

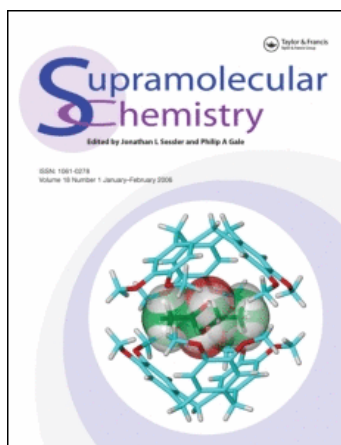
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COMMUNICATION

Inter-domain movement of spin labels in the vesicle monolayers of hybrid bolaamphiphiles

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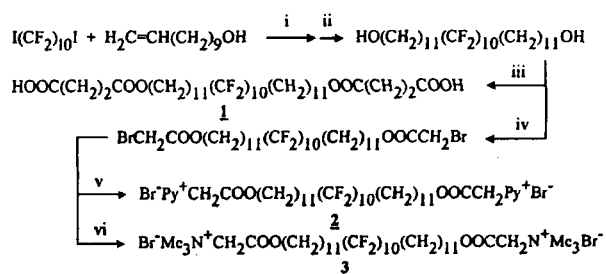
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Vesicle monolayers with a fluorocarbon domain between two hydrocarbon domains were prepared, in which spin labels bearing a hydrocarbon, a fluorocarbon, or a half-hydrocarbon half-fluorocarbon hybrid methylene chain, are located and move differently.

Synthetic vesicles formed by aggregation of a single amphiphile can be regarded as extremely simple models of highly organized multifunctional biological cells.^{1,2} In biological systems, fixation of reaction partners at appropriate distances from one another is a structural prerequisite for vectorial reactions and reaction sequences.^{1,3} The positions of the reaction centers are fixed by membrane-protein complexes. Compared with the rapidly, selectively reacting proteins, the lipid aggregates constitute a chemically inert filling material. They merely act as a layer separating the two aqueous volumes and as a solvent for the hydrophobic protein moieties. Functional vesicle membranes were obtained from specially designed synthetic amphiphiles.¹ Only when reactive domains are achieved in synthetic vesicle membranes will it be possible to couple two or more reactions in a vectorial reaction chain. In this communication, we report that stable vesicles with three domains of monolayer membranes are formed by synthetic, single chain hybrid bolaamphiphiles which have a fluorocarbon segment of nearly one third of their total length intercalated in the middle of a hydrocarbon chain. It is known that fluorocarbon chains have behaviors very different from those of the corresponding hydrocarbon chains,^{4–8} including strong hydrophobic interactions with each other⁴ and limited miscibility with hydrocarbon chains.^{5,6}

Furthermore, vesicle monolayers formed by bolaamphiphiles provide many more intriguing properties than usual bilayer membranes.^{8–11} Extremely stable, ultrathin, porous, or unsymmetrical monolayer lipid membranes have been formed from bolaamphiphiles.¹¹

The bolaamphiphiles **1**, **2** and **3** were synthesized as shown in Scheme 1. Sonication of a suspension of **1**, **2**, or **3** (~2 mg in 1 mL H₂O, 50 °C, 75 Watt, 1 min.) gave clear, colorless dispersions. Electron micrographs confirmed the formation of vesicles (Fig. 1). The vesicles of **1** were single-walled, but those formed from **2** or **3** were double-walled. Their diameters all ranged between 500 and 2000 Å with a layer thickness of about 50 Å, which is consistent with the length of a single bolaamphiphile. The vesicles were so stable that their solutions could be stored at room temperature for one year without sedimentation or any other visible change. No phase transition temperature could be measured by DSC or by turbidity measurement. The average distance between bolaamphiphiles in a curved vesicle monolayer is larger



Scheme 1 Synthesis of the hybrid bolaamphiphiles; Reagents and conditions: i. Na₂S₂O₈/NaHCO₃/CH₃CN/H₂O, r.t., 30min.; ii. Zn/EtOH, reflux, 6h.; iii. Succinic anhydride/DMAP/Py, 100°C, 5h.; iv. BrCH₂COBr/Py/THF, r.t., 30min.; v. Py, 50°C, 2min.; vi. Me₃N/THF, r.t., overnight.

