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Supramolecular Membranes. Spontaneous Assembly of Aqueous Bilayer Membrane via Formation of Hydrogen Bonded Pairs of Melamine and Cyanuric Acid Derivatives

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Abstract: Amphiphilic hydrogen bond networks consisting of alkylated melamines and ammonium headgroup-appended cyanuric acids are stably dispersed in water as supramolecular membranes. Electron micrographs of these aqueous dispersions indicated the formation of supramolecular assemblies of mesoscopic dimension. Their aggregate morphologies, molecular orientation, and thermal characteristics are markedly dependent on the chemical structure of constituent molecules. Self-supporting multilayer films were obtainable by casting the aqueous dispersions, like the conventional aqueous bilayer. X-ray diffraction of the cast films indicated that hydrogen bonded pairs of ammonium-appended cyanuric acid and double-chained melamine adopted the bilayer structure. On the other hand, complementary pairs formed from single-chained melamines adopted partially or completely interdigitated bilayers. The long period of the former cast film (ca. 9 nm) is in good agreement with the thickness of disklike aggregates observed in electron microscopy, indicating that bilayer structures mediated by complementary hydrogen bonds are maintained in water. Thermal characteristics of aqueous dispersions were investigated by differential scanning calorimetry and spectroscopically by using 1,6-diphenyl-1,3,5-hexatriene as a fluorescence probe. The observed spectral characteristics indicate that supramolecular membranes display phase transition from a highly ordered state to a liquid crystalline phase. In addition, reversible dissociation and irreversible segregation of complementary pairs proceeded at higher temperatures. These supramolecular membranes are the first example of water-soluble supermolecules directed by complementary hydrogen bonds and constitute a new family of amphiphilically designed supramolecular assemblies.

Introduction

Formation of multiple hydrogen bonds between complementary molecular components has been widely used as a driving force for the fabrication of artificial supramolecular assemblies.[1,2] They may be soluble oligomers in organic media,[3,4] organic gels,[5] liquid crystals,[6] crystalline organic solids,[7] or hollow tubular aggregates.[8] In these systems, however, hydrogen bonding between complementary molecules is effective only in nonpolar hydrocarbon media, and aqueous environments interfere with their formation due to competition of water molecules for the hydrogen bond used in the self-assembly.[9] This situation is in remarkable contrast with biological self-assemblies—DNA multiplexes, multimeric proteins, nucleic acid/protein complexes, and viruses—which display a wealth of hierarchical supramolecular structures in the mesoscopic range (10−1000 nm size). These biological self-organizations are achieved in aqueous media through effective integration of weak noncovalent interactions—Coulombic and hydrophobic interactions in addition to hydrogen bonds—to compensate the entropic

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disadvantage of the integration processes.[10] These superstructures can exist in aqueous media as independent entities without being segregated as insoluble aggregates, because of their amphiphilic supramolecular structures. It is only within past several years that molecular recognition via complementary hydrogen bonding in the presence of water has emerged as a challenging issue. Strategies for achieving facilitated hydrogen bonding in aqueous environments require the help of hydrophobic interactions that have been provided by aromatic surfaces[11] and the hydrophobic core of aqueous micelles.[12]

Monolayers at the air−water interface provide a unique environment for the facilitated formation of complementary hydrogen bonds.[13,14] Binding of nucleotides by the guanidinium unit at the surface of monolayers (binding constant; 10^6−10^7 M^{-1}) was efficient much more than those observed for aqueous micelles and bilayers (binding constant; 10^2−10^4 M^{-1}),[15] indicating a unique nature of the macroscopic interface in the molecular recognition process. However, there have been no reports on hydrogen bond-mediated supramolecular assemblies in aqueous media, except for our previous short communications.[16] We have demonstrated that preformed amphiphilic complexes of suitably designed cyanuric acid derivatives and substituted melamines are dispersed in water as mesoscopic supramolecular assemblies containing extended arrays of complementary hydrogen bonds.[16] In this paper, we provide a full account of supramolecular organization of these aqueous assemblies and their physicochemical characteristics in relation to the chemical structure of constituent molecules. We demonstrate “hierarchical self-assembly of amphiphilic supermolecules” as a key strategy in the fabrication of soluble supramolecular assemblies of mesoscopic dimensions.

Results and Discussion

Molecular Design of Complementary Subunits. A mesoscopic supramolecular assembly would be obtainable, when aggregates mediated by complementary hydrogen bonds undergo further self-organization to form *soluble* supramolecular assemblies of higher hierarchy. We previously reported that hydrogen bond networks containing solvophilic alkyl chains and a solvophobic aromatic imide moiety formed mesoscopic supramolecular assemblies in organic media.[17] In these studies, proper amphiphilicity in relation to solvents used was an indispensable feature in order to obtain mesoscopic molecular assemblies. Formation of complementary hydrogen bond pairs in water must overcome the difficulty that they are subject to deterioration caused by water molecules. Additional assembling forces should effectively operate in order to keep hydrogen bond-mediated supramolecular assemblies intact in water. In this respect, hydrogen bond-directed biological supermolecules such as DNA duplex provide useful guidelines. First, hydrogen bonded pairs should be positioned in the hydrophobic interior of the supermolecules, so that they are effectively shielded from bulk water. Second, the supermolecules should possess hydrophilic surfaces so that they are stably dispersed in aqueous media. We have demonstrated that synthetic bilayers are formed from a large variety of synthetic amphiphiles in water,[18] in binary water−organic media,[19] in polar organic media,[20] and also in nonpolar organic media.[21] By introducing the concept of amphiphilic pair to aqueous bilayer membranes, we propose a novel class of supramolecular assembly—*supramolecular membrane*. As schematically shown in Figure 1, conventional aqueous bilayer membranes are formed through self-assembly of amphiphilic molecules that possess both a hydrophilic headgroup and hydrophobic alkyl chains covalently connected in a single molecule. In contrast, a bilayer-forming amphiphilic pair is designed by dividing a bilayer-forming amphiphile into two complementary subunits—a hydrophilic moiety and a hydrophobic moiety. Each of the two components is designed so that the most stable amphiphilic superstructure is produced only via formation of complementary hydrogen bonds.

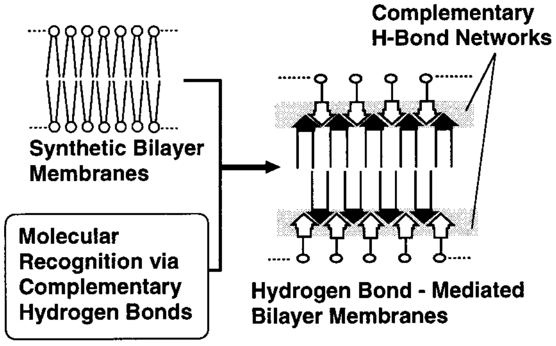

Figure 1. Design of complementary hydrogn bond-directed supramolecular membrane in water.

In this study, hydrophilic subunits were appended with quarternary ammonium headgroups in order to create hydrophilic supramolecular surfaces. This molecular design is crucial to the preparation of stable supramolecular dispersions in water. On the other hand, the hydrophobic building block is equipped with alkyl chains that improve molecular association. This would help association of complementary hydrogen bond networks in the bilayer interior, leading to its enhanced stability in water. A pair of cyanuric acid/melamine was chosen as

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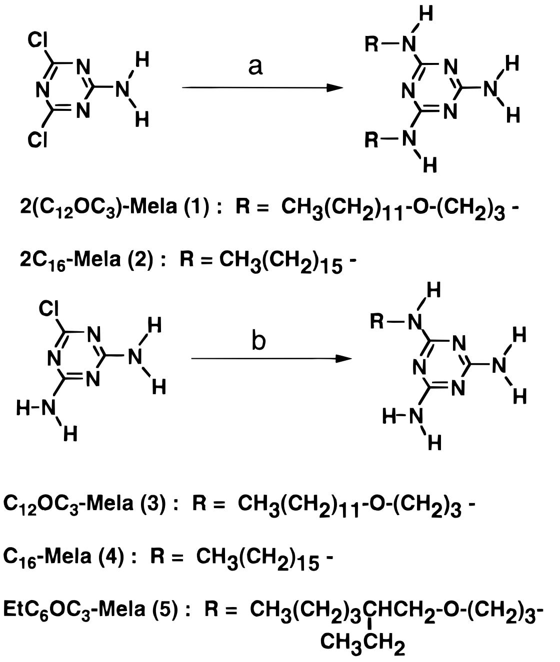
Scheme 1. Synthesis of Alkylated Melamines

