drophobic forces, or a syn orientation of the complexing chromophores. The origin of this cooperativity and applicability to new host–guest complexes is the subject of current investigation.[5]

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Supplementary Material Available: Schemes detailing the preparation of **1**–**5**, a table of "cyclization shifts" for **2**–**4**, and positional and thermal parameters from the X-ray analysis of compound **4** (9 pages). Ordering information is given on any current masthead page.

Self-Assembly of Bilayer Membranes in Organic Solvents by Novel "Amphiphilic" Compounds[1]

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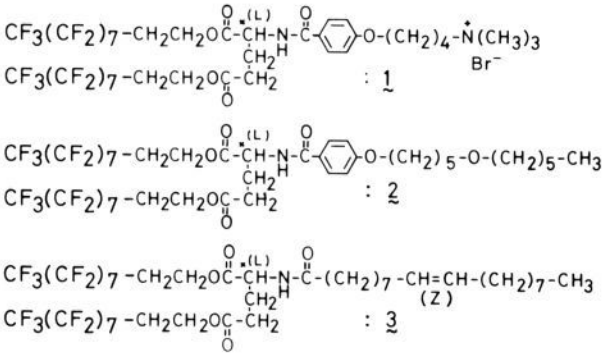
We describe herein spontaneous bilayer formation by perfluoroalkyl derivatives in nonaqueous media. The synthetic bilayer membrane[2] has been shown to be useful as biomembrane models and as novel functional materials, because of its unique molecular organizations and a rich variety of component molecules.[3] The bilayer structure is produced spontaneously when component amphiphiles are dispersed in water. However, it is usually not preserved in organic media, since the hydrophobic interaction is a major driving force for this assembly. Should stable molecular bilayers be produced in organic media, one could expect emergence of a wholly new branch of organic chemistry.

Some fluorocarbon amphiphiles have been shown to form stable bilayer membranes in water.[4-6] The limited miscibility between the fluorocarbon and hydrocarbon components led to reduced permeation of probe molecules into fluorocarbon vesicles and to controlled phase separation. The limited miscibility was also crucial in recent findings that semifluorinated *n*-alkanes, F-$(CF_2)_n(CH_2)_mH$, possessed bilayer-type crystal structures[7] and that they formed micellar aggregates in toluene and in fluorinated solvents.[8]

Ammonium amphiphile **1** (Chart I) forms stable bilayer vesicles in water.[9] Therefore, we adopted a similar molecular design and synthesized compounds **2** and **3** as components of molecular assemblies to be organized in organic media.[10] The ammonium head group in **1** is replaced by solvophilic units in **2** and **3**. The fluorocarbon tails should provide the solvophobic property.

Chart I



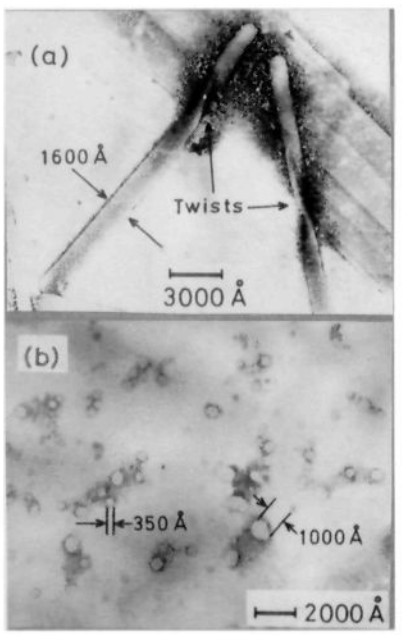


Figure 1. Electron micrographs of **2** in cyclohexane. **2** was poststained with lead(II) bis(acetylacetonate). [**2**] = (0.5 – 1.0) × 10^{-4} M, ca. 17 °C. (a) Twisted tapes. (b) Vesicles.

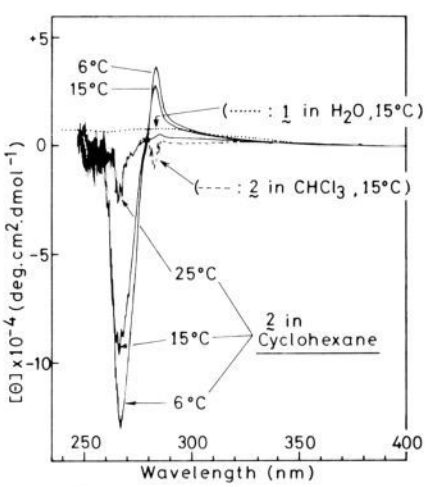


Figure 2. Circular dichroism spectra of **2** in organic solvent and aqueous **1**. [**1**] = [**2**] = 1.0 × 10^{-4} M.

Compound **2** gave a colorless, transparent solution in cyclohexane at 6–25 °C upon dispersion by warming.[11] A few drops

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(10) Compounds **2** and **3** were prepared from bis(perfluoroalkyl) glutamate and the corresponding acid chlorides, according to the procedures employed for **1**. For **2**: Anal. Found: C, 38.98; H, 3.12; N, 1.08. Calcd for $C_{43}H_{41}O_7NF_{34}$: C, 38.84; H, 3.11; N, 1.05. For **3**: Anal. Found: C, 39.74; H, 3.65; N, 1.09. Calcd for $C_{43}H_{47}O_5NF_{34}$: C, 39.61; H, 3.63; N, 1.07. IR and NMR data are consistent with the respective structures.