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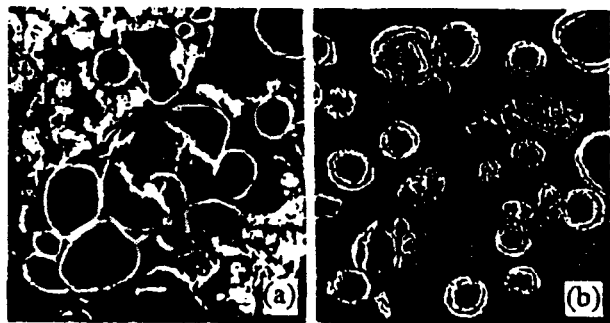
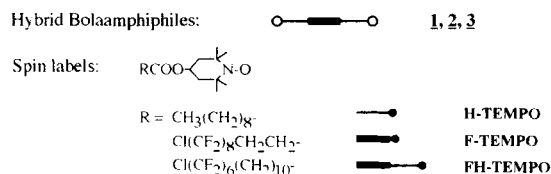
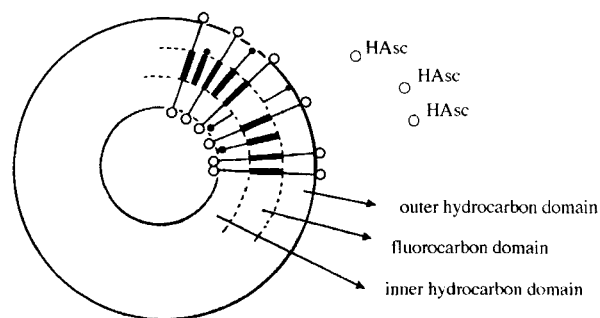


Figure 1 Electron micrographs. (a) single-walled vesicle of **1**. (b) double-walled vesicle of **2**. Negatively stained, magnification 100,000.

than found in bilayers, and results in weaker interactions. Therefore, no sign of liquid crystal formation has so far been observed in any vesicle monolayers made of bolaamphiphiles except in the case of the wedge-shaped, fluorinated amphiphiles we reported previously.⁸

Synthetic spin labels with a hydrocarbon methylene chain (H-TEMPO), a fluorocarbon chain (F-TEMPO), or a half-hydrocarbon half-fluorocarbon hybrid chain (FH-TEMPO) were entrapped in vesicles of **1** by cosonication of **1** and the spin labels. The range of concentration ratios of **1** and spin labels was 400:1 to 550:1. These vesicles were also very stable, and the optically transparent suspensions could be kept at room temperature for several weeks without any visible change. The vesicle shapes were the same as when the spin labels were absent as judged by electron micrographs. Because the spin labels are water insoluble, they are contained within the vesicle monolayer. The EPR peaks at high field of the trapped labels were broad and became sharper with increasing temperatures from 20 °C to 80 °C. The free rotation of the label molecules is indeed hindered in the vesicle membrane, which became more mobile when the temperature increased. Ascorbic acid when added to the bulk solution could only come into contact with the nitroxide labels located on the outer surface of the vesicle monolayer and reduce them to non-paramagnetic hydroxylamine derivatives. Mutual "phobicity" between hydro- and fluorocarbon species causes the hydro- and fluorocarbon chains of the labels to be located in the hydrocarbon and fluorocarbon domains in the vesicle monolayer, respectively (Scheme 2).