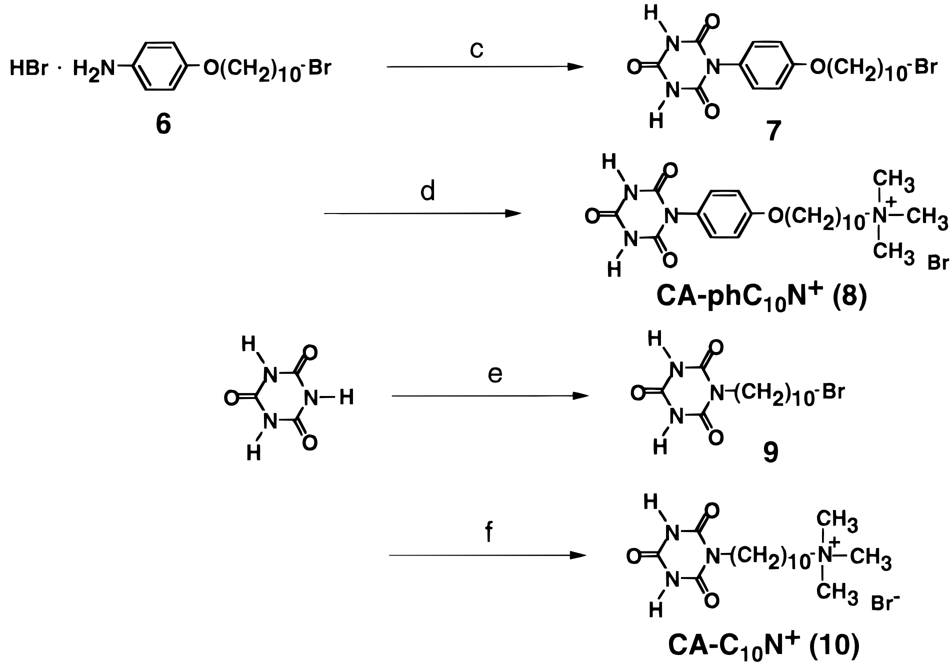


complementary units, because of their ability to form polymeric hydrogen bond networks.[3] The polymeric hydrogen bond produces an enthalpic advantage to maintain hydrogen bond-mediated assemblies even in aqueous media. On the basis of these considerations, alkylated melamines **2(C$_{12}$OC$_3$)-Mela** (**1**), **2C$_{16}$-Mela** (**2**), **C$_{12}$OC$_3$-Mela** (**3**), **C$_{16}$-Mela** (**4**), and **EtC$_6$OC$_3$-Mela** (**5**) and cyanuric acid derivatives **CA-phC$_{10}$N$^+$** (**8**) and **CA-C$_{10}$N$^+$** (**10**) were designed and synthesized as shown in Schemes 1 and 2.

Solubility of Hydrogen Bond-Mediated Complexes in Water. At first, the solubility of equimolar mixtures in water was examined for combinations of double-chained melamines, **2C$_{16}$-Mela** and **2(C$_{12}$OC$_3$)-Mela**, and cyanuric acid derivatives, **CA-C$_{10}$N$^+$** and **CA-phC$_{10}$N$^+$**. Among the four equimolar complexes of **2C$_{16}$-Mela/CA-C$_{10}$N$^+$**, **2(C$_{12}$OC$_3$)-Mela/CA-C$_{10}$N$^+$**, **2C$_{16}$-Mela/CA-phC$_{10}$N$^+$**, and **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$**, only **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** gave a transparent dispersion in water (ca. 30 mM) upon ultrasonication. This aqueous dispersion was stable over a period of 1 month. In contrast, the other complexes and the individual components of **2C$_{16}$-Mela**, **2(C$_{12}$OC$_3$)-Mela**, and **CA-phC$_{10}$N$^+$** displayed very poor solubilities in water, and they could not be dispersed even at a concentration of 5 mM. From comparison of these component structures, we suggest that the phenyl group in **CA-phC$_{10}$N$^+$** stabilized complementary hydrogen bond networks in water by placing them in the hydrophobic interior of bilayer membrane. In addition, the presence of the ether linkage in **2(C$_{12}$OC$_3$)-Mela** much improved the solubility of the complementary pairs, as is apparent from the comparison of **2C$_{16}$-Mela/CA-phC$_{10}$N$^+$** and **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$**. We have already reported that introduction of ether linkages in alkyl chains of bilayer-forming amphiphile imparted the aggregation morphology with surprising flexibility without losing the regular side-chain alignment.[22] Superior bilayer matrixes were formed from such amphiphiles for the organization of heme proteins without denaturation.[23a] This molecular design was also successfully utilized to produce highly polymerizable bilayer membranes, in which organization of polymerizable units in the bilayer headgroup is effectively decoupled from the alkyl chain packing.[23b] In the present case, packing of alkyl chains in bilayer must be compatible with the hydrogen bonded structure of melamine and cyanuric acid groups. The flexible ether linkage in the alkyl chain can probably promote decoupling of chain packing from the hydrogen bond network, facilitating coexistence of alkyl chain packing and complementary hydrogen bonds. Apparently, this is not the case with **2C$_{16}$-Mela/CA-phC$_{10}$N$^+$** that lacks the ether linkage, as it is not stably dispersed in water.

The equimolar composition was essential for producing stable dispersions, since nonequimolar mixtures (**2(C$_{12}$OC$_3$)-Mela: CA-phC$_{10}$N$^+$** $= 2{:}1$ or 1:2 (mol:mol), [**2(C$_{12}$OC$_3$)-Mela**] $=$ 20 mM) did not give homogeneous dispersions. The solubility in water of equimolar mixtures of single-chained melamine derivatives—**C$_{12}$OC$_3$-Mela**, **C$_{16}$-Mela**, and **EtC$_6$OC$_3$-Mela**—was

Scheme 2. Synthesis of Cyanuric Acid Derivatives



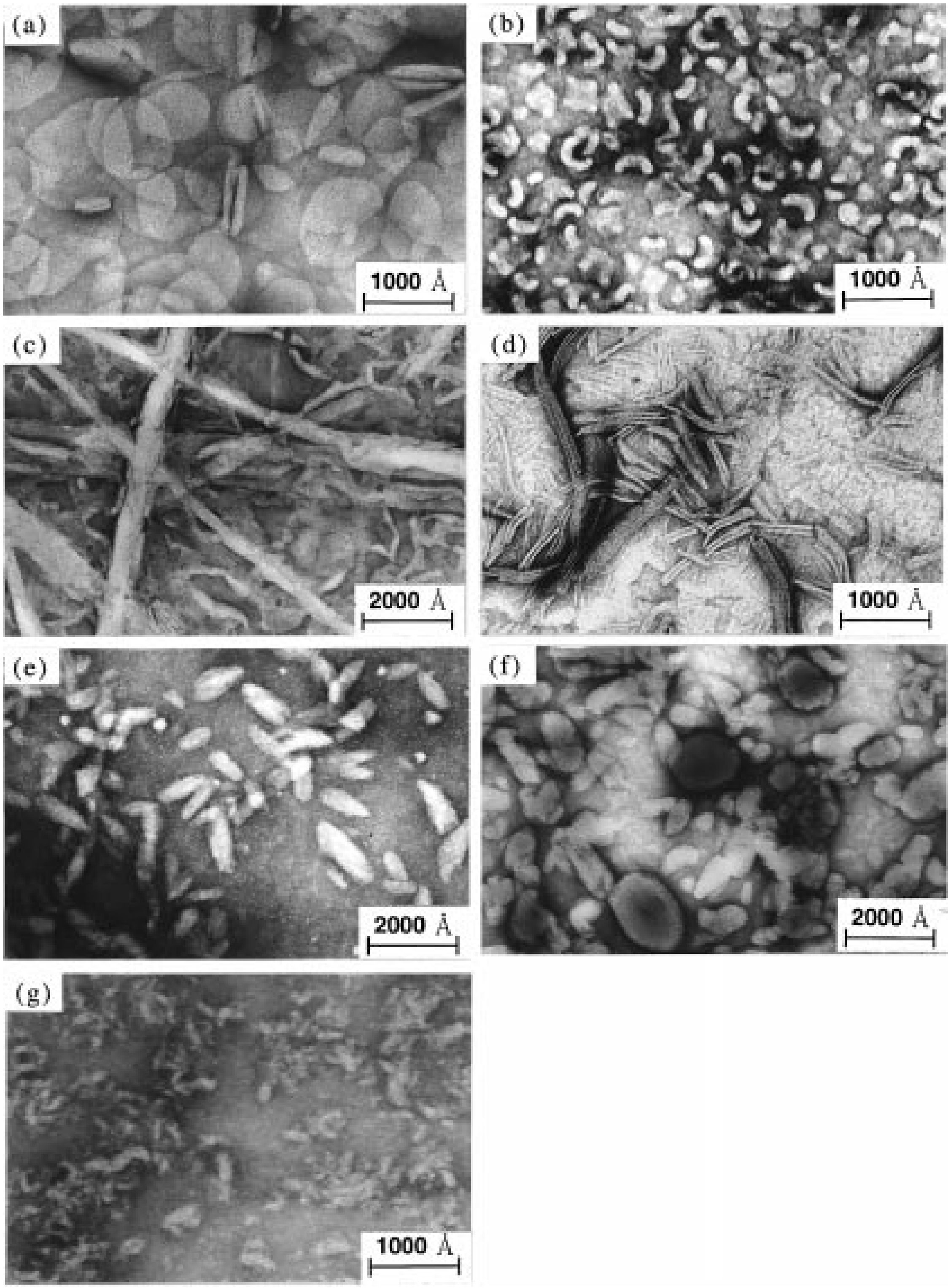


Figure 2. Electron micrographs of aqueous dispersions: (a) **2($C_{12}OC_3$)-Mela**/**CA-phC$_{10}$N$^+$**, (b) **$C_{12}OC_3$-Mela**/**CA-phC$_{10}$N$^+$**, (c) **C_{16}-Mela**/**CA-phC$_{10}$N$^+$**, (d) **EtC_6OC_3-Mela**/**CA-ph-C$_{10}$N$^+$**, (e) **CA-phC$_{10}$N$^+$**, (f) **2($C_{12}OC_3$)-Mela**, (g) **$C_{12}OC_3$-Mela**. Stained by uranyl acetate.