(11) **2** was not soluble at all in hexane and decane. It gave clear solutions in hot alcohols, ethylene glycol, CH_3CN, DMF, and DMSO, but crystals precipitated at room temperature. $CHCl_3$, acetone, ethyl ether, dioxane, THF, and CF_2CCl_2 were good solvents.

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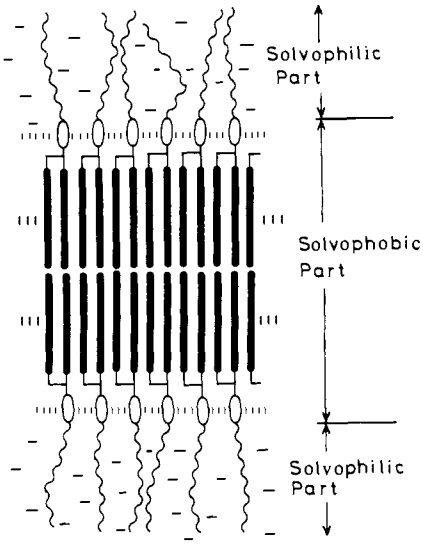

Figure 3. Schematic illustration of the bilayer structure of **2** and **3** in organic media.

of the solution were applied to carbon-coated Cu grids and dried. A few drops of lead(II) bis(acetylacetonate) in CH_3OH were then added as the staining agent, and the samples were observed by a transmission electron microscope (Hitachi, H600). As shown by Figure 1, the stained samples reproducibly contained twisted tapes (width, 1600 Å) and smaller vesicles (diameter, 200–1000 Å). The inner core of the vesicles cannot be seen in Figure 1b, because of the poststaining method we employed. In a direct observation of the cyclohexane dispersion by a dark-field optical microscope (Olympus BH-2), numerous fiber-like aggregates (width less than 1 μm) were found. These microscopic observations of varied morphologies reflect different degrees of development of the molecular aggregate, since vesicles were dominant in samples prepared at 25 °C and the tape and lamella morphologies were abundant at 15 °C.

Compound **3** gave lamellar and rod-like morphologies in benzene (layer thickness, ca. 100 Å), as will be discussed in detail elsewhere.[12]

Figure 2 compares circular dichroism (CD) spectra of **1** in water and **2** in $CHCl_3$ and cyclohexane. CD peaks due to the phenylene unit are observed at 250–300 nm. The fluorocarbon bilayer of **1** in water displays a very small peak ($[\theta]_{266}$(15 °C) 7000), in contrast with a related hydrocarbon bilayer which gives a $[\theta]_{260}$ value of 4×10^5 at temperatures below the phase transition.[13] On the other hand, fluorocarbon compound **2** at low temperatures gives strong CD peaks in cyclohexane: $[\theta]_{266} = 1.3 \times 10^5$ at 6 °C. The intensity is lessened with rising temperature. The solvent used is crucial, and the signal is much smaller in $CHCl_3$. It has been shown that much-enhanced CD spectra of *aqueous* chiral bilayers are derived from exciton coupling among the organized chromophore.[13] Thus, the observed CD data indicate that the component molecules in the aggregate are highly organized in *cyclohexane*.

The data shown in Figures 1 and 2, together with the structural similarity of component molecules with common, bilayer-forming compounds, strongly suggest that the molecular bilayer is the fundamental building unit of the aggregate, as schematically illustrated in Figure 3. Macroscopic and microscopic assemblage of amphiphilic molecules in organic media has been reported in the past. For example, a phospholipid (dipalmitoylphosphatidylcholine) formed reversed micelles in aromatic solvents[14] and macroscopic gels in aliphatic solvents.[15] *N*-Octylaldonamides similarly formed gels in xylene.[16] We demonstrated recently that the Ca^{2+} complex of synthetic phosphate bilayers retained their molecular organization in organic solvents.[17] The polar interaction is the dominant driving force of molecular assembly in these instances. In contrast, the organized molecular assembly in the present case is formed by the use of the solvophobic property of the fluorocarbon chain.

The present study together with our previous finding implies that compartmentalization of the molecular space can be realized even in organic media.

Registry No. 2, 122948-36-1; **3**, 122948-37-2.

Supplementary Material Available: Electron micrographs of bilayer aggregates of related fluorocarbon amphiphiles (1 page). Ordering information is given on any current masthead page.

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Convenient Procedure for the Preparation of Specific Mixed DNA–RNA Polymers

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The chemical synthesis of specific DNA oligomers[1] and, more recently, RNA oligomers[2] has become routine in many laboratories. With the development of the alkylsilyl groups as the 2′-hydroxyl protecting groups, in combination with the phosphoramidite coupling procedure for assembling the oligoribonucleotide chain, the synthesis of RNA oligomers can be achieved as efficiently as is the case for DNA oligomers.[3,4] In this communication, we describe a convenient procedure for the solid-phase synthesis of specific DNA–RNA mixed polymers using deoxyribonucleoside phosphoramidite and 2′-silylated ribonucleoside phosphoramidite intermediates. While van Boom[5] has recently reported the solution synthesis of a mixed polymer where a deoxyribonucleotide fragment is linked to a ribonucleotide fragment, the method we describe allows for the synthesis of specific nucleotide sequences with deoxyribonucleotides and ribonucleotides being interspersed. Such mixed DNA and RNA nucleotide polymers will be useful in the study of biological processes and

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