imidazole, which functions as an axial ligand for Mn^{III}. This system was used to catalyze the epoxidation of water-soluble (2,5-dihydrofuran, **3**) and -insoluble (styrene, **4**) alkenes.[5] The reactions followed first-order kinetics. GCMS and comparison with authentic samples showed that for **3** the reaction products are 3,4-epoxytetrahydrofuran and the ring-opened compound *trans*-3,4-dihydroxytetrahydrofuran (molar ratio 1:2.5). For **4** only the ring-opened product 1,2-dihydroxy-1-phenylethane could be detected. Turnover numbers (mol of oxygenated product/(mol of Mn^{III}·h)) for **3** and **4** amounted to 8 and 1.3, respectively. As a side reaction, the catalytic system produces water out of H_2 and O_2. The selectivity of substrate conversion vs. water formation was 2.5%. In separate experiments we checked that no oxygenation took place when any of the aforementioned components were omitted.

In summary, catalytic systems that mimic complex enzyme functions can be designed by using polymerized vesicles as microreactors.

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Registry No. 1, 103794-75-8; **2**, 103794-74-7; **3**, 1708-29-8; **4**, 100-42-5; Pt, 7440-06-4; *N*-methylimidazole, 616-47-7; methylene blue, 61-73-4; cytochrome P-450, 9035-51-2; monooxygenase, 9038-14-6.

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(4) Experiments done with the water-soluble porphyrin [tetrakis(1-methylpyridinium-4-yl)porphyrinato]manganese(III) pentaiodide prove that no Pt is present in the outer aqueous compartments. Vesicles containing Pt to which this porphyrin was externally added required methylene blue to reduce Mn^{III} to Mn^{II}. Vesicles that also had K_2PtCl_4 added externally could function without the electron carrier.

(5) In a typical experiment a polymerized vesicle dispersion (2 mL, 5×10^{-3} M **2**) containing **1** (2.7×10^{-5} M), *N*-methylimidazole (5.0×10^{-4} M), methylene blue (6.2×10^{-6} M), Pt (3.5×10^{-4} M), and 2,5-dihydrofuran (4×10^{-2} M) or styrene (4.3×10^{-3} M) was stirred magnetically at 20.0 °C under an atmosphere of O_2 and H_2 (1:1 v/v). From time to time samples were taken and analyzed by GLC (Tenax-GC column). The products were identified by GCMS and by comparison with authentic samples. The pH of the reaction mixture varied between 4.5 and 5.0. In separate experiments we checked that under our conditions no H_2O_2 is produced from H_2 and O_2.

Spontaneous Assembly of Phospholipid Monolayers via Adsorption onto Gold[1]

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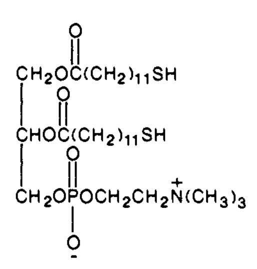
Supported phospholipid monolayers and multilayers [Langmuir–Blodgett (LB) films] represent powerful tools for probing structure–activity relationships of biomembranes.[3-5] While the preparation of such assemblies is, in theory, straightforward, monolayer transfers using film-balance techniques are nontrivial, do not always proceed with high efficiency, and are limited to planar surfaces. Moreover, the formation of supported monolayers having polar head groups extending away from the support in air is particularly difficult.[6] In this paper we describe a simple and reliable method for constructing phospholipid monolayers, based on the principle of spontaneous organization via thiol (or disulfide) adsorption onto gold surfaces.[7] Our procedure employs 1,2-bis(11-mercaptoundecanoyl)-*sn*-glycero-3-phosphocholine (**1**).[8,9]



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Resulting monolayers represent unique biomembrane models which are formed with ease and with high reproducibility and which *cannot be prepared using conventional LB methods.*

In a typical experiment, a clean glass microscope slide (75 × 25 × 1 mm) was coated with a thin layer of chromium metal (ca. 100 Å) and then coated with gold (ca. 550 Å), using a deposition rate of ca. 5 Å s^{-1}. The resulting surface was completely wetted by water (stationary contact angle was <10°), indicating the absence of contamination.[10] The slide was then immersed in 40 mL of a 4×10^{-5} M methanolic solution of **1** (chloroform or *n*-hexane can also be used) for 60 min at room temperature, removed, and rinsed by gentle agitation in an equal volume of the same solvent for 2 min. The slide was then allowed to remain in air for 0.5 h; reproducibility of lipid adsorption, as judged by ellipsometry and contact angle measurements described below, was excellent.