similarly examined by using **CA-phC$_{10}$N$^+$** as a complementary unit. Unlike double-chained **2($C_{12}OC_3$)-Mela**, all the equimolar mixtures of **$C_{12}OC_3$-Mela**/**CA-phC$_{10}$N$^+$**, **C_{16}-Mela**/**CA-phC$_{10}$N$^+$** and **EtC_6OC_3-Mela**/**CA-phC$_{10}$N$^+$** gave homogeneous dispersions (ca. 20 mM) upon ultrasonication. Interestingly, single-chained melamines provide water-soluble complexes regardless of the presence of ether linkages. The single chained − melamines are not soluble by themselves at the employed concentration range. It is clear that water-soluble complementary mixtures are obtainable more readily from single-chained melamines, implying that the mode of supramolecular organization is different between the single- and double-chained melamines.

Electron Microscopy. Figure 2 displays transmission electron micrographs of aqueous dispersions of **2($C_{12}OC_3$)-Mela**/**CA-phC$_{10}$N$^+$** (a), **$C_{12}OC_3$-Mela**/**CA-phC$_{10}$N$^+$** (b), **C_{16}-Mela**/

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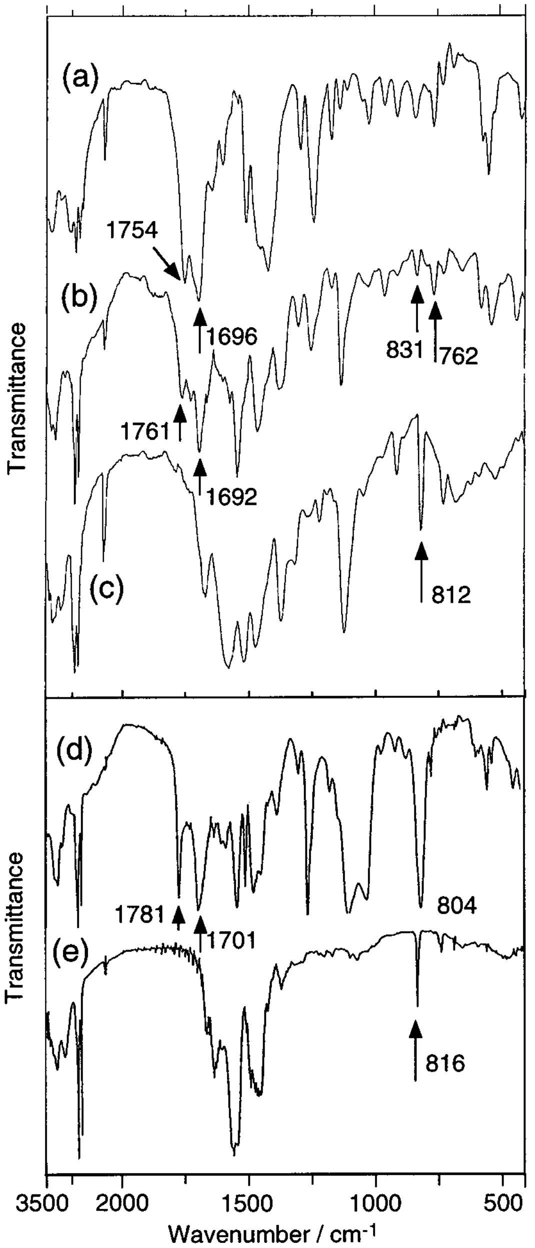

Figure 3. IR spectra (KBr) of cast films: (a) **CA-pHC$_{10}$N$^+$, (b) 2(C$_{12}$OC$_3$)-Mela/CA-pH$_{10}$N$^+$**, (c) **2(C$_{12}$OC$_3$)-Mela**, (d) **C$_{16}$-Mela/phC$_{10}$N$^+$**, and (e) **C$_{16}$-Mela**.

CA-phC$_{10}$N$^+$ (c), and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$** (d), together with those observed for single-component dispersions of **CA-phC$_{10}$N$^+$** (e), **2(C$_{12}$OC$_3$)-Mela** (f), and **C$_{12}$OC$_3$-Mela** (g). These samples were prepared from dilute aqueous dispersions (ca. 0.2−0.5 mM). Disklike aggregates with diameters of several hundred angstroms and a thickness of ca. 100 Å are found for **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** (Figure 2a). On the other hand, croissantlike aggregates with lengths of 300 to 440 Å and width of ca. 125 Å are observed for **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$** (Figure 2b). An aqueous mixture of **C$_{16}$-Mela/CA-phC$_{10}$N$^+$** displayed tapelike aggregates (Figure 2c) and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$** gave short ropelike aggregates with lengths of 600−2500 Å and a thickness of ca. 44 Å (Figure 2d). These morphologies are obtained upon self-assembly of complementary hydrogen bond networks, since they are cleary distinguished from those observed for the single-component dispersions. Ellipsoidal aggregates with long axes of 750−1900 Å are observed for aqueous **CA-phC$_{10}$N$^+$** (Figure 2e), and a dilute dispersion of **2(C$_{12}$OC$_3$)-Mela** (0.2 mM) displayed ellipsoidal aggregates with long axes of 600−2200 Å (Figure 2f). Single-chained **C$_{12}$OC$_3$-Mela** displayed irregular fragments (Figure 2g), and the presence of aggregates were not cleary noticed for **C$_{16}$-Mela** and **EtC$_6$OC$_3$-Mela** (data not shown). The disklike structure observed for **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** is different from those observed for the single-component dispersion of either **2(C$_{12}$OC$_3$)-Mela** or **CA-phC$_{10}$N$^+$**. Similarly, the croissantlike structure of **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$** is not observed for either of the single-component dispersions. In addition, ellipsoidal aggregates of **CA-phC$_{10}$N$^+$** are not present for the equimolar mixtures of **C$_{16}$-Mela/CA-phC$_{10}$N$^+$** and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$.** These TEM observations clearly demonstrate that the complementary pairs are dispersed in water without separation of the two components. Aggregate morphologies of the four complementary mixtures in which the ammonium component is common vary depending on the melamine subunit employed; see Figures 2a−d. It is apparent that aggregation characteristics are determined by the chemical structure of both constituents.

IR Spectra of Cast Films. We have reported that macroscopically oriented multibilayer films are obtainable by casting aqueous dispersions of ordered bilayer membranes on solid supports. In these cast films, the molecular orientation existing in aqueous bilayers are well preserved.[24] Interestingly, self-supporting cast films were also obtainable from aqueous dispersions of **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$**, **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$**, **C$_{16}$-Mela/CA-phC$_{10}$N$^+$**, and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$** on fluorocarbon membrane filters. IR spectra of these films were measured in order to confirm formation of complementary hydrogen bonds. In the case of the **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** film, its IR spectrum contained a group of the C=O stretching bands at 1761 and 1692 cm^{-1} (Figure 3b) which were altered from those observed for **CA-phC$_{10}$N$^+$** alone (1754 and 1696 cm^{-1}, Figure 3a). In addition, the triazine ring vibration[25] observed at 812 cm^{-1} in **2(C$_{12}$OC$_3$)-Mela** alone (Figure 3c) was weakened significantly in the equimolar cast film. These IR changes suggest that complementary hydrogen bonds are formed between the two components. Similarly, cast films of **C$_{12}$OC$_3$-Mela/ICA-phC$_{10}$N$^+$**, **C$_{16}$-Mela/CA-phC$_{10}$N$^+$**, and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$** displayed C=O stretching bands at 1780 and 1692 cm^{-1} (**C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$**) and at 1781 and 1701 cm^{-1} (**C$_{16}$-Mela/CA-phC$_{10}$N$^+$**, **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$**). These stretching bands are again altered from those observed for **CA-phC$_{10}$N$^+$** alone. In the case of **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$**, the intensity of the triazine ring vibration was significantly weakened compared to that of **C$_{12}$OC$_3$-Mela** alone (812 cm^{-1}). This spectral change is similar to that observed for **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$**, and it is suggested that these films possess analogous hydrogen bonding modes. In contrast to these combinations, intensities of the triazine ring vibration observed for single-chained melamines **C$_{16}$-Mela** (816 cm^{-1}, Figure 3e) and **EtC$_6$OC$_3$-Mela** (813 cm^{-1}) are remarkably enhanced and shifted in pairs of **C$_{16}$-Mela/CA-phC$_{10}$N$^+$** (804 cm^{-1}, Figure 3d) and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$** (802 cm^{-1}). Apparently, the nature of hydrogen bonds formed in the cast films of **C$_{16}$-Mela/CA-phC$_{10}$N$^+$** and

