Effect of Melamine-Amphiphile Structure on the Extent of Two-Dimensional Hydrogen-Bonded Networks Incorporating Barbituric Acid

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Abstract: Four alkyl melamine amphiphiles each containing identical triads of hydrogen-bonding sites (hydrogen donor, acceptor, and donor) but different numbers of alkyl chains were examined in order to determine their monolayer properties and binding behavior towards barbituric acid (BA). Their structural organization in supramolecular assemblies at the air–water interface was affected by the bulkiness of the hydrophobic part of the amphiphile. Aqueous BA and amphiphiles with two or three alkyl chains formed a 1:1 alternate network structure. In contrast, a melamine amphiphile with four alkyl chains formed a 2:1 (BA:amphiphile) complex rather than a 1:1 alternate network structure. The 2:1 complex appears to behave like an independent molecular entity without further networking. The results point to the importance of size matching between the hydrophobic part of the monolayer and the underlying hydrogen-bonded network in order to maintain the overall supramolecular structure.

Keywords
amphiphiles · barbituric acid · hydrogen bonds · melamines · molecular recognition · monolayers

Introduction

The complementary hydrogen bonds between 2,4,6-triamino-1,3,5-triazines (melamines) and cyclic imides or between 2,6-diaminopyrimidines and cyclic imides are a useful tool for the construction of supramolecular network structures in various phases.[1] In the solid state, for instance, *N*,*N*′-diphenylmelamine forms a 1:1 alternate network structure with barbiturate. When *N*,*N*′-di-(*tert*-butyl)melamine is used, the structure of the supramolecular species is altered to a 1:1 crinkled complex in order to relieve the steric hindrance of bulky *tert*-butyl groups.[1a]

Amphiphilic barbituric acid (BA) derivatives and aqueous melamine or triaminopyrimidine have been proposed to form supramolecular 1:1 alternate network structures at the air–water interface.[2] We recently showed, by means of atomic force microscopy (AFM), that an *N*,*N*′-didodecylmelamine monolayer transferred from an aqueous BA solution onto a mica plate has the supramolecular network structure shown in Figure 1.[3] In this system, the molecular cross-section of two alkyl chains attached to one melamine ring supplies an appropriate distance between melamine units to allow BA to be accommodated in a 1:1 alternate network. The introduction of a bulkier group on the melamine ring is expected to change the supramolecular structure at the interface. In surface monolayers, the orientation of the melamine ring in relation to the alkyl chains is spatially restricted by alkyl chain packing within the monolayer assembly. Therefore, the inter-melamine distance can be controlled precisely in order to provide information on the spatial requirements in supramolecular architectures.

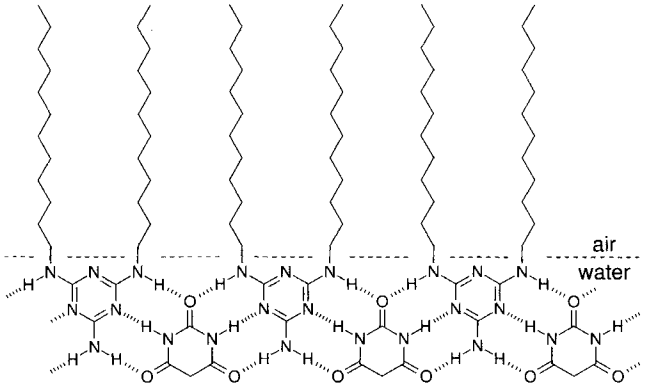

Figure 1. The 1:1 alternate network structure of BA/2C_{12}mela.

Results and Discussion

We employed four alkyl melamine amphiphiles (2C_{12}mela, 2$C_{12}OC_3$mela, 3C_{12}mela, and 4C_{12}mela) each containing identical triads of hydrogen-bonding sites (hydrogen donor, ac-

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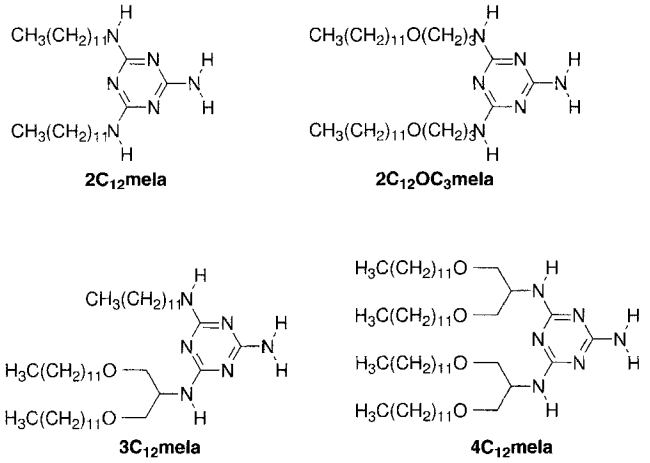

ceptor, and donor), but different numbers of alkyl chains, and examined their monolayer properties and binding behavior towards BA. These amphiphiles were synthesized by aminoalkylation of 2-amino-4,6-dichloro-1,3,5-triazine,[4] directly or in a stepwise manner (see Experimental Section).