The advancing contact angle (θ_a) for water on this lipid-modified surface was 0°.[11] Examination of Θ_a, as a function of time of surface treatment, indicated that adsorption equilibrium was reached within 5 min. The film thickness of **1**, determined by using a Rudolph Model Auto-EL-II computerized ellipsometer (6328 Å) and assuming an index of refraction (n) of 1.52,[7] was 21.6 ± 1.9 Å (nine measurements); for $n = 1.50$, the thickness was 22.0 ± 2 Å. Space-filling models (CPK) for **1**, where the α and β chains are fully extended and perpendicular to the head group, indicate a maximum length of 24 Å. The measured thickness is, therefore, very close to that which is predicted for an assembly of **1** having *an orientation which is perpendicular*

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(2) On leave from (a) Technical University of Warsaw, Poland, and (b) A. Mickiewicz University, Poznan, Poland.

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(8) Samuel, N. K. P.; Singh, M.; Yamaguchi, K.; Regen, S. L. *J. Am. Chem. Soc.* **1985**, *107*, 42.

(9) In a recent publication, it was disclosed that organic thiols of structures $HS(CH_2)_{10-20}CO_2H$ adsorb onto gold films with essentially monolayer coverage; no experimental details were, however, provided: Randall, S.; Farley, H.; Reamey, R. H.; McCarthy, T. J., Deutch, J.; Whitesides, G. M. *Langmuir*, **1985**, *1*, 725.

(10) Smith, T. *J. Colloid Interface Sci.* **1980**, *75*, 51. Gaines, G. L., Jr. *Ibid.* **1981**, *79*, 295. Schneegans, M.; Menzel, E. *Ibid.* **1982**, *88*, 97.

(11) When chloroform was used as the solvent for adsorption and washing, the advancing angle was 17° after 0.5 h in air. All contact angles reported are averages of a minimum of six independent measurements on the surface and were made after 30 s of contact with water.

(12) Foltynowicz, Z.; Yamaguchi, K.; Czajka, B.; Regen, S. L. *Macromolecules* **1985**, *18*, 1394.

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to the plane of the metal surface and a bulk packing density.

Further evidence for lipid organization comes from the measured site density of **1**. Treatment of the lipid-modified surface with 5.4 M HCl for 6 h at 40 °C and subsequent analysis of the solution for phosphorus[12] indicated the presence of $2.7 \times 10^{14} \pm 1.4 \times 10^{14}$ lipids cm^{-2} of geometric surface [average of six preparations, using three different batches of gold-coated slides and lipid concentrations in the range of 4×10^{-7} to 4×10^{-5} M]. By use of one freshly prepared batch of slides and a constant lipid concentration (4×10^{-5} M), five independent surface treatments afforded a phosphorus content of 1.8 ± 0.25 lipids/cm^2. In a control experiment, a gold-coated slide was treated with a 10^{-5} M methanolic solution of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine; examination by ellipsometry and phosphorus analysis indicated negligible lipid association.

Scanning electron microscopy of untreated and **1**-modified gold slides (70000×) did not reveal any detectable morphology. To a first approximation, the true area of these surfaces can be estimated to be within a factor of 2 of the geometrical surface.[7] Based on the measured collisional area of **1** (82 $Å^2$/molecule, film balance determination), a tightly packed monolayer contains 1.2×10^{14} lipids cm^{-2}. While the uncertainty of the true surface area for each gold sample precludes a quantitative assessment of the compactness of monolayers of **1** on gold, the observed loading is clearly in the range expected for a packed monolayer.