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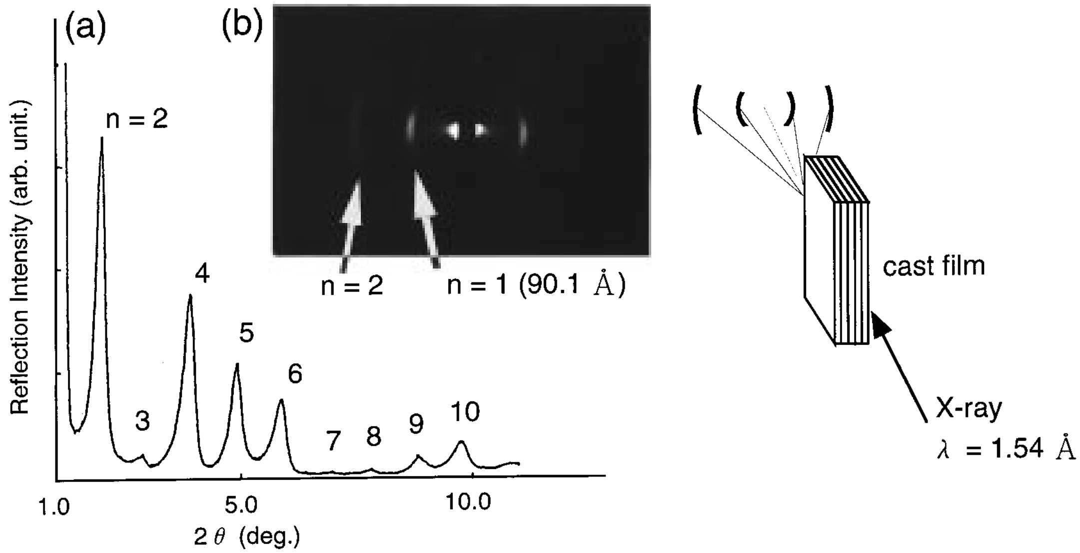

Figure 4. X-ray diffraction patterns of a **$2(C_{12}OC_3)$-Mela/CA-ph$C_{10}N^+$** cast film: (a) reflection diffraction; (b) edge view, small-angle, transmission diffraction.

EtC_6OC_3-Mela/CA-ph$C_{10}N^+$ are different from those of **$2(C_{12}OC_3)$-Mela/CA-ph$C_{10}N^+$** and **$C_{12}OC_3$-Mela/CA-ph$C_{10}N^+$**.

X-ray Diffraction of Cast Films. X-ray diffraction patterns of the cast film of **$2(C_{12}OC_3)$-Mela/CA-ph$C_{10}N^+$** are shown in Figure 4. In the transmission method, pieces of cast films were piled up and the X-ray beam was irradiated parallel to the vertically set film plane (edge view). Equatorial diffractions are observed up to 10th order with a long period of 90.1 Å. This spacing is close to the bilayer thickness of the hydrogen bonded array of **$2(C_{12}OC_3)$-Mela/CA-ph$C_{10}N^+$**, as estimated from a CPK molecular model. It is clear that regular multibilayers exist parallel to the film plane. IR and X-ray diffraction data indicate that a hydrogen bonded molecular array as schematically illustrated in Figure 6a is formed in the cast film. A similar network structure is probably present in the aqueous dispersion, since the thickness of the disklike aggregate (90–100 Å) observed in electron microscopy (Figure 2a) is consistent with the long period observed for the corresponding cast film. Stacking of the complementary hydrogen bond networks and of the phenyl groups would contribute to stabilization of these hydrogen bonds in water.

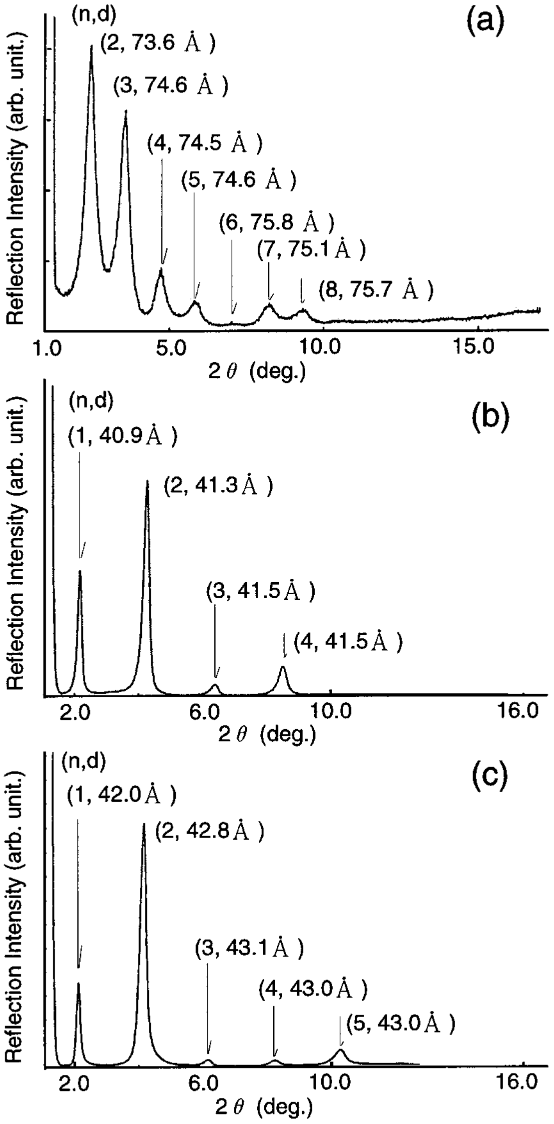

Figure 5. X-ray diffraction patterns (reflection mode) of cast films: (a) **$C_{12}OC_3$-Mela/CA-ph$C_{10}N^+$**, (b) **C_{16}-Mela/CA-ph$C_{10}N^+$**, (c) **EtC_6OC_3-Mela/CA-ph-$C_{10}N^+$**. n = the order of diffraction; d = long period. The n and d values are given in parentheses.

Similarly, cast films of **$C_{12}OC_3$-Mela/CA-ph$C_{10}N^+$**, **C_{16}-Mela/CA-ph$C_{10}N^+$**, and **EtC_6OC_3-Mela/CA-ph$C_{10}N^+$** displayed lamellar X-ray diffraction patterns with long periods of 75.3, 41.3, and 42.9 Å, respectively (Figure 5). These long spacings are smaller than that observed for **$2(C_{12}OC_3)$-Mela/CA-ph$C_{10}N^+$**. In the case of **$C_{12}OC_3$-Mela/CA-ph$C_{10}N^+$**, the observed long spacing (75.3 Å) is shorter than that of the dialkyl counterpart, **$2(C_{12}OC_3)$-Mela/CA-ph$C_{10}N^+$**, by 14.8 Å, although these two pairs appear to give analogous hydrogen bond networks from their IR spectra. These conflicting observations are reasonably explained by assuming the interdigitation of alkyl chain moieties in **$C_{12}OC_3$-Mela/CA-ph$C_{10}N^+$** as shown in Figure 6b. In this supramolecular structure, a melamine unit in **$C_{12}OC_3$-Mela/CA-ph$C_{10}N^+$** is still associated with two alkyl chains (one of them from the other hydrogen bond network), and as a result, the distance between melamine and cyanuric acid moieties become comparable to that of **$2(C_{12}OC_3)$-Mela/CA-ph$C_{10}N^+$**. A similar interdigitation has been noticed in alanate-derived azobenzene amphiphiles.[27] We have reported

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(26) Xu, G.; Okuyama, K.; Shimomura, M. *Mol. Cryst. Liq. Cryst.* **1991**, *213*, 105.