$\pi-A$ Isotherms of monolayers: The $\pi-A$ isotherm of $2C_{12}$mela (Figure 2a) shows that this dialkylmelamine amphiphile has a condensed phase on pure water with a limiting molecular area of 0.42 nm^2. This value is close to the theoretical cross-section of the two alkyl chains, and indicates formation of a well-packed monolayer. The isotherm of $2C_{12}OC_3$mela, a dialkylmelamine with ether linkages in its alkyl chains, shows an inflection point at approximately 20 $mN\,m^{-1}$ on pure water (Figure 2b), and the limiting area of the condensed phase is 0.40 nm^2. At low surface pressures, it forms a more expanded phase. The trialkylmelamine $3C_{12}$mela on pure water shows monolayer properties similar to those of $2C_{12}OC_3$mela (Figure 2c). Its isotherm has an inflection point at approximately 5 $mN\,m^{-1}$ marking the transformation from an expanded to a condensed phase; a well-packed phase is formed at high surface pressures with a limiting area of 0.61 nm^2. This value again corresponds to the theoretical cross-section of three alkyl chains

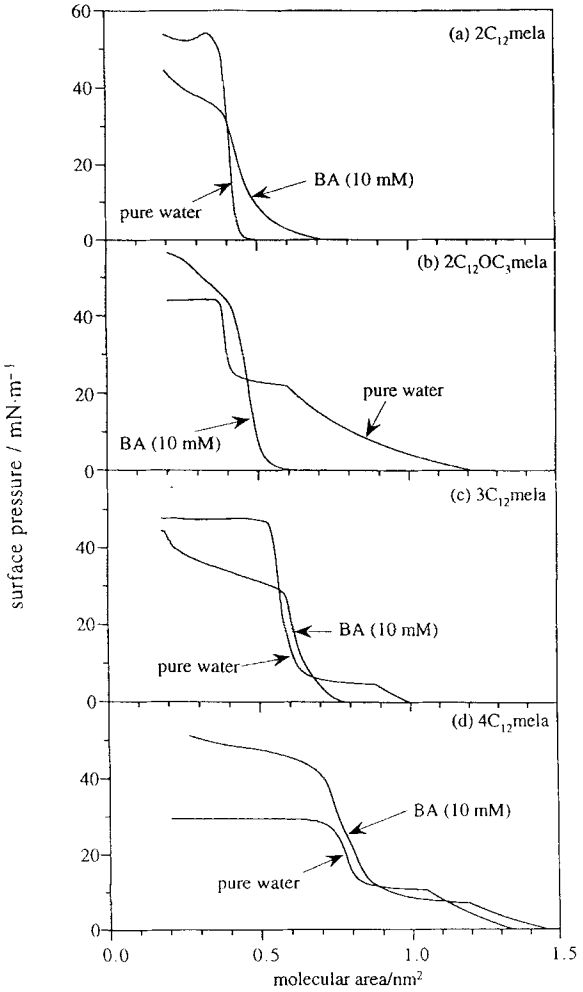

Figure 2. $\pi-A$ Isotherms of a) $2C_{12}$mela, b) $2C_{12}OC_3$mela, c) $3C_{12}$mela, d) $4C_{12}$mela on pure water and on a 10 mM BA solution at 20.0±0.2 °C.

$(0.2\times3 = 0.6\ nm^2)$. The tetraalkylmelamine $4C_{12}$mela has a lower collapse pressure (ca. 30 $mN\,m^{-1}$, Figure 2d) than the other three amphiphiles, but the shape of the isotherm is not very different. A condensed phase with a limiting area of 0.84 nm^2 is formed above inflection point at ca. 10 $mN\,m^{-1}$.

The presence of 10 mM BA in the subphase changes the $\pi-A$ isotherms in all cases. The isotherms of $2C_{12}$mela, $2C_{12}OC_3$mela, and $3C_{12}$mela monolayers on aqueous BA display lower collapse pressures, larger molecular areas, and slopes with lower gradients than the corresponding isotherms on pure water. The inflection point observed on pure water disappears on aqueous BA. Apparently, binding with aqueous BA induces formation of island structures (i.e., two-dimensional aggregates of the melamine amphiphile).[5] The $4C_{12}$mela monolayer on aqueous BA behaves differently from the other monolayers. It has a higher collapse pressure than on pure water, and the phase-transition pressure is clearly observed at around 8 $mN\,m^{-1}$. This observation indicates that the $4C_{12}$mela monolayer maintains its distinct structure and molecular mobility even on aqueous BA.