Attempted "horizontal lifting"[13] of a monolayer of **1**, formed at the air-water interface with a surface pressure of 16 dyn/cm and a subphase temperature of 20 °C (collapse point is ca. 33 dyn/cm), onto a gold slide resulted in a severe and unavoidable disruption (observable waves) of the quiet liquid surface, due to the strong hydrophilicity of the surface. The observed film thickness and Θ_a for the transferred monolayer were 17 ± 3 Å and 58 ± 6°, respectively. Taken together; this lower film thickness, higher value of Θ_a, and higher standard deviation of Θ_a, relative to the spontaneously assembled monolayer of **1** on gold, indicate a less organized and less homogeneous assembly. In view of the hydrophilic nature of the gold, meaningful monolayer transfer, via vertical dipping from air into water, was precluded. Interestingly, however, monolayers of **1** transferred to gold slides via pulling from water into air exhibited an initial Θ_a of 44°; after 42 h in air, Θ_a reached a limiting value of 25 ± 5°. In contrast, when a clean hydrophilic glass slide was used as the substrate, a *stable* surface ($\Theta_a = 55°$) was obtained. These results imply that **1** "flips over" on gold with time, to form a more thermodynmically favored assembly in which the thiol moiety binds to gold and the more polar choline head group extends away from the surface.

In preliminary studies, we have found that spontaneous assembly of 1-palmitoyl-2-(16-mercaptohexadecanoyl)-*sn*-glycero-3-phosphocholine (**2**) on gold using a 4×10^{-6} M methanolic solution of the lipid resulted in a loading, Θ_a, and film thickness of 1.0×10^{14} lipids cm^{-2}, 47 ± 6°, and 17.7 Å, respectively (CPK models predict a maximum length of 28 Å). These results imply a looser packed monolayer compared with **1** and that each "leg" of the lipid needs to be adsorbed onto the gold surface for maximal chain packing.

Efforts which are now in progress are aimed at gaining further insight into the degree of compactness, uniformity, and orientation of monolayers of **1** and **2** (and related analogues) on gold and exploiting such surfaces as biomembrane models.[14]

Acknowledgment. We thank Drs. Ralph Nuzzo (Bell Laboratories) and Dave Allara (Bell Communications Research) for essential discussions concerning the adsorption properties and surface chemistry of gold.

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(13) Gaines, G. L. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966.

(14) Reflectance IR and XPS spectra confirm the presence of **1** and **2** adsorbed on gold. Detailed analysis of these spectra, with regard to precise orientational information, will be reported in due course: Allara, D. L.; Diem, T.; Regen, S. L., unpublished results.

Synthesis and X-ray Crystal Structure of a Soluble Pentametallic Organoyttrium Alkoxide Oxide Complex, $(C_5H_5)_5Y_5(\mu\text{-}OCH_3)_4(\mu_3\text{-}OCH_3)_4(\mu_5\text{-}O)$[1]

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As part of a general program to make oxygen-stabilized organoyttrium and organolanthanide complexes, we have examined synthetic routes to the simple prototypical organometallic alkoxide complex dicyclopentadienylyttrium methoxide (**1**). Although **1** can be produced in the reaction of $[(C_5H_5)_2Y(\mu\text{-}H)(THF)]_2$ with CH_3OH or CH_2O, the potentially more direct synthesis from $(C_5H_5)_2YCl(THF)$ and alkali-metal methoxides can take a different course. A remarkable polymetallic oxide complex can be obtained whose synthesis and structure may have important implications in organometallic oxide/alkoxide chemistry.

$(C_5H_5)_2YCl(THF)$[3] reacts with desolvated $KOCH_3$[5] in THF overnight at 30 °C to form a mixture of products containing some dicyclopentadienylyttrium methoxide.[6] By use of the solvate $KOCH_3{\cdot}CH_3OH$,[5] complex **1** can also be obtained from $(C_5H_5)_2YCl(THF)$ at -78 °C, but when the reaction is run at 30 °C for a 2-day period, the formation of complex **1** is not observed. Instead, a complex, **2**, which is a minor component at low temperature, is obtained as the predominant product. **2** can be isolated in 60–70% yield by removing THF from the reaction mixture and extracting with toluene.[7] The ^1H NMR spectrum of **2** contains two cyclopentadienyl resonances in a 4:1 ratio and two methoxide resonances of equal intensity corresponding to a total of eight methoxide ligands per five cyclopentadienyl groups.[8] **2** is soluble in hexane and sublimes at 260 °C at 10^{-5} torr.