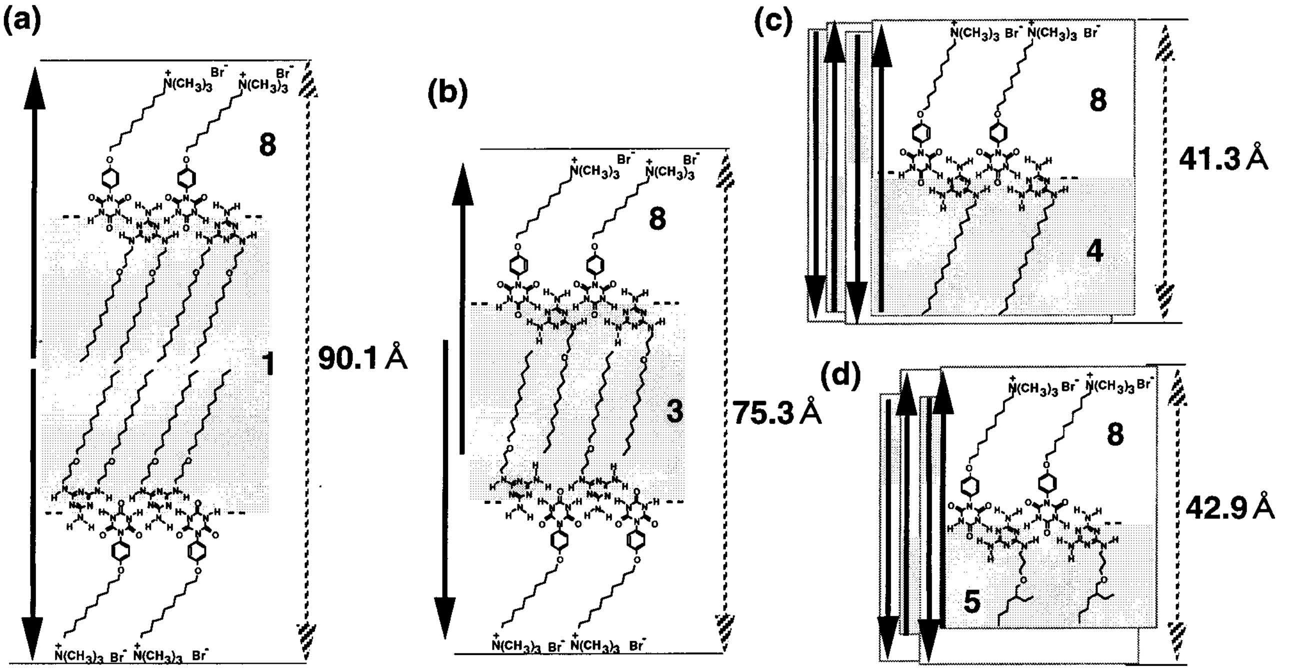
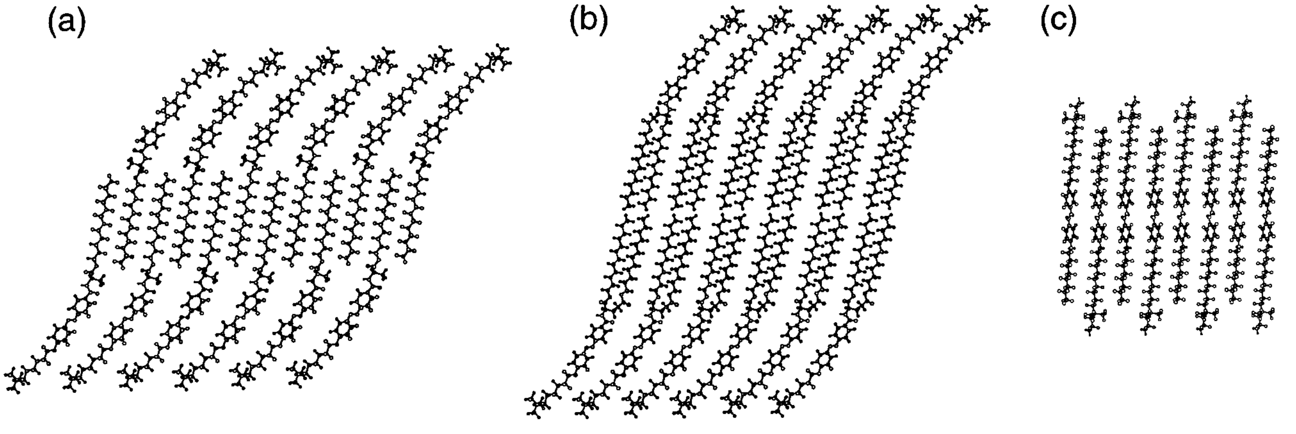


Figure 6. Schematic illustration of molecular organization in cast films: (a) **2($C_{12}OC_3$)-Mela/CA-ph$C_{10}N^+$**, (b) **$C_{12}OC_3$-Mela/CA-ph$C_{10}N^+$**, (c) **C_{16}-Mela/CA-ph$C_{10}N^+$**, (d) **EtC_6OC_3-Mela/CA-ph-$C_{10}N^+$**. Arrows indicate directions of molecular orientation from melamine subunits to ammonium headgroups in a single hydrogen bond network.

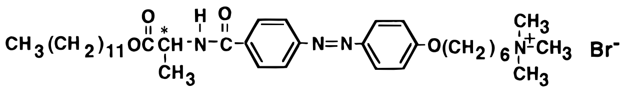


11
partial interdigitation

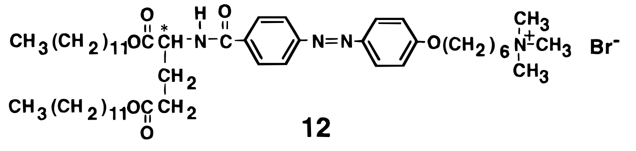
12
bilayer structure

13
full interdigitation

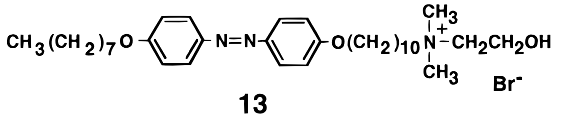
Figure 7. Schematic illustration of molecular orientation in azobenzene-containing bilayer membranes: (a) **11**, (b) **12**, (c) **13**. Bromide ions are omitted for clarity.



11



12



13

that a partially interdigitated structure as schematically shown in Figure 7a is conceivable in the bilayer of single-chained azobenzene amphiphile **11**, which possess a chromophore orientation similar to that of double-chained azobenzene amphiphile **12**.[27] The partial interdigitation in **11** is favored, since it effectively alleviates steric repulsion between alanate methyl groups in the normal bilayer orientation. Interdigitation helps in attaining van der Waals interactions stable enough to form bilayer assemblies, whereas intermolecular force is not sufficient if a noninterdigitated bilayer structure is adopted.[27,28]

In the case of **C_{16}-Mela/CA-ph$C_{10}N^+$** and **EtC_6OC_3-Mela/CA-ph$C_{10}N^+$**, intensities of the first-order diffraction peaks are considerably smaller than those of the second-order peaks. A similar X-ray diffraction pattern has been typically observed for a multibilayer film of azobenzene-containing ammonium

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[27] (a) Kimizuka, N.; Kunitake, T. *Polymer Preprints Jpn.* **1988**, *37*, 3303. (b) Kimizuka, N. Ph.D. Thesis, Faculty of Engineering, Kyushu University, 1990.

[28] Kimizuka, N.; Kunitake, T. *Colloids Surfaces* **1989**, *38*, 79.

amphiphile **13**, which displayed perpendicularly packed amphiphiles with a fully interdigitated structure (Figure 7c).[24a,b,26] Therefore, it is strongly suggested that these amphiphilic pairs adopt perpendicularly packed hydrogen bond networks as schematically shown in Figures 6c,d. The observed small long spacings of 41.3 and 42.9 Å are consistent with antiparallel packing of the adjacent complementary hydrogen bond networks. These supramolecular orientations give a good account of their IR spectra which are distinguished from those observed for **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** and **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$**. Modes of hydrogen bond network must be affected by the distance and mutual orientation between the melamine and cyanuric acid units.

It is noteworthy that branched chain **EtC$_6$OC$_3$-Mela** provides an ordered multibilayer film as well as water-soluble supramolecular aggregates (Figure 2d) by complexation with **CA-phC$_{10}$N$^+$**. It is well-known that amphiphiles containing branched short alkyl chains, such as sodium di(2-ethylhexyl) sulfosuccinate, cannot form stable bilayer assemblies in water due to inferior interaction among the alkyl chains. Thus, the formation of a stable superstructure from **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$** must be ascribed to improved molecular alignment due to complementary hydrogen bond networks.

These results indicate that formation of ordered supramolecular membranes is promoted by complementary hydrogen bond networks in water. It is noteworthy that all these supramolecular assemblies adopt linear hydrogen bond motifs. Whitesides and others reported that cocrystals of melamine and barbituric acid derivatives display polymorphism of hydrogen bonded motifs such as crinkled tape and rosette, in addition to the linear tape structure.[7e] The hydrogen bonded motifs in cocrystals are strongly dependent on the structure of substituents in the constituent molecule. They simultaneously affect the mode of molecular packing in the crystal and the hydrogen bond motif, and it is difficult to rationally explain the substituent effect on the packing of tapes.[7g] On the other hand, the present amphiphilic complementary pairs all possess 2D motifs of aggregation with linearly extended hydrogen bond networks. Changes in the number of alkyl chains in melamine subunits are accompanied by the structural transformation from bilayer (parallel alkyl packing) to interdigitated structures (antiparallel alkyl packing), although the linear hydrogen bonded motif is preserved. The linear hydrogen bond motif is likely to be involved in most amphiphilic supramolecular structures.