Mode and stoichiometry of BA binding: The reflection–absorption (RAS) FT-IR spectra of $2C_{12}$mela LB films transferred from pure water and from 10 mM aqueous BA solution were

Abstract in Japanese:

アルキル鎖の本数は異なるが同一の水素結合部位を持つ四種類のアルキルメラミン脂質の単分子膜挙動と水中のバルビツール酸に対する結合挙動を調べた。その結果、気水界面に発現する分子組織体(超分子)の構造はメラミン脂質の疎水部の高さに影響されることが分かった。すなわち、二本あるいは三本のアルキル鎖をもつメラミン脂質と水中のバルビツール酸は両者が互い違いに並んだネットワーク構造を形成する。一方、四本のアルキル鎖をもつメラミン脂質($4C_{12}$mela)はこのようなネットワーク構造を形成することなく、2:1バルビツール酸/$4C_{12}$mela複合体を形成することが分かった。この2:1複合体はネットワーク構造を伸張することなく、独立の化学種として存在しているようである。これらの結果から、気水界面での分子組織体(超分子)形成には、脂質の疎水部とその下部にある水素結合性ネットワークの大きさが一致することが重要であることが結論される。

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compared (Figure 3a and b, respectively). The changes observed are typical for hydrogen-bond formation. A strong C=O peak of bound BA is observed at $\tilde{\nu} = 1719\ cm^{-1}$ in Figure 3b, which is absent in Figure 3a. The C=O peak of BA in an argon matrix appears at $\tilde{\nu} = 1754$ (for the monomer) and 1732 (for the dimer) cm^{-1}, but these peaks shift to $1694\ cm^{-1}$ in the solid state at 20 K, owing to hydrogen-bond formation between molecules of BA.[6] A shift in the C=O peak of a BA derivative as a result of hydrogen bonding with a melamine derivative (1:1 BA derivative/$2C_{12}$mela) has also been reported in KBr, from $\tilde{\nu} = 1737$ to $1715\ cm^{-1}$.[7] In addition, a shift is observed for the $(CN)_{ring}$ peak ($\tilde{\nu} = 1606$ to $1545\ cm^{-1}$), and broadening is seen for the NH peak (at $\tilde{\nu} = 1653\ cm^{-1}$ in Figure 3a).[8] The shift in the $(CN)_{ring}$ peak is similar to that observed when thymidine binds to a diaminotriazine monolayer through complementary hydrogen bonding (from $\tilde{\nu} = 1571$ to $1557\ cm^{-1}$).[9] These changes in the IR spectra indicate the formation of complementary hydrogen bonds between BA and $2C_{12}$mela.

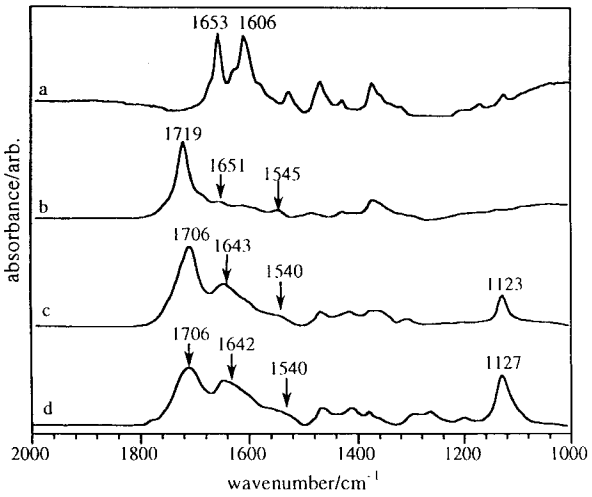

Figure 3. FT-IR Spectra of LB films: a) $2C_{12}$mela transferred from pure water; b) $2C_{12}$mela transferred from BA solution; c) $3C_{12}$mela transferred from BA solution; d) $4C_{12}$mela transferred from BA solution.

The IR spectra of $3C_{12}$mela and $4C_{12}$mela LB films transferred from 10 mM aqueous BA show characteristics similar to those of $2C_{12}$mela, namely, shifted C=O and $(CN)_{ring}$ peaks and a broadened NH peak (Figure 3c,d). The additional peak around $1125\ cm^{-1}$ is assigned to $\tilde{\nu}$(C–O). In the spectrum of $4C_{12}$mela, the C=O peak of bound BA is broad and weak relative to the other peaks. This suggests the presence of C=O in different chemical environment(s). It is also possible that the C=O groups assume a more horizontal orientation relative to the film surface, because the RAS-mode IR measurement is only sensitive to vertically oriented vibrations.[10]

Figure 4 shows the dependency of the amount of bound BA per amphiphile on BA concentration, obtained from the oxygen/nitrogen (O/N) ratio measured by X-ray photoelectron spectroscopy (XPS) of the LB films. Saturation of BA binding at higher concentrations suggests that BA molecules are specifically bound to the monolayer. The binding constant (K) and the binding ratio at saturation (α) are calculated by curve fitting according to the Langmuir adsorption isotherm and are shown in Table 1, along with the correlation coefficient. The α value of

