Atomic force microscopic observation of a dialkylmelamine monolayer on barbituric acid

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A monolayer of 2-amino-4,6-di(dodecylamino)-1,3,5-triazine 1 transferred from barbituric acid solution onto a mica plate is observed by atomic force microscopy (AFM) to show regularly arrayed terminal methyl groups of 1 as a result of hydrogen-bond networking.

We have recently reported multisite molecular recognition between multicomponent monolayers on water and flavin adenine dinucleotide (FAD) in water.[1] This result opened the possibility to control the alignment of component amphiphiles within a monolayer.[2] We extended this concept one step further in the present study and examined extended hydrogen-bond network formation between a monolayer of 2-amino-4,6-di(dodecylamino)-1,3,5-triazine **1**† and aqueous barbituric acid. Related supramolecular structures were found by Lehn *et al.* in the solid phase,[3] by Seto *et al.* in bulk solution,[4] and by Kimizuka *et al.* in aqueous bilayer membranes.[5] Ahuja *et al.* reported the formation of a network similar to ours at the air/water interface on the basis of UV–VIS reflection spectroscopy.[6]

Hydrogen bonds between monolayer **1** and barbituric acid were detected in the FTIR spectrum‡ of an LB film of **1** (nine-layer Y film, transfer ratio of unity) transferred from 1 mmol dm^{-3} barbituric acid solution onto a gold-coated glass plate. A peak at 1713 cm^{-1} assigned to $\nu_{C=O}$ of barbituric acid showed a significant shift caused by hydrogen-bond formation, relative to that reported for monomeric barbituric acid in an argon matrix (1754 cm^{-1}).[7] This peak was not observed in a spectrum of a LB film transferred from pure water in the same manner as that from barbituric acid solution. X-Ray photoelectron spectroscopy (XPS)§ of the LB films transferred from 0.1, 0.5, 1, 5, and 10 mmol dm^{-3} barbituric acid solutions onto gold-coated glass plates gave the oxygen : nitrogen ratio for each film. The component ratios (barbituric acid : **1**) were derived from this elemental ratio¶ and plotted against barbituric acid concentration. The plots showed binding saturation of barbituric acid to monolayer **1**. Curve-fitting according to the Langmuir adsorption isotherm revealed that the maximum binding ratio was 1.1 ± 0.1 : 1 with a binding constant of 3000 dm^3 mol^{-1}. Surface pressure *vs.* molecular area (π–A) isotherms‖ showed that the molecular area of **1** on pure water at 15 mN m^{-1} was 0.42 nm^2, implying that the monolayer formed a well packed condensed phase. Barbituric acid in the subphase (1 mmol dm^{-3}) caused the expansion of the π–A isotherm with an increase in the molecular area to 0.45 nm^2 at the same surface pressure.

Fig. 1 shows non-filtered and Fourier-filtered AFM images (5 nm × 5 nm)** of monolayer **1**. The single monolayer was transferred from 10 mmol dm^{-3} barbituric acid solution at 15 mN m^{-1} onto a freshly cleaved mica (10 × 20 mm) by the horizontal drawing-up method.[8] The same image was observed over almost all the mica plate. The monolayer was not damaged by the AFM tip even after repeated scannings. However, a hole could be artificially pierced through the monolayer with an applied force stronger than 10^{-9} N. The hole was about 2 nm deep, and was comparable to the calculated molecular length based on the extended CPK molecular model. The hole depth, apparently, represents the thickness of the monolayer. It is clear that brighter portions, which correspond to individual terminal methyl groups of **1**, are regularly arranged in a two-dimensional oblique array with a nearest-neighbour spacing of 0.40 ± 0.02 nm (*a*-axis), next-neighbour spacing of 0.48 ± 0.02 nm (*b*-axis) and an interaxis angle γ of 105 ± 5°. The occupied molecular area of **1** in the monolayer was evaluated from these data as 0.19 ± 0.01 nm^2 per molecule, indicating that one brighter portion in the AFM images was composed of one terminal methyl group of **1**. Based on these geometrical data, a plausible packing state of alkyl chains is drawn as Fig. 2.

The monolayer was similarly transferred from pure water. However, the AFM image was not obtained because the monolayer was destroyed by tip scanning with the same applied force as before, resulting in a hole corresponding to the monolayer thickness (*ca.* 2 nm depth). Therefore, successful AFM observation appears to be made possible by the rigidity conferred by the supramolecular network based on complementary hydrogen bonds among **1** and barbituric acid as shown in Fig. 3.