Differential Scanning Calorimetry of Aqueous Dispersions. Bilayers covalently polymerized in the middle portion of amphiphilic structures are known to lose gel-to-liquid crystal phase transition characteristics.[29] As the complementary hydrogen bond network in the present supramolecular membranes can be regarded as noncovalent polymers, it was expected also to suppress the phase transition phenomena. Interestingly, however, differential scanning calorimetry of aqueous **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** showed endothermic peaks and they were concentration dependent. At a concentration of 20 mM, a broad endothermic peak was observed between 65 and 100 °C (ΔH; ca. 70 kJ mol^{-1}) in the first heating process (Figure 8), whereas a 5 mM dispersion possessed a broad peak which was located at a lower temperature range of ca. 50 to 80 °C with ΔH of 58−75 kJ mol^{-1} (data not shown). These ΔH values are larger than those of conventional aqueous bilayers (ΔH is typically 20−50 kJ mol^{-1}),[30] and this endothermic peak is likely to involve a dissociation process of the hydrogen bonded pair of **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$**, as is described in a later section. When the heating scan was repeated up to 100 °C, a new endothermic peak gradually grew at 53 °C in addition to the original broad peak (Figure 8, 20 mM sample). Isotherms become reproducible after the third scan, ΔH of the 53 °C peak amounting to 18% of the total heat absorption. The new endothermic peak is ascribed to the gel-to-liquid crystal phase transition of the self-aggregate of **2(C$_{12}$OC$_3$)-Mela**, since an aqueous dispersion of **2(C$_{12}$OC$_3$)-Mela** alone (below 5 mM) gave an endothermic peak at the same temperature range. The heat-induced segregation of **2(C$_{12}$OC$_3$)-Mela** was reflected in the appearance of the aqueous dispersion. An aqueous dispersion of **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** is transparent below 80 °C, but it turned turbid by further heating to 90 °C. Due to limited solubility of **2(C$_{12}$OC$_3$)-Mela** in water, the **2(C$_{12}$OC$_3$)-Mela** moiety that is thermally dissociated at 80 °C starts to segregate. On the other hand, when the heating scan was repeated up to below 80 °C, the original broad peak remained intact without the appearance of a new peak, and reversible phase transition was observed. From these observations, we conclude that the **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** composite undergoes segregation of the dissociated melamine subunit at temperatures of 80−100 °C. This thermal change can be regarded as an irreversible *denaturation* process of the hydrogen bond-mediated supramolecular membrane. The hydrogen bonded pair appears to be less prone to segregate at 5 mM, since reproducible endothermic peaks were obtained without appearance of the 53 °C peak even when the heating scan was repeated up to 100 °C.

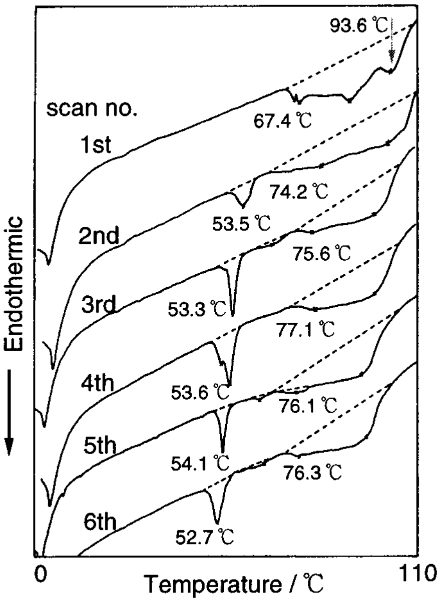

Figure 8. DSC thermograms for aqueous **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** (20 mM).

In the case of other aqueous complementary pairs, dissociation phenomena were not so evident. In the case of **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$** (20 mM), a sharp endothermic peak was observed at 79.4 °C (ΔH; 10.1 kJ mol^{-1}) in the first heating process, while it was transformed to a broad peak centered at ca. 73.0 °C (ΔH; 10.0 kJ mol^{-1}) after the second heating cycle. These endothermic peaks were not observed for its lower-concentration

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(29) (a) Gros, L.; Ringsdorf, H.; Schupp, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 305. (b) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Ibid.* **1988**, *27*, 113.

(30) (a) Okahata, Y.; Ando, R.; Kunitake, T. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 789. (b) Kunitake, T.; Ando, R.; Ishikawa, Y. *Memoirs. Fac. Eng. Kyushu University* **1986**, *46*, 221.

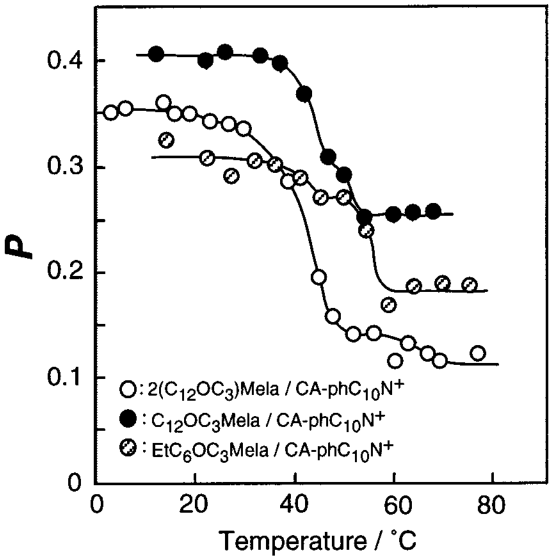

Figure 9. Temperature dependence of fluoresence depolarization (*P*) of DPH in aqueous dispersions of **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$**, **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$**, and **EtC$_6$OC$_3$-Mela/CA-ph-C$_{10}$N$^+$**. [**2-(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$**] = [**C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$**] = [**EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$**] = 2 × 10^{-4} M, [DPH] = 2 × 10^{-7} M.

samples (10 and 5 mM). Similarly, endothermic peaks were not observed for aqueous dispersions of **C$_{16}$-Mela/CA-phC$_{10}$N$^+$** and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$** (20 mM). As is discussed in the following section, fluorescence depolarization of 1,6-diphenyl-1,3,5-hexatriene (DPH) bound to these supramolecular membranes displays temperature dependent changes which are indicative of the presence of phase transition processes. Therefore, the absence of endothermic peaks for these complementary pairs is probably ascribed to inferior packing of melamine alkyl chains in their alternating hydrogen bond sheets. Especially, branched short alkyl chains of **EtC$_6$OC$_3$-Mela** would not be aligned so as to give an endothermic peak in the hydrogen bonded supramolecular pair.

Fluorescence Depolarization of Membrane-Bound Dye. Figure 9 displays the effect of temperature on the fluorescence depolarization of 1,6-diphenyl-1,3,5-hexatriene (DPH) bound to aqueous dispersions of **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$**, **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$**, and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$**. In the case of **2C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$**, a drop in fluorescence depolarization (*P*) of DPH was observed from 0.35 (at 20 °C) to 0.15 (at 55 °C), and it was followed by a further drop to ca. 0.12 (above 70 °C). Similarly, aqueous dispersions of **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$** and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$** displayed decreases in *P* between 40 and 60 °C. The observed temperature dependences of *P* are comparable to those reported for the phase transition of conventional aqueous bilayer aggregates.[31] Furthermore, the temperature dependence of *P* observed for **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** is consistent with the reported absorption spectral change of membrane-bound cyanine dye aggregates.[16b] The observed *P* value of 0.15 at 57 °C indicates that **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** is in the fluid (liquid crystalline) state.[31] A second drop in the *P* value in Figure 9 indicates that aqueous **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** underwent transition from the liquid crystalline state to a less ordered state. This change is accompanied by a spectral change of membrane-bound cyanine dye,[16b] and we presume that these spectral changes reflect dissociation of the complementary pair to micellar aggregates, as schematically shown in Figure 10. As is clearly indicated by the spectroscopic observations, **2-(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** is in the liquid crystalline state already at 55 °C, and therefore, the endothermic peak observed in DSC at the higher temperature range (50 to 80 °C, 5 mM-dispersion) may be related to the dissociation enthalpy of the hydrogen bonded bilayer assembly.