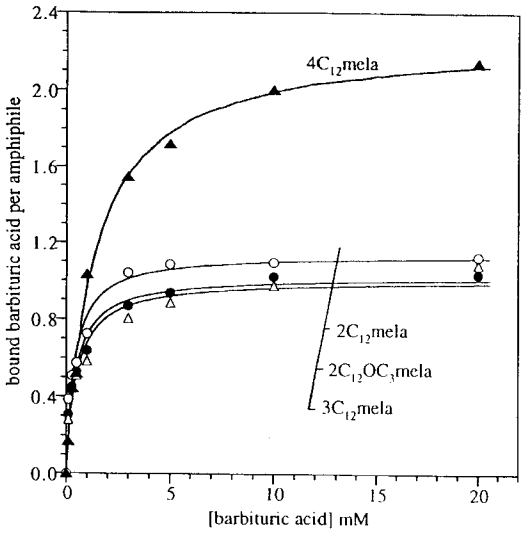

Figure 4. Binding of BA to monolayers of $2C_{12}$mela, $2C_{12}OC_3$mela, $3C_{12}$mela, and $4C_{12}$mela.

Table 1. Binding constants (K) and binding stoichiometry (α, BA/amphiphile).

Monolayer	K ($10^3\ M^{-1}$) [a]	α [a]	R [b]
$2C_{12}$mela	2.53±0.48	1.14±0.05	0.984
$2C_{12}OC_3$mela	2.33±0.38	1.03±0.04	0.988
$3C_{12}$mela	2.06±0.45	1.01±0.05	0.980
$4C_{12}$mela	0.73±0.06	2.27±0.05	0.998

[a] Error values represent standard deviation. [b] Correlation coefficient in curve fitting.

unity observed in $2C_{12}$mela, $2C_{12}OC_3$mela, and $3C_{12}$mela LB films is consistent with the 1:1 alternate network structure shown in Figure 1. In contrast, the $4C_{12}$mela LB film shows a definite difference in the α value. The observed value of $\alpha = 2.27$ suggests the formation of a 2:1 BA/$4C_{12}$mela complex rather than the 1:1 complex formed for the other monolayers. The structure of the new complex may be represented by Figure 5. The four alkyl chains attached to one melamine function are quite bulky, and the bound BA are not capable of hydrogen bonding with additional $4C_{12}$mela amphiphiles. Restriction of the molecular alignment to two dimension is crucial in this case. The discrepancy of the α value from integer cannot be explained by limitation of the XPS analysis, since the O/N ratio of an LB film of pure $4C_{12}$mela agreed with the theoretical value. It is probable that the non-hydrogen-bonded faces of the bound BA in the 2:1 complex are loosely associated with other (free) BA or water molecules.[11] This effect can explain the observed α value of greater than two, by assuming that 30% of the 2:1 complexes are bound to addition-

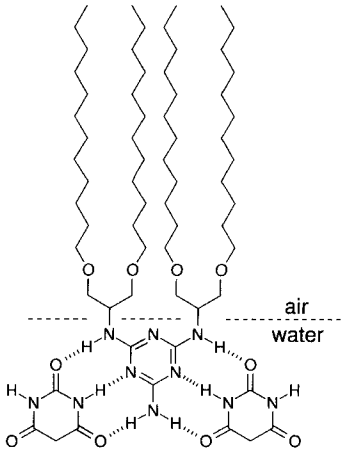

Figure 5. A schematic illustration of the 2:1 BA/$4C_{12}$mela complex.

al BA. The 2:1 complex behaves as an independent molecular entity without any network formation. This model is supported by the phase-transition behavior of $4C_{12}$mela monolayers in the presence of aqueous BA (see Figure 2d). Other networked monolayers display only condensed phases (Figure 2a–c).

Size matching of the hydrophobic alkyl chains and underlying supramolecular network: The structural organization of a supramolecular assembly at the air–water interface is expected to be affected by the bulkiness of the hydrophobic part of the amphiphile. This is unmistakably demonstrated by the preceding results where supramolecular structures are assembled through specific hydrogen bonding. Aqueous BA and amphiphiles with two or three alkyl chains adopt the 1:1 alternate network structure. The analogous binding properties of $2C_{12}$mela and $2C_{12}OC_3$mela show that the ether linkage in the alkyl chain does not affect binding behavior. The melamine amphiphile with four alkyl chains, $4C_{12}$mela, cannot form a 1:1 alternate network structure, owing to the bulkiness of the alkyl chains. Based on the molecular sizes derived with the Corey–Pauling–Koltun (CPK) molecular model, the distance between two carbonyl oxygens of BA in the 1:1 alternate network structure was estimated to be 1.0 nm, and that between two alkyl chains of dialkylmelamine approximately 0.5 nm. Assuming that an alkyl chain is about 0.5 nm wide, two alkyl chains of dialkylmelamine are snugly aligned on the network structure (Figure 6). In contrast, the two outermost alkyl chains are