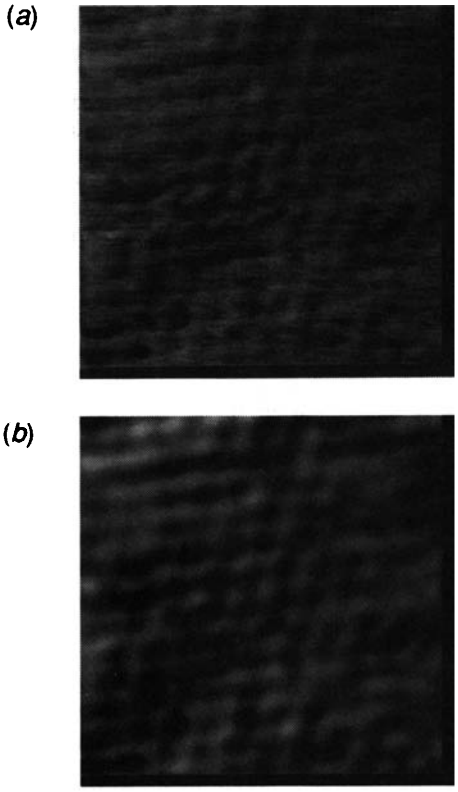

Fig. 1 Non-filtered (*a*) and Fourier-filtered (*b*) AFM images (5 × 5 nm)

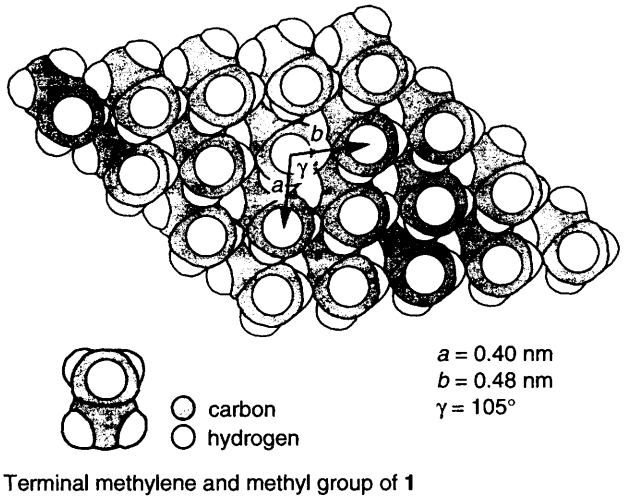

Fig. 2 A plausible packing state of alkyl chains

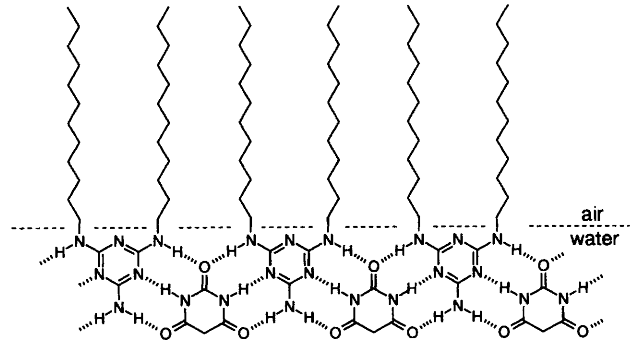

Fig. 3 Supramolecular strands of **1** and barbituric acid

Construction of supramolecular architecture or surfaces by spontaneous, non-covalent self-organization has been extensively studied in the past decade.[9] The ordered molecular alignment on solid surfaces has great application potentials.[10] We demonstrated in this study that specific disposition of individual monolayer components becomes feasible by the use of rationally designed amphiphiles in combination with hydrogen-bonding partners. The preparation of unique molecular patterns is in progress in these laboratories.

Footnotes

† Detailed description of the synthetic procedure for **1** will be reported elsewhere. **1**: colourless powder, mp, 92.6–93.2 °C; TLC, R_f 0.43 (10:1 CH$_2$Cl–MeOH); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.88 (t, 6 H, J 6.7 Hz), 1.2–1.4 (m, 36 H), 1.4–1.6 (m, 4 H), 3.34 (br s, 4 H), 4.8–5.3 (br, 4 H). Anal. Calc. for $C_{27}H_{54}N_6$: C, 70.08; H, 11.76; N, 18.18. Found: C, 69.92; H, 11.72; N, 17.91%.

‡ Measured in reflection–absorption spectrum (RAS) mode with a Nicolet 710 FTIR spectrometer at the digital resolution of 4 cm^{-1}.

§ Recorded on a Perkin–Elmer PHI 5300, X-ray source: Mg-Kα 300 W, take-off angle = 45°.

¶ The numerical relationship between the oxygen : nitrogen ratio (O : N) and the component ratio (barbituric acid : **1**), y, is given by $O:N = 3y:(6 + 2y)$.

|| Measured with a computer-controlled film balance system FSD-50 (USI System, Fukuoka). Benzene–ethanol (80:20) was used as a spreading solvent. Compression was started 10 min after spreading at a rate of 0.2 mm s^{-1} (or 30 mm^2 s^{-1} based on area). The temperature of the subphase was kept at 20 ± 0.2 °C. Surface pressures were measured by a Wilhelmy plate which was calibrated with the transition pressure of an octadecanoic acid monolayer.

** Obtained on a Seiko Instrument SFA300 at 293 K in air in constant-height mode, in which the feedback electronics and corresponding software were used to keep the sample height and to measure the cantilever deflection. A 0.8 × 0.8 μm scan head and a silicon nitride tip on a cantilever with a spring constant of 0.022 N m^{-1} were used. The applied force on scanning was *ca.* 10^{-10} N.

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Received, 23rd April 1996; Com. 6/02817I