In the case of single-chain pairs of **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$** and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$**, it is not clear if these bilayers similarly undergo dissociation of hydrogen bonds at elevated temperatures, since endothermic peaks are absent in DSC. However, fluoresence depolarization data and absorption spectral characteristics of membrane-bound cyanine dyes[16b] (given in Supporting Information) indicate the presence of gel-to-liquid crystal phase transition, while *P* values observed at 70 °C for **C$_{12}$OC$_3$-Mela/CA-phC$_{10}$N$^+$** (0.26) and **EtC$_6$OC$_3$-Mela/CA-phC$_{10}$N$^+$** (0.18) are slightly higher than that observed for the dissociated mixture of **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$** (0.12, Figure 9). These observations imply that the microviscosities of these fluid assemblies vary depending on the chemical structure of melamine subunits. We have reported that interdigitated bilayers of **11** and **13** undergo de-interdigitation during the gel-to-liquid crystal phase transition, and they exist as non-interdigitated bilayers in the liquid crystalline state.[27] Thus,

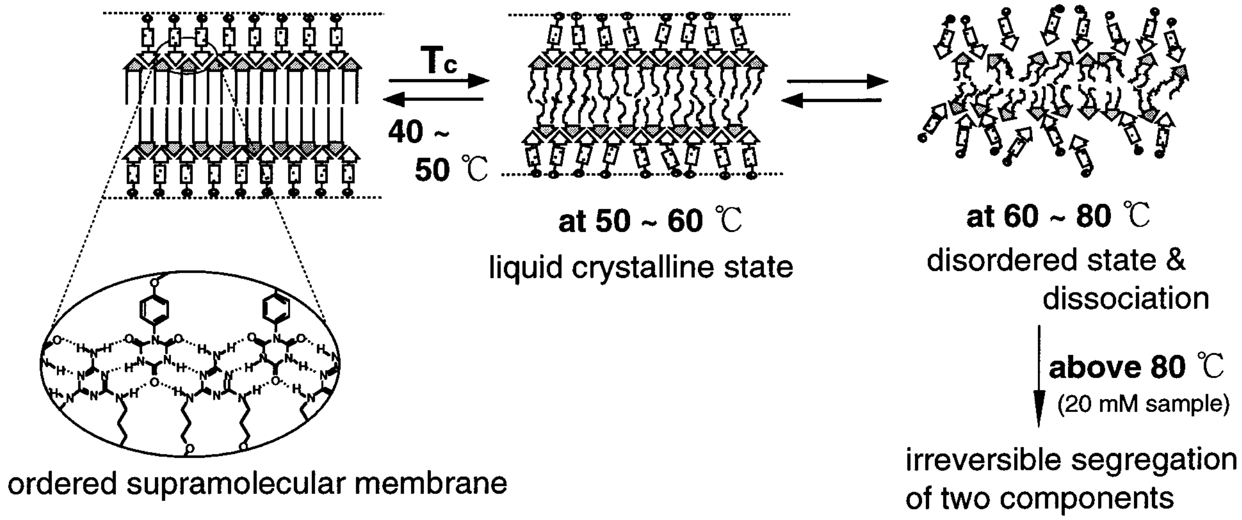

Figure 10. Schematic illustration of phase transition characteristics of aqueous **2(C$_{12}$OC$_3$)-Mela/CA-phC$_{10}$N$^+$**. Reversible dissociation was observed with a dilute (5 mM) dispersion.

bilayers of **$C_{12}OC_3$-Mela/CA-ph$C_{10}N^+$** and **EtC_6OC_3-Mela/CA-ph$C_{10}N^+$** are similarly de-interdigitated during the phase transition and are further converted to disordered states as illustrated in Figure 10.

Conclusions

The preceding results establish that complementary hydrogen bonding pairs form bilayer membranes in water. These supramolecular membranes are the first example of water-soluble supermolecules directed by complementary hydrogen bonds. Maintenance of the complementary hydrogen bonds in aqueous environments was achieved by using molecular subunits that are designed on the basis of the concept of "*amphiphilic supramolecular assembly*". Amphiphilicity is an indispensable requirement for fabrication of self-assembled supermolecules as independent entities. This principle is commonly applicable to aqueous and organic media. In aqueous systems, the amphiphilic nature is imparted by structural combination of hydrophilic and hydrophobic moieties in which the former moiety surrounds the latter to ensure stability of the molecular assembly in water. In the same vein, a combination of the solvophilic moiety surrounding the solvophobic core gives rise to amphiphilicity in organic media.[17] The same reasoning applies to supramolecular assemblies in water−alcohol mixtures.[32]

Thermal, reversible dissociation of hydrogen bond-mediated subunits and irreversible segregation at higher temperatures observed for the present system are architectural features characteristic of biological supermolecules such as nucleic acids and proteins. These molecular assembly directed by complementary hydrogen bonding lead to dynamic functions *in water*, such as reconstitution and cooperative subunit exchanges, that have been regarded as unique and essential characteristics of biological self-assemblies.

Experimental Section

Materials. Long-chain derivatives of melamine and cyanuric acid were synthesized according to Schemes 1 and 2. The structures of the intermediates and the final products were confirmed by thin-layer chromatography, IR and NMR spectroscopies, and elemental analysis. 2-Chloro-4,6-diamino-1,3,5-triazine (Aldrich), isocyanuric acid, 3-(2-ethylhexyloxy)propylamine (Tokyo Kasei), and 3′-(dodecyloxy)propylamine (Wako Pure Chemical) were used as received. Ethanol used for spectral measurements and for preparation of hydrogen bonded complexes was of spectral grade (Kishida Chemical). 1,10-Dibromodecane (Tokyo Kasei) was purified by distillation. 1,6-Diphenyl-1,3,5-hexatriene (DPH, Tokyo Kasei) was used as received.

2($C_{12}OC_3$)-Mela (1). 2-Amino-4,6-dichloro-1,3,5-triazine was prepared from cyanuric chloride according to the literature.[33] 2-Amino-4,6-dichloro-1,3,5-triazine (3.7 g, 22.9 mmol) was added to 3′-(dodecyloxy)propylamine (22.3 g, 91.5 mmol). An exothermic reaction sets in upon mixing, and the mixture was stirred at room temperature for 30 min. Sodium hydroxide (1.83 g, 45.8 mmol) in 150 mL of water was added to this mixture, and the resultant heterogeneous mixture was refluxed for 14 h. After cooling, the crude product was extracted with chloroform, and the organic layer was washed with water three times and dried over Na_2SO_4, and the solvent was removed in vacuo. The resulting crude product was chromatographed on silica gel (32:2 $CHCl_3$/methanol), and recrystallization from ethanol and hexane afforded the colorless powders of **1** (9.8 g, 74%): mp 56 → 60 °C (arrow indicates the liquid crystalline temperature range); TLC (silica gel, 10:1 $CHCl_3$/methanol) $R_f = 0.78$; IR (KBr) (N−H) 3354, 3197, (C−H) 2923, 2849, (N−H) 1572, (triazine) 1514, 1468, 812 cm^{-1}; ^1H NMR ($CDCl_3$) 1.0−2.0 (m, 50H, CH_3, CH_2), 3.1−3.6 (t + t, 12H, OCH_2, $NHCH_2$), 4.95−5.25 (br, 4H, NH_2, NH). Anal. Calcd for $C_{33}H_{66}O_2N_6$: C, 68.47; H, 11.49; N, 14.52. Found: C, 68.20; H, 11.41; N, 14.31.

2C_{16}-Mela (2). This compound was synthesized by adopting the procedure used for **$C_{12}OC_3$-Mela (1)**. **2:** TLC (silica gel, 10:1 $CHCl_3$/methanol) $R_f = 0.5$; mp 91.0−94.5 °C; IR (KBr) (N−H) 3350, 3150, (C−H) 2925, 2850, (triazine) 1465, 810 cm^{-1}; ^1H NMR ($CDCl_3$) 0.6−2.0 (m, 31H, CH_3, CH_2), 3.0−3.8 (t, 2H, $NHCH_2$),4.2−5.2 (br, 5H, NH_2, NH). Anal. Calcd for $C_{19}H_{38}N_6$: C, 65.10; H, 10.09; N, 23.97. Found: C, 65.04; H, 10.84; N, 23.83.

$C_{12}OC_3$-Mela (3). 2-Chloro-4,6-diamino-1,3,5-triazine (3.0 g, 20.6 mmol) was added to 3′-(dodecyloxy)propylamine (5.02 g, 20.6 mmol), and 150 mL of aqueous sodium hydroxide (0.85 g, 21.3 mmol) was further added. The heterogeneous mixture was then refluxed for 48 h, and after the solution was cooled to room temperature, precipitates were collected by filtration. The crude material was chromatographed on silica gel (20:1 to 10:1 $CHCl_3$/methanol). Recrystallization from 140 mL of ethanol/water mixture (5:2 by volume) afforded a colorless powder of **3** (3.2 g, 44%): mp 114.9−116.3; TLC (silica gel, 10:1 $CHCl_3$/methanol) $R_f = 0.34$; IR (KBr) (N−H) 3450, 3350, 3150, (C−H) 2925, 2850, (C−O) 1115, (triazine) 815 cm^{-1}; ^1H NMR ($CDCl_3$) 0.7−1.1 (t, CH_3), 1.1−1.5 (m, 20H, CH_2), 1.5−2.0 (m, 2H, $NHCH_2$-CH_2), 3.2−3.6 (t + t, 6H, $NHCH_2$, OCH_2), 5.6−6.0 (s + t, NH, NH_2). Anal. Calcd for $C_{15}H_{36}ON_6$: C, 61.32; H, 10.29; N,23.84. Found: C, 61.44; H, 10.25; N, 23.84.