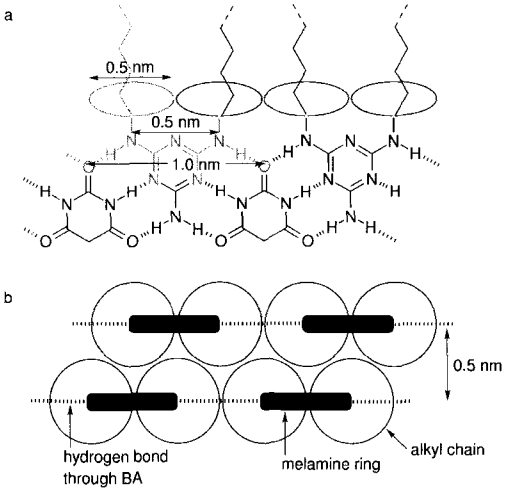

Figure 6. Estimation of molecular sizes in the 1:1 alternate network from BA and dialkylmelamine: a) side view and b) top view. Elipsoids represent the width of an alkyl chain.

0.8 nm apart in a $4C_{12}$mela molecule, resulting in a width of 1.3 nm (Figure 7a,b), which is sufficient to prevent the formation of an extended 1:1 alternate network. It is possible that individual $4C_{12}$mela molecules assume another conformation in which the two alkyl chains in each pair are aligned perpendicular to the melamine ring, as shown in Figure 7c,d. Formation of an extended hydrogen-bonded network is feasible in this case. However, the distance between the neighboring linear networks (1.0 nm) is much greater than that in an ideal network structure (0.5 nm, Figure 6b), and this effect would be detrimental to the stable two-dimensional packing of alkyl chains.

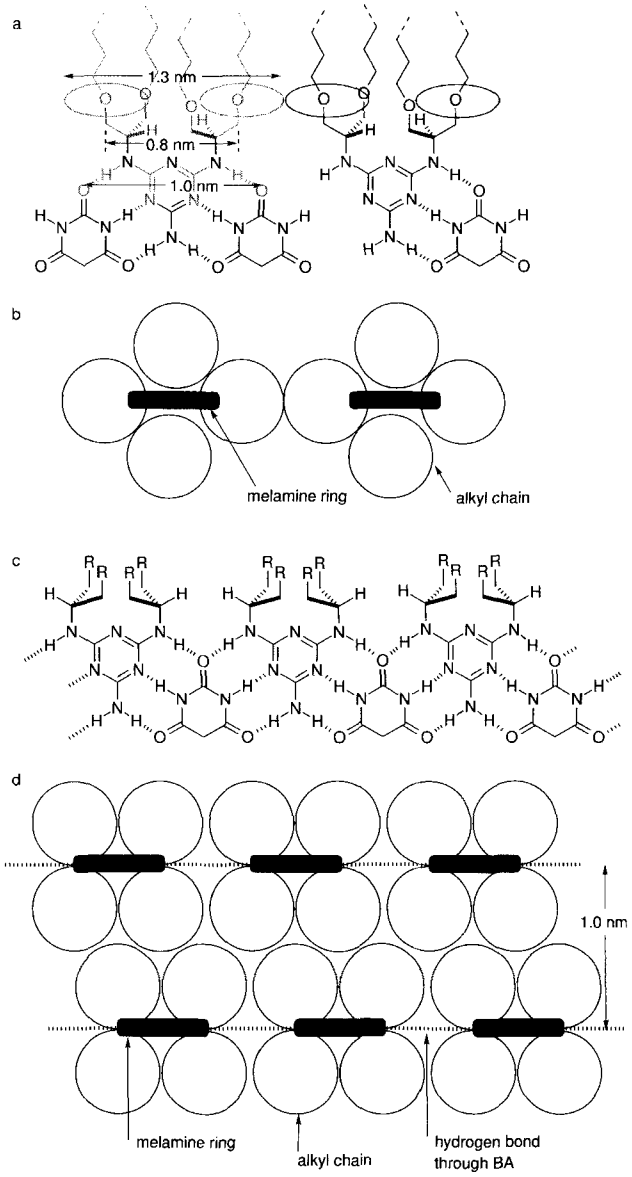

Figure 7. A plausible model of the molecular arrangement in the 2:1 BA/$4C_{12}$mela complex: a) side view, b) top view. Hypothetical 1:1 BA/$4C_{12}$mela alternate network: c) side view, d) top view (R = $(CH_2)_3O(CH_2)_{11}CH_3$).

