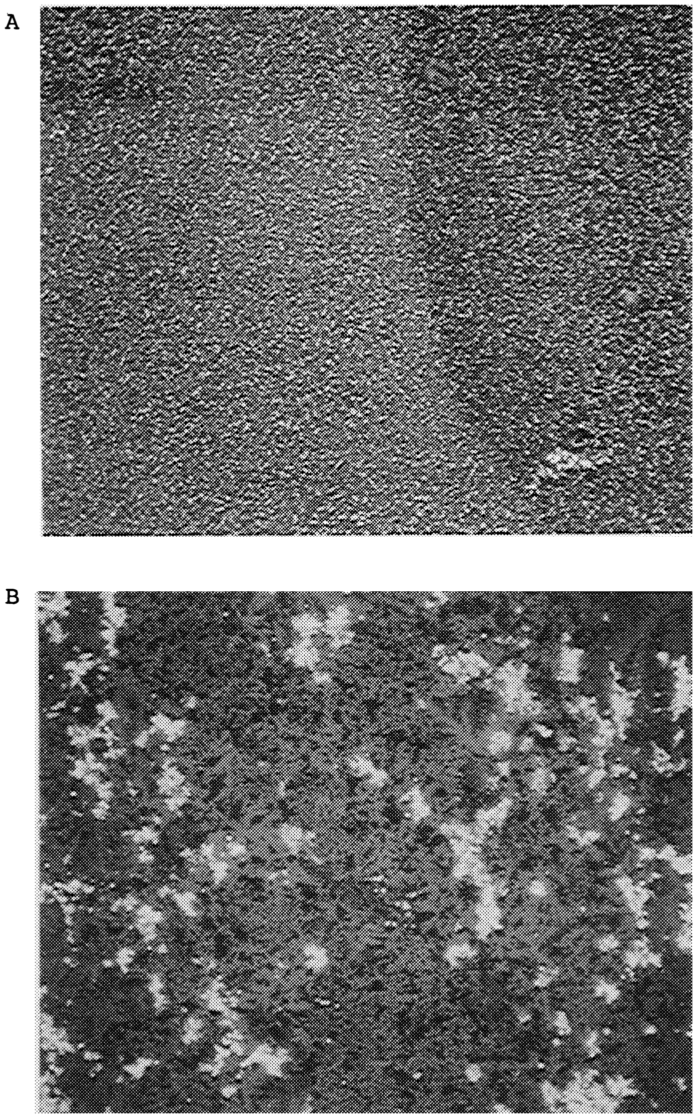

Fig. 3. The fluorescence micrographs of the same mixed monolayers as those used in Figs. 1 and 2. (A) PDA - AA, (B) PHA - PA

⊢—⊣ 50 μm

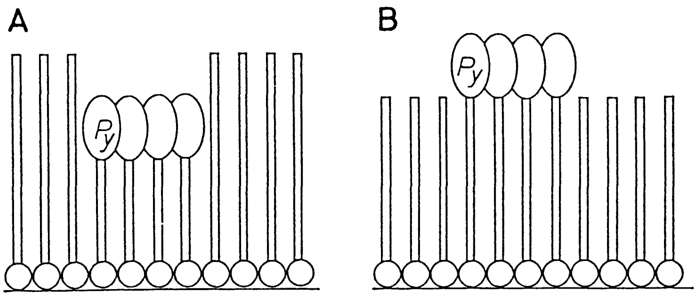

Fig. 4. The schematic representation of aggregation of pyrene moieties. (A) PDA - AA, (B) PHA - PA.

to control the cluster size as a function of the chain-length difference and the monolayer-forming conditions such as subphase compositions (pH, electrolyte), spreading solvents, compressing rates, temperatures, etc.

The authors wish to thank Mr. Toshihito Takahashi and Mr. Kazuhisa Suzuki of Nippon Kogaku Kogyo Co. for the use of the Nikon XF-EFD2 fluorescence microscope. This work was partially supported by Grant-in-Aid for Scientific Research No. 61470076 from the Ministry of Education, Science, and Culture.

References

1) G. L. Gaines, Jr., "Insoluble Monolayers at Liquid-Gas Interfaces," Interscience Publishers, New York (1966).
2) "Molecular Electronic Devices," ed by F. L. Carter, Marcel Dekker, New York (1982).
3) F. L. Carter, J. Vac. Sci. Technol. B, 1, 959 (1983).
4) H. Kuhn, D. Möbius, and H. Bücher, "Techniques of Chemistry," ed by A. Weissberger and B. W. Rossiter, Wiley, New York (1973), Vol. 1, Part 3B, p.577.
5) H. Kuhn, J. Photochem., 10, 111 (1979).
6) H. Kuhn, Thin Solid Films, 99, 1 (1983).
7) D. Möbius, Ber. Bunsenges. Phys. Chem., 82, 848 (1978).
8) D. Möbius, Acc. Chem. Res., 14, 63 (1981).
9) T. L. Penner and D. Möbius, J. Am. Chem. soc., 104, 7407 (1982).
10) W. Arden and P. Fromherz, Ber. Bunsenges. Phys. Chem., 82, 868 (1978).
11) W. Arden and P. Fromherz, J. Electrochem. Soc., 127, 370 (1980).
12) H. Nakahara and K. Fukuda, Thin Solid Films, 99, 45 (1983).
13) M. Saito, M. Sugi, T. Fukui, and S. Iizima, Thin Solid Films, 100, 117 (1983).
14) K. Sakai, M. Saito, M. Sugi, and S. Iizima, Jpn. J. Appl. Phys., 24, 865 (1985).
15) M. Sugi, K. Sakai, M. Saito, Y. Kawabata, and S. Iizima, Thin Solid Films, 132, 69 (1985).
16) M. Fujihira, K. Nishiyama, and H. Yamada, Thin Solid Films, 132, 77 (1985).
17) T. Yamazaki, N. Tamai, and I. Yamazaki, Chem. Phys. Lett., 124, 326 (1986).
18) M. Fujihira, K. Nishiyama, and Y. Hamaguchi, J. Chem. Soc., Chem. Commun., 1986, 823.
19)
20) S. S. Atik and L. A. Singer, J. Am. Chem. Soc., 101, 6795 (1979).
21) S. Hashimoto and J. K. Thomas, Chem. Phys. Lett., 109, 115 (1984).
22) Y. Takahashi and M. Tomura, J. Phys. Soc. Jpn., 34, 1014 (1973).
23) A. Matsui, M. Iemura, and H. Nishimura, J. Luminescence, 24,25, 445 (1981).
24) M. Lösche, E. Sackmann, and H. Möhwald, Ber. Bunsenges. Phys. Chem., 87, 848 (1983).
25) M. Lösche and H. Möhwald, Rev. Sci. Instrum., 55, 1968 (1984).

(Received October 6, 1986)