C_{16}-Mela (4). This compound was synthesized according to the procedure used for **$C_{12}OC_3$-Mela (3)**. **4:** TLC (silica gel, 10:1 $CHCl_3$/methanol) $R_f = 0.5$; mp 91.0−94.5 °C; IR (KBr) (N−H) 3350, 3150, (C−H) 2925, 2850, (triazine) 1465, 810 cm^{-1}; ^1H NMR ($CDCl_3$) 0.6−2.0 (m, 31H, CH_3, CH_2, $NHCH_2CH_2$), 3.0−3.8 (t, 2H, $NHCH_2$), 4.2−5.2 (s + t, NH, NH_2). Anal. Calcd for $C_{10}H_{38}N_6$: C, 65.10; H, 10.09; N, 23.97. Found: C, 65.04; H, 10.84; N, 23.83.

EtC_6OC_3-Mela (5). This compound was synthesized according to the procedure used for **$C_{12}OC_3$-Mela (3)**. **5:** TLC (silica gel, 10:1 $CHCl_3$/methanol) $R_f = 0.43$; mp 80.0−83.0 °C; IR (KBr) (N−H) 3440, 3320, 3140, (C−H) 2950, 2925, 2850, (C−O−C) 1103, (triazine) 1460, 810 cm^{-1}; ^1H NMR ($CDCl_3$) 0.5−1.0 (t, 6H, CH_3),1.0−2.1 (m, 11H, CH_2, CH, CH−CH_2, $NHCH_2CH_2$), 3.1−3.8 (t + t + t, 6H, $NHCH_2$, CH_2 OCH_2). Anal. Calcd for $C_{14}H_{28}ON_6$: C, 56.73; H, 9.52; N, 28.35. Found: C, 56.84; H, 9.39; N, 28.10.

CA-ph-C_{10}Br (7). *p*-(10-Bromodecyloxy)aniline hydrobromide (**6**) was prepared according to the reported procedure.[34] *p*-(10-Bromodecyloxy)aniline hydrobromide (**6**) (1.5 g, 4.6 mmol) was dissolved in 40 mL of anhydrous THF, and triethylamine (0.46 mL, 4.6 mmol) was added. Triethylamine hydrobromide formed was removed by filtration, and *N*-chlorocarbonyl isocyanate (0.74 mL, 9.2 mmol) was added to the filtrate. The solution was stirred for 2 h at room temperature and then refluxed for 2 days. Waxy residues obtained by solvent removal under reduced pressure were chromatographed on silica gel (CH_3Cl_3 to 29:1 $CHCl_3$/methanol). Recrystallization from ethanol afforded a colorless powder of **7** (0.4 g, 22%): mp 245−248.5 °C; TLC (silica gel, $CHCl_3$) $R_f = 0.05$; IR (KBr) (N−H) 3200, 3175, (C−H) 2920, 2850, (C−O)1800, 1770, 1700, (phenyl ring) 1520, (C−O−C) 1260 cm^{-1}; ^1H NMR ($CDCl_3$) 0.8−2.2 (m,16H, CH_2), 3.3−3.8 (m, 2H, $BrCH_2$),3.8−4.2 (t, OCH_2), 6.8−7.4 (t, 4H, −CH=),11.4 (s, 2H, NH).

CA-ph-$C_{10}N^+$ (8). *p*-(10-Bromodecyloxy)phenyl cyanuric acid (**7**) (2.0 g, 5.0 mmol) was dissolved in 100 mL of anhydrous THF, and 3.5 g of gaseous trimethylamine was introduced. The reaction vessel was then sealed, and the mixture was stirred for 9 days. Solvent removal and recrystallization of the residue from ethanol afforded a pale yellow powder of **8** (1.6 g, 62%): mp 255−259 °C; IR (KBr) (N−H) 3200, 3175, (C−H) 2920, 2850, (C=O) 1750, 1700 cm^{-1} (phenyl ring), 1520, (C−O−C) 1240 cm^{-1}; ^1H NMR ($CDCl_3$) 1.2−2.0 (m, 16H, CH_2), 3.07 (m, 11H, CH_2N, NCH_3), 3.99 (t, 2H, OCH_2), 6.8−7.4 (d + d, 4H, −CH=), 11.4 (s, 2H, NH) Anal. Calcd for

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$C_{22}H_{35}O_4N_4Br\cdot1.5H_2O$: C, 50.19; H, 7.28; N, 10.64. Found: C, 49.94; H, 7.41; N, 10.49.

CA-$C_{10}N^+$ (10). Cyanuric acid dihydrate10.0 g (60.6 mmol) was dehydrated by heating to 100 °C under reduced pressure. Then 300 mL of anhydrous DMF, 18.35 g (61.2 mmol) of distilled 1,10-dibromodecane, and 9.2 g (60.6 mmol) of 1,8-diazabicyclo[5.4.0]-7-undecene were added, and the mixture was stirred for 7 h at 70 °C. After removal of DMF under reduced pressure, the residue was recrystallized from ethanol to give N-(10-bromodecyl)isocyanuric acid (**9**). The product (2.96 g, 8.5 mmol) was then quarternized according to the procedure described for **8**, to give **10** as a colorless powder (3.10 g, 92.7%): mp 189.5−192.5 °C; IR (KBr) (N−H) 3509, 3080, (C−H) 2922, 2849, (C═O) 1765, 1788, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) 1.2−2.0 (m, 16H, CH_2), 3.35 (m, 11H, CH_2N, NCH_3), 3.80 (m, 2H, NCH_2). Anal. Calcd for $C_{16}H_{31}O_3N_4Br\cdot0.25H_2O$: C, 46.66; H, 7.71; N, 13.60. Found: C, 46.79; H, 7.75; N, 13.38.

Sample Preparation. Hydrogen bonded complexes of alkylated melamine and isocyanuric acid derivatives were prepared by mixing equimolar amounts of each component in ethanol and removing the solvent under reduced pressure. This procedure was repeated three times, and the resultant complexes were finally dried at 60 °C in vacuo. Formation of complementary hydrogen bonds in these samples was confirmed by IR spectra. Pure water was added to the complexes, and the mixtures were dispersed in water by ultrasonication (Branson Sonifier Model 185, sonic power 45 W, 5−10 min at 0 °C. Water was purified with a Milli-Q system. Multibilayer cast films were obtained by casting aqueous dispersions (ca. 20 mM) on glass plates or on fluorocarbon membrane filters (Fluoropore filters, Sumitomo Electric Co.).

Measurements. Transmission electron microscopy (TEM) was conducted on a Hitachi H-600 instrument by the negative staining method. Aqueous dispersions (ca. 0.4 mM) of complexes were prepared by ultrasonication. One drop of the dispersions was placed on a carbon-coated grid and dried in air. Subsequently, a drop of 2% aqueous uranyl acetate was placed on each of the grids and dried in vacuo (post-staining method). Alternately, 500 μL of aqueous dispersions was mixed with 500 μL of 2% aqueous uranyl acetate, sonicated for 1 min, and applied to carbon-coated grids. The Cu meshes were subjected to TEM observation with an acceleration voltage of 75 kV and magnifications of 10000−50000. IR spectra were measured on a Shimadzu FTIR model DR-8000 (KBr pellet, resolution: 2 cm^{-1}). Peak positions were determined by a peak-search program. X-ray diffraction of cast films was obtained by the reflection method ($2\theta-\theta$ scan) and by the transmisson method (edge view) with a Rigaku Denki RAD-R-32 X-ray diffractometer and a Rigaku Dinki Rotaflex R-200, respectively. The X-ray beam was generated with a Cu anode, and the Cu Kα beam was taken out via a graphite monochromator (reflection method) and with a nickel filter (transmission method). The edge-view diffraction was obtained by directing the X-ray beam parallel to the film surface and by photographing by a plate camera. Differential scanning calorimetry (DSC) was conducted on Seiko Electronics SSC-5200 instrument. The dispersions (56 μL) were sealed in Ag sample pans, and DSC thermograms were scanned at a heating rate of 1 °C min^{-1}. Fluorescence depolarization of DPH was obtained on a Hitachi 650-10S spectrofluorimeter.

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Supporting Information Available: UV−vis absorption spectral data of membrane-bound cyanine dye (NK2012, Nihon Kankoh Sikiso) and their temperature dependence, a table giving the absorption λ_{max} values of NK2012 in aqueous dispersions of complementary hydrogen bond-mediated bilayers (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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