A condensed monolayer of asymmetrically substituted melamine, $3C_{12}$mela may contain a unique molecular arrangement in combination with bound BA. The elemental composition of the transferred monolayer indicates the formation of a 1:1 BA/$3C_{12}$mela complex. Within the framework of an alternately extended network of BA and $3C_{12}$mela, the three alkyl chains of $3C_{12}$mela molecule will be most stably arranged as shown in Figure 8. The trialkyl units may be arranged alternately (Figure 8, left) or regularly (Figure 8, right). The distance between the neighboring extended networks is estimated to be 0.8 nm. This distance appears to be sufficient for side-by-side stacking of polar moieties and the consequent stabilization of the monolayer. This arrangement is in contrast with that for the BA/$4C_{12}$mela system, where a 2:1 complex is formed rather than a 1:1 extended network. The inability of this system to form a hydrogen-bonded network such as that shown in Figure 7c,d is ascribable to the separation of the neighboring linear

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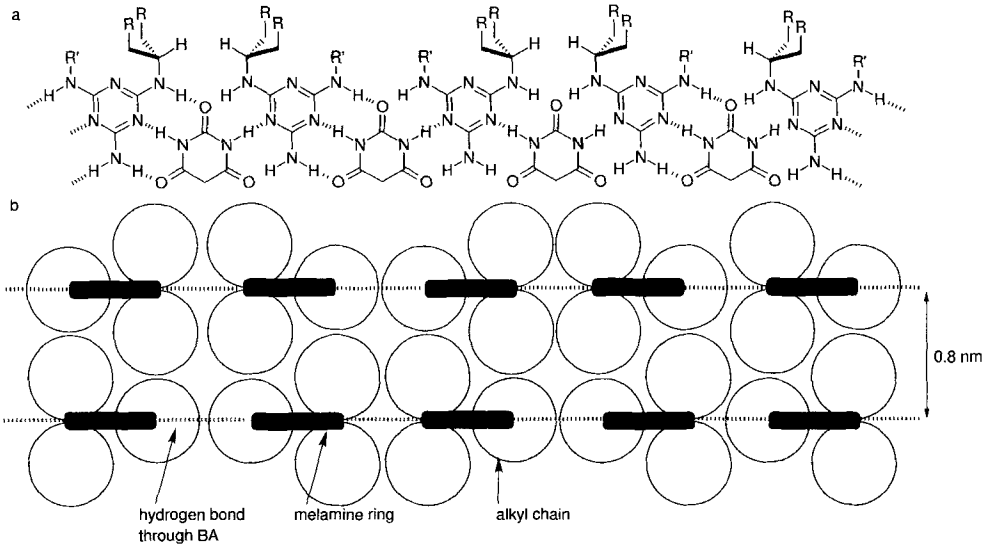

Figure 8. Possible arrangements in a 1:1 BA/3C_{12}mela alternate network: a) side view (R = $(CH_2)_3O(CH_2)_{11}CH_3$, R′ = $(CH_2)_{11}CH_3$) and b) top view.

networks (1.0 nm), as discussed above. The critical separation for stabilization of a monolayer must lie in the range 0.8–1.0 nm.

Concluding Remarks

The results obtained in this study show the importance of size matching between the hydrophobic part of the monolayer and the underlying supramolecular structure in maintaining the extended hydrogen-bonded network. This information will make it possible to design two-dimensionally extended supramolecular structures, and open up the way for their practical applications.[12] The structure of monolayers can be elucidated to molecular precision by the combination of scanning probe microscopy, vibrational spectroscopy, and electron microscopy. The AFM image gives the top view of a monolayer with molecular resolution,[13] and IR spectra and electron diffraction (ED) patterns give conformational and packing information of alkyl chains within monolayer.[10, 14] In particular, AFM molecular images of the monolayer allowed us to suggest a plausible packing model of alkyl chains.[3, 15] These measurements on the present system are a subject of continuing investigation and will be published elsewhere.

Experimental Section

Synthesis of amphiphiles—general: 2-Amino-4,6-dichloro-1,3,5-triazine was prepared from cyanuric chloride according to the literature.[4] 1,3-Didodecoxy-2-propanol was prepared from dodecyl alcohol and epichlorohydrin in 56% yield according to the literature.[16] Dodecylamine (>99%) (Aldrich) was used without purification. $2C_{12}OC_3$mela was donated from Dr. Kawasaki of Kyushu University.[17] The melting points were uncorrected. ^{1}H NMR spectra were recorded on a Bruker ARX-300 (300 MHz) spectrometer.

$2C_{12}$mela: A solution of 2-amino-4,6-dichloro-1,3,5-triazine (1.0 g, 6.1 mmol), dodecylamine (2.36 g, 12.7 mmol), and $NaHCO_3$ (1.07 g, 12.7 mmol) in 1,4-dioxane (60 mL) was placed in a round-bottomed flask. This mixture was refluxed for 24 h. The precipitate was removed by filtration through a Celite pad and washed with $CHCl_3$. The filtrate was concentrated to give a yellow oil, and hot ethanol was added until a clear solution was obtained. The resulting solution was allowed to stand at room temperature until the product had precipitated out as a powder. This was collected on a filter, was washed with ethanol, and dried in vacuum to give $2C_{12}$mela (2.1 g, 75%). Concentration of the mother liquor gave a second crop (0.42 g, 15%). M.p. 92.6–93.2 °C; TLC: $R_f = 0.43$ (10:1 CH_2Cl_2/CH_3OH); ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 6H), 1.2–1.4 (m, 36H), 1.4–1.6 (m, 4H), 3.34 (brs, 4H), 4.8–5.3 (br, 4H); $C_{27}H_{54}N_6$ (462.76): calcd C 70.08, H 11.76, N 18.18; found C 69.92, H 11.72, N 17.91.