X-ray quality crystals of **2** were grown from toluene at 30 °C and the complex was identified as $(C_5H_5)_5Y_5(\mu\text{-}OCH_3)_4(\mu_3\text{-}OCH_3)_4(\mu_5\text{-}O)$ by X-ray diffraction.[9] Figure 1 shows that **2** is comprised of a square pyramid of yttrium atoms each of which is coordinated to one C_5H_5 group. Upon each triangular face of the square pyramid is a triply bridging methoxide ligand and attached to each edge of the square base is a doubly bridging

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(2) Alfred P. Sloan Research Fellow.

(3) Prepared from YCl_3 and NaC_5H_5 as previously described[4] except for the following. Solvent is removed from the crude reaction mixture and the solids are washed with hexane. The solids are extracted with THF and the THF extract is filtered or centrifuged leaving the NaCl behind.

(4) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008–2014.

(5) The potassium methoxide is prepared in THF by adding potassium to CH_3OH previously distilled from a vessel containing CH_3OH which was dried first with CaH_2 and then with sodium. Removal of THF and excess CH_3OH by rotary evaporation leaves $KOCH_3{\cdot}CH_3OH$. This can be desolvated by heating at 80–90 °C under vacuum for several hours. The methoxides were characterized by ^1H NMR and elemental analysis.

(6) Anal. Calcd for $YC_{11}H_{13}O$: Y, 35.54. Found (complexometric analysis[4]): Y, 35.0. ^1H NMR (THF-d_8) δ 6.17 (s, 10 H, C_5H_5), 3.34 (s, 3 H, OCH_3); (C_6D_6) δ 6.14 (s, 10 H, C_5H_5), 2.84 (s, 3 H, OCH_3).

(7) Typically, in the glovebox, $[(C_5H_5)_2YCl]_2$ (250 mg, 0.49 mmol) dissolved in 8 mL of THF was added to a stirred suspension of $KOCH_3{\cdot}CH_3OH$ (69 mg, 0.68 mmol) in 8 mL of THF. After 2 days, the mixture was centrifuged, the supernatant was decanted, the solvent was removed, and the solids were extracted with toluene. Removal of toluene gives **2** (127 mg, 63%). The yield and purity of the product is quite sensitive to reaction time, reaction temperature, purity of starting materials, and the alkali-metal salt used.

(8) ^1H NMR (C_6D_6) δ 6.26 (s, 20 H, C_5H_5), 6.16 (s, 5 H, C_5H_5), 3.67 (s, 12 H, μ_3-OCH_3), 3.47 (s, 12 H, μ-OCH_3). IR (KBr) 3090 w, 2920 s br, 2810 s, 1457 m, 1258 *m*, 1154 *w*, 1072 s br, 1018 s br, 770 s br cm^{-1}. Anal. Calcd for $Y_5C_{33}H_{49}O_9$: Y, 42.98%. Found: Y, 41.0%. Attempts to obtain a melting point resulted in decomposition at 320 °C.

(9) The space group is monoclinic $P2_1/c$ with $a = 11.402$ (2) Å, $b = 19.502$ (3) Å, $c = 20.922$ (5) Å, $\beta = 95.41$ (2)°, $U = 4631$ (2) $Å^3$, and $D_{calcd} = 1.48$ g cm^{-3} for $Z = 4$. Full-matrix least-squares refinement on the basis of 2477 unique reflections with $I > 3\sigma(I)$ yielded a final $R = 0.087$, $R_w = 0.108$. All non-hydrogen atoms except those of the cyclopentadienyl rings and C1 were refined with anisotropic temperature factors.

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