Consequently, the H-TEMPO is located either in the outer or the inner hydrocarbon domain. The EPR signals of the H-TEMPO located in the outer layer disappeared within 2 min after the addition of ascorbic acid. Meanwhile the EPR signals of the probe present in the inner layer were not affected until the H-TEMPO diffused through the middle fluorocarbon barrier into the outer hydrocarbon layer. The time course of the EPR signals of these labels decreased steadily (Fig. 2). Their first-order kinetics, with a rate constant of 0.044 min^{-1} , was almost the same as the rate of the outward flip-flop



Scheme 2 Schematic illustration of the vesicle monolayer of bolaamphiphiles and the distribution of the spin labels in the hydrocarbon and fluorocarbon domains.

of the H-TEMPO in a biphased hydro-fluorocarbon vesicle monolayer (0.047 min^{-1})⁸.

The F-TEMPO molecules, which are located in the fluorocarbon domain, were not reduced by ascorbic acid until they penetrated the outer hydrocarbon domain. The reaction time course is comparable to that of the inner-located H-TEMPOs (Fig. 2). The rate constant was cal-

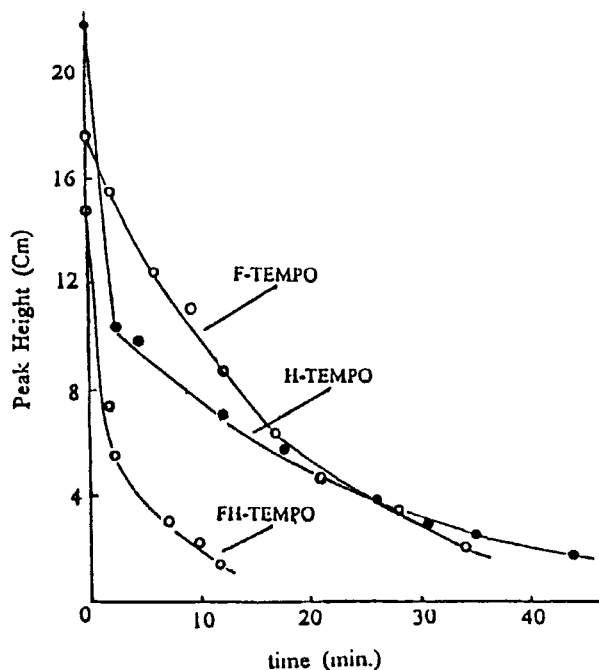


Figure 2 Time courses of the EPR signals of spin labels in vesicle monolayers after the addition of ascorbic acid at 20°C. The concentrations of F-TEMPO, H-TEMPO, FH-TEMPO, ascorbic acid, **1**, and NaHCO_3 are 2.31×10^{-5} , 1.76×10^{-5} , 1.81×10^{-5} , 0.01, 9.60×10^{-3} , $5.0 \times 10^{-3} \text{ M}$, respectively.

culated to be 0.062 min^{-1} , *i.e.* only slightly faster than that for the inner-located H-TEMPO.

Finally, we examined the case of the FH-TEMPO which is located either inner-facing or out-facing. The out-facing FH-TEMPO molecules were reduced rapidly ($< 2 \text{ min}$) while the inner-facing ones were not affected until they underwent a flip-flop movement into the outer layer. The flip-flop rate constant of the FH-TEMPO was calculated to be 0.15 min^{-1} . It shows a much faster process than for the inner-located H-TEMPO or F-TEMPO, and is a little slower than for a fluorocarbon label in a fluorocarbon vesicle bilayer (0.25 min^{-1})⁷. Therefore, the hybrid chain of the FH-TEMPO might be considered as a phase transfer carrier which easily crosses the fluorocarbon domain. After the spin labels had been reduced, the shapes of the vesicles were observed to be unchanged by electron microscopy.

In conclusion, the formation of vesicle monolayers with a fluorocarbon domain between two hydrocarbon domains was established. The exact location of the functional molecules in the different domains of the vesicle monolayer, and their interactions, including charge and energy transfer, are the object of our current attention.

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