1,3-Didodecoxy-2-propyl methanesulfonate: A solution of methanesulfonyl chloride (6.68 g, 58.3 mmol) in CH_2Cl_2 (50 mL) at room temperature was added to a solution of 1,3-didodecoxy-2-propanol (20.0 g, 46.7 mmol) and triethylamine (5.90 g, 58.3 mmol) in CH_2Cl_2 (100 mL). The whole mixture was stirred for 18 h. Most of solvent was removed by evaporation and the residue was diluted with ethyl acetate (150 mL). This was washed with water (×3) and brine. After the solution had been dried over Na_2SO_4, the solvent was removed to give the title compound (23.47 g, 99%) as a slightly yellow powder. M.p. 58.0–59.0 °C; TLC: $R_f = 0.50$ (4:1 hexane/ethyl acetate); ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 6H), 1.1–1.4 (m, 36H), 1.5–1.6 (m, 4H), 3.09 (s, 3H), 3.4–3.5 (m, 4H), 3.6–3.7 (m, 4H), 4.82 (tt, $J = 5.3$, 5.3 Hz, 1H); $C_{28}H_{58}O_5S$ (506.82): calcd C 66.36, H 11.53; found C 66.11, H 11.44.

15-Azido-13,17-dioxanonacosane: A mixture of 1,3-didodecoxy-2-propyl methanesulfonate (23.39 g, 46.15 mmol), NaN_3 (9.00 g, 138.5 mmol), and dimethyl formamide (DMF) (50 mL) was stirred at 100 °C for 18 h. After cooling to room temperature, it was diluted with ethyl acetate (200 mL). The solution was washed with water (×5) and brine, dried over Na_2SO_4, and concentrated to give the title compound (20.45 g, 98%) as a yellow oil. TLC: $R_f = 0.84$ (4:1 hexane/ethyl acetate); ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 6H), 1.1–1.4 (m, 36H), 1.5–1.6 (m, 4H), 3.4–3.6 (m, 8H), 3.6–3.8 (m, 1H); $C_{27}H_{55}N_3O_2$ (453.75): calcd C 71.47, H 12.22, N 9.26; found C 71.53, H 12.18, N 9.25.

1,3-Didodecoxy-2-propylamine: A mixture of 15-azido-13,17-dioxanonacosane (20.42 g, 45.00 mmol), 5% Pd on charcoal (Pd/C) (1.0 g), CH_3OH (200 mL), and ether (100 mL) was stirred at room temperature for 20 h under H_2. Pd/C was removed by filtration and washed with ether. The filtrate and washings were concentrated to give 1,3-didodecoxy-2-propylamine (18.36 g, 95%) as a colorless solid. M.p. 32.0–33.0 °C; TLC: $R_f = 0.24$ (20:1 CH_2Cl_2/CH_3OH); ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (t, $J = 6.7$ Hz, 6H), 1.1–1.4 (m, 36H), 1.5–1.6 (m, 6H), 3.1–3.2 (m, 1H), 3.3–3.5 (m, 8H); $C_{27}H_{57}NO_2$ (427.75): calcd C 75.81, H 13.43, N 3.27; found C 75.76, H 13.35, N 3.16.

2-Amino-4-chloro-6-(1,3-didodecoxy-2-propylamino)-1,3,5-triazine: A mixture of 2-amino-4,6-dichloro-1,3,5-triazine (163 mg, 1.0 mmol), 1,3-didodecoxy-2-propylamine (427 mg, 1.0 mmol), and $NaHCO_3$ (84 mg, 1.0 mmol) in 1,4-dioxane was refluxed for 48 h and then diluted with $CHCl_3$ (50 mL). The organic layer was washed with water (3 × 50 mL) and brine (3 × 50 mL), and dried over Na_2SO_4. The crude product was purified by chromatography on SiO_2 (98:2 $CHCl_3/CH_3OH$) to give the title compound as a colorless solid (790 mg, 75%). M.p. 53–54 °C; ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (t, $J = 6.9$ Hz, 6H), 1.20–1.40 (m, 36H), 1.40–1.60 (m, 4H), 3.30–3.60 (m, 8H), 4.10 (br, 1H), 4.95 (br, 2H), 5.70 (br, 1H); $C_{30}H_{58}N_5O_2Cl$ (556.27): calcd C 64.78, H 10.51, N 12.59; found C 64.65, H 10.40, N 12.57.

$3C_{12}$mela: A mixture of 2-amino-4-chloro-6-(1,3-didodecoxy-2-propylamino)-1,3,5-triazine (100 mg, 0.18 mmol), dodecylamine (36 mg, 0.20 mmol), and $NaHCO_3$ (17 mg, 0.20 mmol) in 1,4-dioxane (5 mL) was refluxed for 16 h and then diluted with $CHCl_3$ (10 mL). The organic layer was washed with water (3×10 mL) and brine (3×10 mL), and dried over Na_2SO_4. The crude product was purified by chromatography on SiO_2 (98:2 $CHCl_3/CH_3OH$) to give $3C_{12}$mela as a colorless oil (105 mg, 83%). ^1H NMR ($CDCl_3$): $\delta = 0.87$ (t, $J = 6.9$ Hz, 9H), 1.20–1.40 (m, 56H), 1.40–1.60 (m, 6H), 3.20–3.60 (m, 10H), 4.10 (br, 1H), 4.95 (br, 4H); $C_{42}H_{84}N_6O_2$ (705.16): calcd C 71.54, H 12.01, N 11.92; found C 71.22, H 11.93, N 11.84.

$4C_{12}$mela: A mixture of 2-amino-4,6-dichloro-1,3,5-triazine (50 mg, 0.3 mmol), 1,3-didodecoxy-2-propylamine (285 mg, 0.65 mmol), and $NaHCO_3$ (56 mg, 0.65 mmol) in 1,4-dioxane (5 mL) was refluxed for 20 h then diluted with $CHCl_3$ (10 mL). The organic layer was washed with water (10 mL × 3) and brine (10 mL × 3), and dried over Na_2SO_4. The crude product was purified by chromatography on SiO_2 (98:2 $CHCl_3/CH_3OH$) to give $4C_{12}$mela as a colorless solid (100 mg, 35%). M.p. 35–36 °C. ^1H NMR ($CDCl_3$): $\delta = 0.87$ (t, $J = 6.9$ Hz, 12H), 1.20–1.40 (m, 72H), 1.40–1.60 (m, 8H), 3.20–3.60 (m, 16H), 4.10 (br, 2H), 4.95 (br, 4H); $C_{57}H_{114}N_6O_4$ (947.57): calcd C 72.25, H 12.13, N 8.87; found C 72.24, H 12.10, N 8.79.

π–A Isotherm measurement: π–A Isotherms were measured with a computer-controlled film balance system FSD-50 (USI System, Fukuoka). A mixture of benzene/ethanol (4/1, v/v) was used as the spreading solvent. Compression was started about 10 min after spreading at a rate of 0.2 mm s^{-1} (or 30 mm^2 s^{-1} based on area). The subphase temperature was kept at 20.0 ± 0.2 °C. Surface pressures were measured by a Wilhelmy plate, which was calibrated with the transition pressure of an octadecanoic acid monolayer.

LB Film preparation: Slide glasses coated with chromium and gold (100 nm Au, 5 nm Cr/slide glass) by the vapor-deposition method were used as substrates for LB film transfer. LB transfer was carried out with an FSD-21 instrument (USI System, Fukuoka) by the vertical dipping method with dipping speeds of 20 mm min^{-1} (down stroke) and 5 mm min^{-1} (up stroke). The $3C_{12}$mela monolayer was transferred at 20 mN m^{-1} and the other monolayers were transferred at 15 mN m^{-1}. Nine layers of $2C_{12}$mela monolayer were transferred with the Y-type transfer from pure water. Ten-layers of the monolayer were transferred with the Z-type transfer from 10 mM BA solution. Transfer ratios were almost unity. These LB films were used in RAS mode FT-IR and XPS measurements.

FT-IR Measurement: RAS Mode FT-IR spectra of the LB films were measured with a Nicolet 710 FT-IR spectrometer with a resolution of 2 cm^{-1}.

Determination of BA binding to monolayers by XPS measurement: X-ray photoelectron spectra (XPS) of the LB films were measured with a Perkin-Elmer PHI 5300 ESCA, and the X-ray source was $Mg_{K\alpha}$ (300 W). Repeated scans over the same surface region at a take-off angle of 45° gave reproducible spectra. The elemental composition was obtained by dividing the observed peak area by the intrinsic sensitivity factor of each element. The amount of bound BA per melamine amphiphile (y) was obtained from O/N ratio. XPS measurements on LB films sometimes need a depth correction;[11,8] however, we assumed that corrections were not necessary, because oxygen and nitrogen atoms, which were used for the y value determination, are located close to each other in the film. The amount of bound BA per melamine amphiphile (y) was obtained from Equation (1), where a and b represent the numbers of nitrogen and oxygen atoms in the amphiphile molecules, respectively (for $2C_{12}$mela, $a = 6$ and $b = 0$; for $2C_{12}OC_3$mela and $3C_{12}$mela, $a = 6$ and $b = 2$; for $4C_{12}$mela, $a = 6$ and $b = 4$). The y values were plotted as a function of BA concentration in the subphase and the plots obtained were analyzed by curve fitting with a Langmuir equation [Eq. (2)] in order to determine the binding constant (K) and the binding ratio at saturation (α).

$$y = [a(O/N) - b]/[3 - 2(O/N)] \quad (1)$$

$$y = \alpha[BA]/(1/K + [BA]) \quad (2)$$

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